Sulfur geochemistry of hydrothermal waters in Yellowstone National Park, Wyoming, USA. III. An anion-exchange resin technique for sampling and preservation of sulfoxyanions in natural waters

Greg K. Druschel,*† Martin A. A. Schoonen, a D. Kirk Nordstrom, b James W. Ball, b Yong Xu c and Corey A. Cohn c

aDept. of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794. E-mail: Martin.Schoonen@SUNYSB.edu
bU.S. Geological Survey, 3215 Marine Street, Boulder, CO 80303
cDept. of Geosciences, SUNY at Stony Brook, Stony Brook, NY 11794

Received 11th December 2002, Accepted 22nd May 2003
First published as an Advance Article on the web 4th June 2003

A sampling protocol for the retention, extraction, and analysis of sulfoxyanions in hydrothermal waters has been developed in the laboratory and tested at Yellowstone National Park and Green Lake, NY. Initial laboratory testing of the anion-exchange resin Bio-Rad® AG1-X8 indicated that the resin was well suited for the sampling, preservation, and extraction of sulfate and thiosulfate. Synthetic solutions containing sulfate and thiosulfate were passed through AG1-X8 resin columns and eluted with 1 and 3 M KCl, respectively. Recovery ranged from 89 to 100%. Comparison of results for water samples collected from five pools in Yellowstone National Park between on-site IC analysis (U.S. Geological Survey mobile lab) and IC analysis of resin-stored sample at SUNY-Stony Brook indicates 96 to 100% agreement for three pools (Cinder, Cistern, and an unnamed pool near Cistern) and 76 and 63% agreement for two pools (Sulfur Dust and Frying Pan). Attempts to extract polythionates from the AG1-X8 resin were made using HCl solutions, but were unsuccessful. Bio-Rad® AG2-X8, an anion-exchange resin with weaker binding sites than the AG1-X8 resin, is better suited for polythionate extraction. Sulfate and thiosulfate extraction with this resin has been accomplished with KCl solutions of 0.1 and 0.5 M, respectively. Trithionate and tetrathionate can be extracted with 4 M KCl. Higher polythionate concentrations can be extracted with 9 M hydrochloric acid. Polythionate concentrations can then be determined directly using ion chromatographic methods, and laboratory results indicate recovery of up to 90% for synthetic polythionate solutions using AG2-X8 resin columns.

Introduction

Presence of inorganic sulfoxyanions in natural waters

Sulfur is predominantly present as sulfate in aerated waters and as sulfidic sulfur (H₂S and HS⁻) in anaerobic waters undergoing sulfate reduction. However, in addition to sulfate and sulfidic sulfur, natural waters may also contain some combination of the following: bisulfite (HSO₃⁻), sulfite (SO₃²⁻), polysulfides (H₂⁻Sₙ⁻S⁻), polythionates (SₙO₄²⁻) and thiosulfate (S₈O₆²⁻). These species are sometimes collectively referred to as intermediate sulfur species (ISS) because the average oxidation state of sulfur in these species is between that of sulfidic-sulfur (−II) and that of sulfate-sulfur (VI).1,2 Except for the polysulfide species all other ISS are sulfoxyanions. On the basis of equilibrium speciation calculations, the concentration of none of the sulfoxyanions is expected to be higher than 0.01% of the total dissolved sulfur concentration, S_{tot}. Hence, if 10⁻⁷ molal are taken as a reasonable upper limit for the concentration of total dissolved sulfur in most fresh waters and hydrothermal waters,3 none of the sulfoxyanions are expected to have concentrations over 1 μM.

However, several studies have reported sulfoxyanion concentrations well in excess of 1 μM. For example, thiosulfate in three brines collected from the French Dogger Formation ranged in concentration from 100 to 200 μM (S_{tot} ranged from 6.88 to 7.3 mM).4 Thiosulfate concentrations of 705 to 875 μM were reported for Champagne Pool, New Zealand (S_{tot} = 2.5 × 10⁻³ M).5,6 A survey of twenty-seven Bulgarian hydrothermal waters found thiosulfate concentrations ranging from 5 to 38 μM along with sulfite concentrations ranging from 5 to 20 μM for waters with S_{tot} less than 3100 μM.7 Thiosulfate concentrations up to 36 μmol L⁻¹ were found in several Italian hot springs with sulfide-bearing waters with a S_{tot} of around 12 mmol L⁻¹.8 In an extensive survey of the hot springs of Yellowstone National Park, Allen and Day9,10 reported thiosulfate concentrations for several alkaline hot-spring waters. For example, a thiosulfate concentration of 45 μM for Ojo Caliente which has a S_{tot} of about 250 μM was reported. Xu et al.11,12 determined thiosulfate in about 40 hot-spring waters in Yellowstone National Park. They found elevated sulfoxyanion concentrations in several pools, including a thiosulfate concentration in Azure Spring at about 20 mol% of S_{tot} and tens of μmol concentrations of polythionate in Cinder Pool.11,12

