Environ. Sci. Technol. **2000**, *34,* 4651−4655

Extraction and Quantitative Analysis of Elemental Sulfur from Sulfide Mineral Surfaces by High-Performance Liquid Chromatography

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A simple method for the quantitative determination of elemental sulfur on oxidized sulfide minerals is described. Extraction of elemental sulfur in perchloroethylene and subsequent analysis with high-performance liquid chromatography were used to ascertain the total elemental sulfur resulting from the oxidation of arsenopyrite, pyrite, marcasite, chalcopyrite, and chalcocite under various conditions. An initial pretreatment to remove any sulfur already present on the mineral surface created a chemically clean surface and guaranteed that any elemental sulfur observed was the result of the laboratory oxidation experiments. Because the extraction method and chromatographic analysis are performed ex situ and are not constrained by the parameters of the experimental oxidation reaction, the method can be used for the quantification of elemental sulfur after any laboratory experiment.

Introduction

Acid mine drainage (AMD), a serious environmental problem resulting from the oxidative dissolution of sulfide minerals, has been the focus of numerous studies and several comprehensive reviews (*1*−*5*). When exposed to air and water (often as a result of mining activity), sulfide minerals are oxidized and produce sulfuric acid. The resulting acidified waters leach heavy metals from surrounding minerals, creating conditions that are often detrimental to the environment. Despite extensive efforts to understand the specific chemical interactions that control the formation of AMD, unresolved issues still exist regarding the mechanism and kinetics of the oxidation process at the mineral surface.

One of the fundamental questions regarding the oxidative dissolution of sulfide minerals is the speciation of the sulfur released from the mineral. The most commonly accepted model of the dissolution of pyrite (FeS_2), the most abundant and well studied of the sulfide minerals, is based on the assumption that all of the oxidized sulfur from the mineral is released as thiosulfate (*6*, *7*). In contrast, other studies have clearly demonstrated that elemental sulfur forms at the pyrite surface under oxidative conditions (*8*−*12*). Because the generally accepted model only accounts for sulfoxy anions and does not account for any other experimentally observed sulfur species, understanding the formation of elemental sulfur and other insoluble sulfur species is critical to deciphering the actual mechanistic steps of the dissolution process.

The amount of sulfur that remains at the surface in the form of elemental sulfur (S_8) or other insoluble species also may have important implications for the dissolution kinetics of sulfide minerals. If a sufficiently impenetrable layer of elemental sulfur was formed on the mineral surface, it has been suggested that this sulfur layer may passivate the surface to further oxidation by preventing the passage of oxidants to the surface (*13*−*16*). In contrast, other studies have demonstrated that removal of the elemental sulfur layer at the surface does not increase the rate of dissolution of the underlying mineral at low concentrations of ferrous iron (*9*, *17*). X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy were used to detect elemental sulfur at the mineral surface in these previous studies, but accurate quantification of the sulfur layer with these techniques is difficult at best. A complete understanding of the role of elemental sulfur in the mechanism and dissolution kinetics of sulfide mineral oxidation ultimately requires a better quantitative determination of the sulfur layer.

Solution phase techniques, by which an organic solvent is used to extract the elemental sulfur from the mineral surface prior to analysis, are one way around the quantification difficulties of surface analyses. Toniazzo et al. reported a method by which the elemental sulfur on pyrite was extracted with either methanol or hexane and then analyzed by gas chromatography coupled with mass spectroscopy (GC-MS) (*18*). As noted in Toniazzo's study, the injection process in GC-MS may generate elemental sulfur fragmentation products, resulting in additional chromatographic peaks that complicate the identification and quantification of surface species.

Liquid chromatographic methods for the quantitative analysis of elemental sulfur have been in use in other fields of study for several decades. Lauren and Watkinson evaluated the performance of different columns for the analysis of elemental sulfur by liquid chromatography, including a C_{18} reverse-phase column with a methanol eluent (*19*). In a variation of this method, Mustin et al. developed a pyrite-packed chromatographic column that was used to clean the pyrite grains by extracting the elemental sulfur with methanol in a high performance liquid chromatography-like device (*20*). Although the pyrite-packed column produced sulfur-free pyrite grains for subsequent experiments, this method is not applicable to the quantification of elemental sulfur after oxidation experiments because of the possible oxidizing effects of conditioning the column with water prior to the methanol treatment.