High polythionate concentrations are often found in acid crater lakes associated with active volcanoes and some acid hot springs. A high total polythionate concentration of 113 μM (average n = 5.5, S_{tot} = 3.1 × 10⁻³ M) was found in a sample taken from Ketetahi Cauldron, Tongariro National Park, New Zealand.8 For Ruapehu Crater Lake, New Zealand, in three brines collected from the French Dogger Formation ranged in concentration from 100 to 200 μM (S_{tot} ranged from 6.88 to 7.3 mM).4 Thiosulfate concentrations of 705 to 875 μM were reported for Champagne Pool, New Zealand (S_{tot} = 2.5 × 10⁻³ M).5,6 A survey of twenty-seven Bulgarian hydrothermal waters found thiosulfate concentrations ranging from 5 to 38 μM along with sulfite concentrations ranging from 5 to 20 μM for waters with S_{tot} less than 3100 μM.7 Thiosulfate concentrations up to 36 μmol L⁻¹ were found in several Italian hot springs with sulfide-bearing waters with a S_{tot} of around 12 mmol L⁻¹.8 In an extensive survey of the hot springs of Yellowstone National Park, Allen and Day9,10 reported thiosulfate concentrations for several alkaline hot-spring waters. For example, a thiosulfate concentration of 45 μM for Ojo Caliente which has a S_{tot} of about 250 μM was reported. Xu et al.11,12 determined thiosulfate in about 40 hot-spring waters in Yellowstone National Park. They found elevated sulfoxyanion concentrations in several pools, including a thiosulfate concentration in Azure Spring at about 20 mol% of S_{tot} and tens of μmol concentrations of polythionate in Cinder Pool.11,12

High polythionate concentrations are often found in acid crater lakes associated with active volcanoes and some acid hot springs. A high total polythionate concentration of 113 μM (average n = 5.5, S_{tot} = 3.1 × 10⁻³ M) was found in a sample taken from Ketetahi Cauldron, Tongariro National Park, New Zealand.8 For Ruapehu Crater Lake, New Zealand,
Hence, there are a number of studies that suggest sulfoxynians persist at higher concentrations in various types of natural waters than expected based on equilibrium thermodynamics. The occurrence of non-equilibrium concentrations of sulfoxynians in natural waters is likely to result from sluggish and often incomplete redox reactions involving hydrogen sulfide, sulfur dioxide, or sulfate. The two most important redox processes in which sulfoxynians form are the oxidation of hydrogen sulfide and the reduction of sulfate. Oxidation of hydrogen sulfide in O$_2$-bearing waters proceeds via the formation of thiosulfate and elemental sulfur as demonstrated in several laboratory studies and field studies. This process has been documented to occur in Cinder Pool, Yellowstone National Park. Reduction of sulfate proceeds via microbial pathways via poorly understood mechanisms. Sulfidic sulfur is typically the main product of microbial sulfate reduction but thiosulfate is also formed in sediments and acts as a link between sulfate reduction and hydrogen sulfide oxidation in sediments. Thermochemoautotrophic sulfate reduction yields elemental sulfur as well as hydrogen sulfide. Interaction of sulfidic water with elemental sulfur can lead to waters with a high thiosulfate concentration.

Incomplete oxidation of SO$_2$ may play a role in the ISS distribution in crater lakes on active volcanoes. Releases of magmatic SO$_2$ gas in a crater lake can lead to complex sulfur speciation dominated by sulfate with polythionates as a minor species. Many acid crater lakes are underlain by a pool of molten sulfur which interacts with the crater-lake water to produce a complex sulfur speciation that includes polythionates. Thus, monitoring of ISS in crater lakes may be a viable method to characterize changes in SO$_2$ release, an important indicator of potential volcanic activity.

The presence and persistence of sulfoxynians in natural waters is potentially of importance in several other processes. Sulfoxynians may play a role in the transport of metals. Experimental studies suggest that sulfite and thiosulfate form stable complexes with gold and silver. Hence, if the concentration of these oxyanions is significant they may account for some of the mobility of gold and silver in natural waters. Sulfoxynians are also thought to play an important role in the isotopic equilibration of sulfate-sulfur and sulfidic-sulfur. The isotopic equilibration of sulfate-sulfur and sulfidic-sulfur in a hydrothermal system must proceed via a sequence of reactions where a sulfur($n$) species is reduced to a sulfur($n$−$n$) species and vice versa. One such scheme involves the formation of thiosulfate. Finally, many microorganisms can use thiosulfate and polythionates as an energy source during oxidation or reduction.

Sampling and analysis of dissolved S species in natural waters

Given the geochemical importance of dissolved sulfide, sulfate, and the potential importance of sulfoxynians in natural water, it is important to be able to determine the sulfur speciation in a wide range of natural solutions. In the last two decades, several studies have been published presenting analytical methods for the determination of sulfidic sulfur, sulfoxynians, sulfur oxyanions and sulfide species, as well as inorganic S-species and thiols in natural waters and waste waters. Analytical schemes for the determination of complete or nearly complete sulfur speciation in aliquots withdrawn from H$_2$S oxidation experiments have been presented in several studies. In addition, several papers have discussed the general problems in sampling and preserving unstable (i.e., volatile or reactive) constituents in natural waters.

The sampling, preservation and analysis of sulfur species in spring waters and hot spring waters presents a major challenge because the discharging water is often far from equilibrium with the atmosphere. Upon discharge, processes such as degassing (e.g., CO$_2$, H$_2$S), mineral precipitation (e.g., BaSO$_4$, CaCO$_3$), and oxidation (H$_2$S) may drastically change the chemical composition, including the sulfur speciation, of the water. Most of these processes proceed even after a sample has been collected and sealed in a bottle. Hence, either the analyses have to be conducted immediately after collection of the sample, which is often impractical, or the sample must be preserved so that later analysis is meaningful. Several studies have evaluated the effect of prolonged storage on preserved, sealed samples.

Previous studies using resins to determine dissolved sulfur species

Resins have been used before in the field and laboratory to concentrate dissolved ionic constituents and sequester redox species (e.g., As(III)). Resins capable of retaining anions have been used in the past to separate sulfoxynians, sulfide and sulfate from waste waters and ground waters. In all these prior studies, the resin was used to sequester the dissolved species, followed by a sequential elution to allow for the analyses of the different types of sulfur species. In one study an anion exchange resin was used to remove dissolved sulfide from an alkaline groundwater.

Present study objectives

The primary objective in this study was to evaluate the use of anionic resins to sequester sulfur oxyanions from hydrothermal solutions and crater lakes. Field tests and laboratory experiments were conducted to evaluate the technique. In addition the technique was used in the determination of the sulfur species of a stratified lake with high dissolved sulfide and sulfate concentrations. Subsequent field studies in Yellowstone National Park and a field study of the hydrothermal springs in Lassen Volcanic National Park using the technique presented in this paper will be published separately.

Methods

Selection of resin

The selection of a resin is dictated by the objectives of the application. In this study the primary objective was to sequester the sulfoxynians from a hydrothermal solution and subsequently elute these species, followed by analysis using ion chromatography (IC). The selectivity of an anion resin is

_Takano et al._ reported an extensive survey of polythionate concentrations. Some of the samples contained considerable amounts of polythionates. For example, sample R18F collected at Ruapehu Crater Lake contained 1.95 mM S$_4$O$_6^{2-}$, 2.1 mM S$_3$O$_8^{2-}$, and 0.82 mM S$_2$O$_4^{2-}$. The total amount of S represented by these three polythionates accounts for 12% of the total dissolved sulfur in this water. There are more studies that report sulfoxynian concentrations than summarized here, but none of these other studies provide enough data to evaluate the abundance of sulfoxynians in relation to the total sulfur in these waters.

Geochem. Trans., 2003, 4(3), 12–19
governed by the type of functional groups present on the resin. Anionic resins, such as the ones used in this study (Bio-Rad\textsuperscript{\textregistered} AG), consist of a styrene divinylbenzene copolymer lattice with quaternary ammonium functional groups saturated with counter ions. Ion exchange takes place at the functional groups if the resin is exposed to a solution that contains anions for which the functional groups have a higher selectivity than the counter ions. Most anion exchange resins are sold with chloride as the counter ion (CI-form). Through exchange it is possible to change the composition of the counter ion; for example, a resin can be converted from the CI-form to the OH-form.\textsuperscript{71} The chloride form of these resins exhibits a significantly better resistance to high temperature (up to 150 °C) applications (Bio-Rad, 1999) than the OH-form. Hence, the CI-form was used in this study because of the high temperature of the waters studied, but for some applications it may be advantageous to convert the resin to, for example, the OH-form.

Two types of AG resins, the Bio-Rad\textsuperscript{\textregistered} AG1-X8 and AG2-X8, both sold in the CI-form, were evaluated in this study. These two resins are analytical-grade Dowex anion exchange resins with the same styrene divinylbenzene copolymer lattice. The percentage of cross-linking in the copolymer lattice controls its porosity. A high porosity allows large molecules, such as proteins and antibodies, to penetrate the resin and exchange, whereas a low porosity excludes large molecules from exchanging with the resin. The two resins used in this study are 8% cross linked and are particularly suitable for the exchange of inorganic anions.\textsuperscript{63} Ion exchange takes place at the functional groups if the resin is exposed to a solution that contains anions with ions of like charge, therefore oppositely charged or neutral species will not be retained on the counterion sites. Hence, the composition of the functional groups (AG2-X8 replaces a sulfonylamide group with quaternary ammonium functional groups saturated with nanoparticles) affects the relative selectivity of the resins.

The relative selectivity of a sample ion with respect to the counterion determines how strongly, if at all, a sample ion will bind to the resin (Table 1). The counterions are only exchanged with ions of like charge, therefore oppositely charged or neutral species will not be retained on the counterion sites. Hence, dissolved H\textsubscript{2}S, O\textsubscript{2}, and potentially reactive transition metals will not be retained on these sites. Though neutral species may be retained to some degree in a resin through a process which forms the basis for ion-exclusion chromatography, it is reasonable to expect separation of neutral and ionic species. As noted above it has been our experience that the presence of these two constituents in a sample changes the sulfoxation speciation upon storage. Therefore, sequestering the sulfoxoanions on a resin and separating these species from H\textsubscript{2}S, O\textsubscript{2}, and transition metal-bearing solutions (by loading the resin and flushing with deoxygenated water) avoids this problem. Chloride counterions are replaced by anions in the sample with higher selectivity, therefore, require a greater concentration, it is important to ensure that there will be enough resin to retain equivalent anions in the sample. Bio-Rad\textsuperscript{\textregistered} AG1-X8 and AG2-X8 resins are listed with a binding capacity of 1.2 meq l\textsuperscript{−1}. As with any analytical technique, care should be exercised that this value is accurate. The volume of resin used to sample any quantity of sample should be chosen so as to ensure that there will be an excess of available sites. Exceeding the capacity of the resin will result in incomplete capture of ions and lowered efficiency of the method.

### Table 1

| Ion          | Selectivity with respect to OH \textsuperscript{−} |
|--------------|-----------------------------------------------|
| Cl\textsuperscript{−} | 22                                            |
| SO\textsubscript{4}\textsuperscript{2−}, HSO\textsubscript{4}\textsuperscript{−} | 85                                            |
| S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−} (n > 2) | Fully retained |

### Column preparation

Bio-Rad\textsuperscript{\textregistered} Anion-exchange resins AG1-X8 and AG2-X8 (both 100–200 mesh size, chloride form), with a 1.2 meq ml\textsuperscript{−1} capacity were used in laboratory experiments and field experiments. Both the Bio-Rad\textsuperscript{\textregistered} AG1-X8 and AG2-X8 resins were obtained in loose form, and were packed in columns of desired length before use. Columns were prepared (see Fig. 1) by cutting pre-made columns of approximately 2 cm diameter to the desired length, and filled with an appropriate volume of resin (Bio-Rad\textsuperscript{\textregistered} resin columns are conveniently marked in ml increments).

To fill the column with resin, a polyethylene frit was inserted into the bottom, and a slurry of the resin (prepared using nanopure water, resistance > 18 MΩ) was poured in. The water was allowed to drip out of the open end, compacting the saturated resin in the column. No air pockets should form in the resin, and the column was re-packed upon observation of any empty spaces. Another frit was inserted onto the top of the resin and a male tubing connector wrapped with Teflon\textsuperscript{®} tape was snugly inserted into the column. The packed column was then flushed with nanopure water through a syringe and connecting tubing, and sealed with plastic caps. The all-plastic construction of the columns is well-suited for fieldwork and shipping.

### Sampling

All laboratory and field samples were collected in 5–60 ml sterile plastic syringes and pressed through a 0.45 μm syringe filter before passing the solution through the prepared exchange resin columns. To improve the interaction between the sample ion and resin, the flow rate did not exceed 3 mL min\textsuperscript{−1} (which can be measured by timing how fast a graduated cylinder or falcon tube is filled). In preliminary lab experiments we found that at higher flow rates the sample ions are not always fully retained, presumably due to the shorter contact time. The volume of each sample was carefully measured by

---

**Fig. 1:** A: Schematic of resin column; B: picture.
collecting the effluent in a volumetric flask of appropriate size. In all laboratory experiments, the sample solution passed through the columns was collected and analyzed for sulfonions to evaluate whether these species were completely retained on the column. These results indicated that the resin retained all of the sulfonions of interest. After the desired volume of sample had been passed through the column, 30–40 ml of nanopure water were passed through the column to displace any remaining sample solution. This step is important because it removes residual H₂S dissolved in the sample fluid. After flushing, the column was capped, shipped, and stored until elution of the retained species could be carried out.

**Elution**

Sequential elutions from the AG2-X8 with 0.1 M KCl, 0.5 M KCl, and 4 M KCl were carried out to remove SO₄²⁻, S₂O₃²⁻, and S₄O₆²⁻, respectively (Fig. 2). Sequential elutions for the AG1-X8 resin were additionally made with 1 and 3 M KCl solutions. KCl eluents were made from reagent grade KCl salt and 18 MΩ water. A peristaltic pump with Tygon tubing was used to pass each eluent through the columns at a flow rate between 0.75 and 2.0 ml min⁻¹. Total sample recovery was found to be independent of flow rate, but the ability to concentrate analyte in smaller volume aliquots was found to be affected by flow rates due to dispersion of the analyte breakthrough curve.

Elution of a column must begin with the lowest eluent concentration (0.1 M KCl) for elution of the SO₄²⁻ while leaving the other sulfonions on the column. Elution for thiosulfate utilizes a 0.5 M KCl solution. Elution for polythionates can be accomplished with a 4 M KCl eluent acidified to 0.01 M HCl for better preservation of the polythionates as they are eluted. 9 M HCl was also used as an eluent for polythionate extraction (from ACS reagent grade 35% HCl). Each eluted aliquot was weighed by difference using a Mettler analytical balance. Samples were diluted by weight on a Mettler analytical balance in the IC autosampler vials and thoroughly mixed by inversion before analysis.

**Analysis**

Eluted aliquots were analyzed using an isocratic elution with a concentrated sodium bicarbonate-sodium carbonate eluent over a run time of 15 minutes with a Dionex DX-500 Ion Chromatography system (ED40 electrochemical detector, GP50 gradient pump, and AS40 Autosampler), employing an AS4A-SC analytical column. Data collection, standardization, and chromatograph manipulation were accomplished using the Dionex PeakNet 5.1 software package. The 18 mM CO₃⁻/28 mM HCO₃⁻ eluent was prepared from the Fischer Scientific analytical grade Na-salts. Polythionates were detected with the same IC system using an isocratic 30% acetonitrile : H₂O eluent containing 2 mM tetrabutylammonium hydroxide, buffered with 3 mM NaHCO₃/3 mM Na₂CO₃ and run through an IonPac NS1 column. The method was modified from Zou et al. Utilizing the reaction of thiosulfate with hydrogen peroxide. Purity of the thionate salt was determined by gravimetry and chromatographic analyses to be greater than 99%. These stock solutions were diluted to yield a series of standards. The standards were matrix-matched to 0.1 M KCl. All standards and samples were analyzed in triplicate for each run, with check standards between every fifth sample (all check standards were analyzed to at least 95% consistency compared to other standards).

The sulfonion concentration in the original solution loaded onto the column is calculated in four steps. First the concentration of the sulfonions in each of the eluted fractions is calculated by correcting for any dilution that was necessary to analyze the fraction. The concentrations are expressed in moles per kilogram of solution. Secondly, the actual number of moles eluted is calculated by dividing the concentration calculated in step one by the mass of the fraction (kg). The number of moles of each species is then summed over all eluted fractions for a given column. That sum is divided by the sample mass that was passed through the column to yield the concentration of each species in the original solution.

**Field tests**

Field tests of the AG1-X8 and AG2-X8 resins were conducted in Yellowstone National Park during the summers of 1997 and 1998. These tests consisted of comparing on-site analyses of sulfonions with analyses of sulfonions eluted from resin columns. The resin columns were loaded at the same time water samples were collected for on-site analyses. The on-site analyses were carried out in a mobile lab equipped with a Dionex 2010I IC. The mobile lab, operated and maintained by the USGS, was parked as close as possible to the hot springs used for the tests (from several meters to several hundred meters away depending on specific location). Procedures for the collection of water samples in Yellowstone National Park and on-site analyses of sulfonions as well as total dissolved sulfide have been described in earlier papers. On-site analysis of H₂S was accomplished using a Hach DR-2000 portable spectrophotometer and a standard colorimetric method (Hach method #8131). Loaded resin samples were collected and transported back to the laboratory where they were analyzed from several days to several weeks after initial collection.

**Results and discussion**

For several years our research team has attempted to develop a sampling strategy that involved the use of additives to stabilize...
thiosulfate in hot-spring waters\textsuperscript{23} and sulfide-rich ground waters.\textsuperscript{60} For example, we experimented with adding zinc or cadmium chloride to water sample to quantitatively remove dissolved sulfide and preserve polythionates and thiosulfate. The expectation was that this would prevent the formation of thiosulfate and polythionates as a result of sulfide oxidation. However, studies of the stability of samples taken at Cinder Pool and Ojo Caliente, Yellowstone National Park, showed that the sulfoxyanion speciation changed over time (Table 2). Results from a study of samples taken at Cinder Pool showed that the concentrations of thiosulfate and polythionates changed over a time scale of weeks to months. We have also found that the thiosulfate concentration can change within minutes after sampling. In a field test at Ojo Caliente, Yellowstone National Park, two samples were taken. To one sample a CdCl\textsubscript{2} solution was added, while the other sample was left untreated (Fig. 3). Immediately after collection (and CdCl\textsubscript{2} addition), both samples were cooled by placing the bottles in ice water. Both samples were analyzed within 10 minutes after sampling using an IC in the mobile lab. The analysis was repeated after five minutes. We found that in the presence of Cd the thiosulfate concentration was higher than the untreated sample, and appeared to increase somewhat over time, whereas the untreated sample gave the same concentration for both analyses. Problems such as these spurred the development of this resin technique.

| Sample | Treatment | Field, 8/23/95 | Lab, 9/21/95 | Lab, 7/20/96 |
|--------|-----------|----------------|--------------|--------------|
| S\textsubscript{2}O\textsubscript{3} | Standard\textsuperscript{a} | 46.5 | 46.7 | 42.9 |
| S\textsubscript{2}O\textsubscript{3} | Standard\textsuperscript{a} | 21.2 | 20.6 | 19.0 |
| SCN | Standard | 9.2 | 9.5 | 9.3 |
| SCN | Standard | 3.5 | 3.6 | 3.7 |
| CD-2 | None | 45.0 | 17.1 | 6.2 |
| CD-2 | ZnCl\textsubscript{2} | 45.5 | 50.4 | 53.3 |
| CD-2 | KCN | 53.2 | 52.0 | 60.3 |
| CD-3 | None | 43.5 | 11.7 | 10.4 |
| CD-3 | ZnCl\textsubscript{2} | 43.8 | 48.2 | 50.0 |
| CD-3 | KCN | 48.9 | 52.1 | 51.9 |
| CD-4 | None | 42.9 | 16.19 | 7.6 |
| CD-4 | ZnCl\textsubscript{2} | 42.8 | 46.1 | 48.3 |
| CD-4 | KCN | 45.5 | 48.3 | 52.4 |

\textsuperscript{a}Thiosulfate standards have pH > 7. In the field KCN was added to the samples to convert polythionates to SCN\textsuperscript{−} using cyanolysis.\textsuperscript{74} Hence, this test pertains to the stability of SCN\textsuperscript{−} over time as a measure of polythionate concentration and the formation of additional polythionate over time, which would be converted to SCN\textsuperscript{−} in the bottle.

![Fig. 3](image_url) Effect of addition of Cd on thiosulfate concentration. Test conducted at Ojo Caliente, YNP. 0.5 mL 0.5 M Cd acetate was added to 60 mL sample. Analysis were conducted on site using a mobile lab parked next to the spring.

![Fig. 4](image_url) Recovery of sulfate and thiosulfate from a synthetic solution loaded on AG1-X8 resin column as a function of eluent (KCl) concentration.

**Laboratory experiments**

AG1-X8 resins were tested in the laboratory using SO\textsubscript{4}\textsuperscript{2−} and S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} eluted with varying concentrations of eluents. The results (Fig. 4) indicate the eluent concentrations most effective for extracting of SO\textsubscript{4}\textsuperscript{2−}, and S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} are 1 and 3 M KCl solutions. Recovery of these two species from the resin was between 89 and 100%. Several eluents were also tested for eluting S\textsubscript{4}O\textsubscript{6}\textsuperscript{2−} from the AG1-X8 resin, including 6 M HCl, 9 M HCl, 12 M HCl, and 6 N H\textsubscript{2}SO\textsubscript{4} without success.

AG2-X8 resins were tested in the laboratory using SO\textsubscript{4}\textsuperscript{2−}, S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}, and S\textsubscript{4}O\textsubscript{6}\textsuperscript{2−}. Several test solutions were formulated to represent hydrothermal solutions from circumneutral to extremely acidic (down to a pH of approximately 0.5) conditions over a range of temperatures (20–75°C). Resin performance was not noticeably affected by any changes in temperature or acidity. Eluents of 0.1 and 0.5 M KCl were found to be efficient in the extraction of SO\textsubscript{4}\textsuperscript{2−}, and S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} from the resin column, respectively. Recovery of these two species from the resin was between 90 and 100% in laboratory tests.

The detection limit of thiosulfate in natural waters can be significantly reduced by increasing the ratio of sample size to aliquot size. By concentrating a majority of the thiosulfate in one or two aliquots of 20–40 mL volume, the sample can be pre-concentrated before analysis by IC. For example, if 1000 mL of a solution containing 1 μmol L\textsuperscript{−1} S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} is loaded on a resin column and all the thiosulfate is eluted in 40 mL, the thiosulfate concentration in this fraction will be 25 μmol L\textsuperscript{−1}. Several concentrations of HCl were tested to determine the
Judicious distribution of eluted aliquots can lower the detection rate and total concentration of anions passed over any volume of resin. The number of anions cannot exceed the total number of binding sites and they must have sufficient time to bind and become immobilized on the resin. Although polythionates were detected at Cinder Pool in the summer of 1997, the AG1-X8 resin exhibited too high a binding capacity with respect to polythionates for those species to be extracted from the resin (Table 1).

Field testing of the AG2-X8 resin was conducted at several hydrothermal pools in Yellowstone National Park in September, 1998. Water samples were collected at pools in Yellowstone National Park and analyzed on-site by IC using the U.S. Geological Survey mobile lab and at SUNY-Stony Brook within two weeks after collection. Sample resin columns were analyzed 1–2 weeks after they were loaded in the field, demonstrating the resin’s ability to stabilize the sulfoxanions in time.

Comparison of thiosulfate results from on-site IC analysis and IC analysis of AG2-X8 resin column elutions at SUNY-Stony Brook indicates agreement between 87 and 96% for 5 samples from pools in the Norris Geyser Basin (Fig. 6). Cinder Pool (in the Norris Geyser basin) was sampled in 2 different locations (outer and inner sections of the pool), and 2 samples in each location were analyzed using the resin columns and the on-site IC. The 4 resin column samples were eluted at SUNY-Stony Brook and analyzed for thiosulfate by IC, resulting in an average concentration of 50.7 μm, a range of 48.1 to 52.2 μm, and a standard deviation of 1.7 μm. No polythionates were detected in Cinder Pool in the summer of 1998 on site, and no polythionates were detected samples taken at the site in 1998 using the AG2-X8 resin columns.

Example application

The AG2-X8 resin also was used at Green Lake, a meromictic glacial lake located at Green Lake State Park in Fayetteville, New York during the summer of 1998. Green Lake is a stratified lake, with a chemocline at about 20 meters depth. The lowest concentration effective for extraction of $S_2O_6^{2-}$ from the AG2-X8 resin. The AS4A-SC column used on the IC can not be used with acid concentrations over 1 M; thus, any sample aliquots will have to be diluted to below 1 M. 9 M HCl was found to be up to 90% efficient in the removal of $S_2O_6^{2-}$. Judicious distribution of eluted aliquots can lower the detection limit for $S_2O_6^{2-}$, but the 10-fold dilution required for IC analysis (due to limits of sample acidity for the column) of $S_2O_6^{2-}$ makes it necessary.

Tetrathionate can also be eluted from the AG2-X8 resin using 4 M KCl. The results of this test are presented in Fig. 5. An acidified tetrathionate solution (pH 0.5) was passed through an AG2-X8 column. Fig. 5A shows the tetrathionate solution before it was loaded onto the column. Fig. 5B shows the tetrathionate solution after it has passed through the column. It is clear from Fig. 5B that all of the tetrathionate is retained. Fig. 5C shows the 4 M KCl elution, which is dominated by tetrathionate but also contains some trithionate. Trithionate is likely a product of a rearrangement reaction which would be important below pH 0.5. About 90% of the initial tetrathionate was recovered in this laboratory test. On the basis of these results, we recommend that the elution of the polythionate fraction on the AG2-X8 fraction be carried out with 4 M KCl, rather than 9 M HCl. The 4 M KCl eluent should also be acidified to approximately 0.01 M HCl in order to better preserve the polythionates in solution before analysis. It is possible that higher polythionates cannot be recovered with a 4 M KCl eluent, because higher polythionates are expected to be more strongly retained than tetrathionate. However, tetrathionate is typically one of the most abundant, if not dominant, $S_2O_6^{2-}$ species in natural waters. If necessary, the 4 M KCl elution can be followed with a 9 M HCl extraction to recover higher polythionates. If the 4 M KCl elution does not yield any tetrathionate, higher polythionates will likely not be measurable. Hence, there is no need to work with 9 M HCl, which requires a great deal of caution.

Field testing

Field testing of the AG1-X8 resin was conducted at Yellowstone National Park in the summer of 1997 at 5 different hydrothermal pools. Water samples were also collected at these pools and analyzed on-site by IC using the U.S. Geological Survey mobile lab and at SUNY-Stony Brook within two to three weeks after collection. Comparison of thiosulfate results from on-site IC analysis and IC analysis of AG1-X8 resin column elutions at SUNY-Stony Brook indicates 96 to 100% agreement for three pools (Cinder Pool, Cistern, and an unnamed pool near Cistern) and 76 and 63% agreement for two pools (Sulfur Dust and Frying Pan). The poor agreement for the last two pools was likely not due to overloading of the anion-exchange resin columns (which should not have become saturated from the anion chemistry reported in Xu et al.17). It is possible that the solution was passed through the columns at too fast a rate for complete binding of the anions. It is important to note that complete binding depends on both the rate and total concentration of anions passed over any volume of resin. The number of anions cannot exceed the total number of binding sites and they must have sufficient time to bind and become immobilized on the resin. Although polythionates were detected at Cinder Pool in the summer of 1997, the AG1-X8 resin exhibited too high a binding capacity with respect to polythionates for those species to be extracted from the resin.

Comparison of thiosulfate results from on-site IC analysis and IC analysis of AG2-X8 resin column elutions at SUNY-Stony Brook indicates agreement between 87 and 96% for 5 samples from pools in the Norris Geyser Basin (Fig. 6). Cinder Pool (in the Norris Geyser basin) was sampled in 2 different locations (outer and inner sections of the pool), and 2 samples in each location were analyzed using the resin columns and the on-site IC. The 4 resin column samples were eluted at SUNY-Stony Brook and analyzed for thiosulfate by IC, resulting in an average concentration of 50.7 μm, a range of 48.1 to 52.2 μm, and a standard deviation of 1.7 μm. No polythionates were detected in Cinder Pool in the summer of 1998 on site, and no polythionates were detected samples taken at the site in 1998 using the AG2-X8 resin columns.

Fig. 5 Results of AG2-X8 resin elution with 4 M KCl elution.

Fig. 6 Comparison of results for three techniques used for thiosulfate analyses for five thermal springs in the Norris Geyser Basin at Yellowstone National Park in September, 1998.

Geochem. Trans., 2003, 4(3), 12–19
Table 3 Results from Green Lake, Fayetteville, NY

| Sample depth/m | H₂S/μmol L⁻¹ | SO₄²⁻/μmol L⁻¹ | S₂O₃²⁻/μmol L⁻¹ |
|---------------|--------------|-----------------|-----------------|
| 15            | 0.7          | 568.7           | 0               |
| 20            | 10.0         | 680.5           | 0               |
| 22            | 343.5        | 690.8           | 22.0            |
| 24            | 406.6        | 684.7           | 0               |
| 30            | 472.7        | 682.0           | 13.6            |

chemocline supports a pink microbial community and contains up to 22 μmol L⁻¹ thiosulfate (Table 3). Using a depth sampler, water was brought up from above, below, and within this transition layer. Each sample was loaded onto an AG2-X8 resin column, taken back to SUNY-Stony Brook, and analyzed for thiosulfate and polythionates by IC after 2–5 days. Hydrogen sulfide concentrations were determined on site (HACH method 8131). No attempt was made to determine sulfur present as FeS, elemental sulfur, polysulfide, or other forms of sulfur that may explain the apparent mass balance fluctuations in the profile.

Conclusions

Sampling of metastable sulfoxyanions may be reliably and reproducibly accomplished under a variety of field conditions using Bio-Rad® AG2-X8 anion-exchange resin columns. Using a series of eluents of increasing Cl concentration, sulfate, thiosulfate, and polythionates can be eluted sequentially. Recoveries of 87–100% for known concentrations of thiosulfate and polythionate in laboratory and field tests indicates that the method is more reliable over time than other methods of sample preservation. Laboratory and field testing over a significant range of temperature and acidity indicates this technique may be readily applied to nearly any environment; use of AG2-X8 resin columns is being planned for use in both highly acidic mine waste waters and in hot, highly acidic crater lake waters. The resin method presented here is particularly useful for the sampling of sulfide-rich waters. Continued reaction of dissolved hydrogen sulfide and molecular oxygen changes the sulfoxyanion concentrations. Field tests have shown that adding of zinc or cadmium to precipitate the sulfide does not prevent these reactions from taking place. In fact, the metal sulfides may catalyze certain reactions.

The ruggedness, as well as small size and weight of the plastic columns facilitates handling in the field. Furthermore, it is possible to ship columns and elute the columns several weeks after sampling.

Acknowledgements

The U.S. National Park Service Staff at Yellowstone National Park is thanked for their help during the field studies. The New York State Department of Parks is thanked for their assistance at Green Lake, NY. The participation of the Stony Brook group in this project was supported through grants from NSF-EAR to M. Schoonen. A few of the laboratory tests were conducted in the Department of Geology and Geophysics, University of Wisconsin-Madison.

References

1. M. A. Schoonen, Mecanisms of pyrite and marcasite formation from solution between 25 and 300°C, in Geology, Pennsylvania State University, University Park, 1989.
2. M. A. Williamson and J. D. Rimstidt, Correlation between structure and thermodynamic properties of aqueous sulfur species, Geochim. Cosmochim. Acta, 1992, 56, 3867-3880.
3. H. L. Barnes, Solubilities of ore minerals, in Geochemistry of Hydrothermal Ore Deposits, ed. H. L. Barnes, John Wiley & Sons, New York, 1979, p. 406-460.
4. J. Boulegue, Metastable Sulfur Species and Trace-Metals (Mn, Fe, Cu, Zn, Cd, Pb) in Hot Brines from French Dogger, Am. J. Sci., 1978, 278(10), 1394-1411.
5. J. G. Webster, Thiosulfate in surficial geothermal waters, North Island, New Zealand, Appl. Geochem., 1987, 2(5-6), 579-584.
6. J. G. Webster, An analytical scheme for the determination of sulfide, polysulfide, thiosulfate, sulfite and polythionate concentrations, DSIR, Petone, New Zealand, 1989.
7. E. Veldeman, L. Vantdack, R. Gijsels and E. N. Pentecheva, Sulfur Species and Associated Trace-Elements in South-West Bulgarian Thermal Waters, Appl. Geochem., 1991, 6(1), 49-62.
8. A. Pentecost, The Microbial Ecology of Some Italian Hot-Spring Travertines, Microbios, 1995, 81(326), 45-58.
9. E. T. Allen, The hot springs of the Yellowstone National Park, Carnegie Inst. Washington News Serv. Bull. School Ed., 1936, 4(1), 1-20.
10. E. T. Allen and A. L. Day, in Hot Springs of the Yellowstone National Park. Microscopic examinations by Herbert Eugene Merwin, Carnegie Institution of Washington, Washington, DC, 1935, vol. 466, p. 525.
11. Y. Xu, M. A. A. Schoonen, D. K. Nordstrom, K. M. Cunningham and J. W. Ball, Sulfur geochemistry of hydrothermal waters in Yellowstone National Park, Wyoming, USA. II. Formation and decomposition of thiosulfate and polythionate in Cinder Pool, J. Volcanol. Geotherm. Res., 2000, 97(1-4), 407-423.
12. Y. Xu, M. A. A. Schoonen, D. K. Nordstrom, K. M. Cunningham and J. W. Ball, Sulfur geochemistry of hydrothermal waters in Yellowstone National Park: I. The origin of thiosulfate in hot spring waters, Geochim. Cosmochim. Acta, 1998, 62(23-24), 3729-3743.
13. D. J. O’Brien and F. B. Birken, Kinetics of oxidation of reduced sulfur species in aqueous solutions, Environ. Sci. Technol., 1977, 11, 1114-1120.
14. J. Z. Zhang and F. J. Millero, The Products from the Oxidation of H₂S in Seawater, Geochim. Cosmochim. Acta, 1993, 57(8), 1705-1718.
15. J.-Z. Zhang, The chemistry of the anoxic waters in the Cariaco Trench, Deep-Sea Res., 1993, 40(5), 1023-1041.
16. J. Z. Zhang and F. J. Millero, Kinetics of Oxidation of Hydrogen-Sulfide in Natural-Water, Environ. Geochemistry of Sulphate Oxidation, ed. C. N. Alpers and D. B. Blowes, American Chemical Society, Washington, DC, 1994, pp. 393-409.
17. J. Z. Zhang and F. J. Millero, Investigation of Metal Sulfide Complexes in Sea-Water Using Cathodic Striping Square-Wave Voltammetry, Anal. Chim. Acta, 1997, 329, 529-537.
18. Y. Xu and M. A. A. Schoonen, The stability of thiosulfate in the presence of pyrite in low-temperature aqueous solutions, Geochim. Cosmochim. Acta, 1995, 59(22), 4605-4622.
19. Y. Xu, M. A. A. Schoonen, D. K. Nordstrom, K. M. Cunningham and J. W. Ball, Formation, reactivity, stability, and analysis of thiosulfate and polythionates in hydrothermal waters, in Crater Lakes, Terrestrial Degassing and Hyper-acid Fluids in the Environment, Crater Lake, Oregon, AGU-Chapman Conference, 1996.
20. D. E. Canfield and D. J. D. Marais, Aerobic sulfate reduction in microbial mats, Science, 1991, 251(5000), 1471-1473.
21. B. B. Jorgensen and F. Bak, Pathways and microbiology of thiosulfate transformations and sulfate reduction in a marine sediment (Kattegat, Denmark), Appl. Environ. Microbiol., 1991, 57(3), 847-856.
22. B. B. Jorgensen, Sulfate reduction and thiosulfate transformations in a cyanobacterial mat during a diel oxygen cycle, FEMS Microb. Ecol., 1994, 13(4), 303-312.
23. M. B. Goldhaber and W. L. Orr, Kinetic controls on thermochemical sulfate reduction as a source of sedimentary H₂S in