To make use of liquid chromatography for the analysis of elemental sulfur formed on sulfide mineral surfaces, an appropriate extraction method must be developed. Previously, extraction of elemental sulfur from coal using perchloroethylene maintained at reflux (120 °C) and subsequent analysis by high-performance liquid chromatography (HPLC) has been demonstrated (*21*). In the case of sulfide minerals, these rather harsh conditions may lead to further oxidation of the mineral and the generation of more elemental sulfur. Nevertheless, the use of perchloroethylene for the extraction of elemental sulfur is advantageous over the extraction methods previously discussed in that elemental sulfur is approximately 50 times more soluble in perchloroethylene than in methanol (*22*).

Because the elemental sulfur on sulfide minerals is readily accessible at the mineral surface, much more gentle condi-

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10.1021/es0011663 CCC: $19.00 © 2000 American Chemical Society
Published on Web 09/29/2000

tions can be employed in the extraction process. This paper describes a simple method for the extraction of elemental sulfur from sulfide mineral surfaces with room-temperature perchloroethylene and subsequent quantitative analysis by HPLC. We demonstrate here that elevated temperatures are not necessary for the extraction of elemental sulfur from sulfide mineral surfaces, and as a result, further oxidation of the mineral during extraction can be avoided.

Experimental Section

Apparatus and Reagents. HPLC Equipment. All HPLC analyses were performed on a Shimadzu LC-10AT high-performance liquid chromatography system with 20 μL injection volume and a Shimadzu SPD-M10AV diode array absorption detector operating at 254 nm with an 8 nm bandwidth. An Alltech Econosphere 5 μ C_{18} reverse-phase column (4.6 × 250 mm) was used with an eluent comprised of 95:5 methanol (Fisher, electronic grade):water at a flow rate of 1 mL/min. Data were collected on a PC running the Shimadzu Class-VP Chromatography Data System.

Raman Spectroscopy. Raman spectroscopy was used as a check of the content of the extract solutions and the efficiency of the process. The Raman detection system consisted of a high-throughput f/1.8 spectrograph from Kaiser Optical Systems with a fixed resolution of ~2 cm^{-1} and a liquid nitrogen-cooled charge coupled device (CCD) detector from Photometrics. Data were collected on a PC using the MAPS spectral data acquisition program (Photometrics). An Ar ion laser (Spectra Physics) operating at 514 nm and ~50 mW power was used as the illumination source. Each spectrum was the result of addition of several shorter acquisitions that were individually analyzed for cosmic ray spikes. All spectra were baseline corrected by fitting to a polynomial function.

Mineral Samples. Arsenopyrite (FeAsS), pyrite (FeS_2), marcasite (FeS_2), chalcopyrite ($FeCuS_2$), and chalcocite (Cu_2S) were obtained from Ward's Natural Science Establishment, Inc. The minerals were crushed by hand with mortar and pestle and sieved. The 75−150 μm fraction was retained. To remove any organic contaminants and adhering smaller particles from the surface, the mineral material was then ultrasonically cleaned in 75% ethanol for 30 min. Subsequent treatment in 50% HCl overnight removed any oxide layer that already existed on the mineral surface. Previous studies have shown that acid-cleaned pyrite samples exhibit reactivity similar to freshly cleaved samples (*23*).

Oxidized Mineral Samples. To duplicate typical laboratory oxidation experiments and produce a mineral surface with a layer of elemental sulfur, several hundred milligrams of the cleaned, crushed minerals were first oxidized in sulfuric acid solutions at pH = 1 and 42 °C. The pH and temperature conditions of the experiment were chosen to mimic extreme acid mine drainage conditions (*24*). Two types of oxidizing solutions were used. One type was saturated with air or oxygen but contained no other oxidizing agents. The second type was saturated with nitrogen to eliminate oxygen and contained an initial concentration of approximately 100−500 ppm ferric iron. The oxidation conditions for each sample are detailed in Tables 1 and 2.

Elemental Sulfur Standards. Twenty-four milligrams of elemental sulfur (Aldrich, 99.998%) were weighed out and added to a beaker containing 30 mL of perchloroethylene (Acros, spectrophotometric grade). The solution was stirred for about 1 h and then quantitatively transferred to a volumetric flask and diluted to 100 mL with perchloroethylene for a final concentration of 240 mg/L. Subsequent dilutions of the stock solution produced additional standards varying in concentration from 5 to 120 mg/L.

Procedure. Treatment to Remove Preexisting Elemental Sulfur. One of the difficulties of laboratory oxidation experiments that attempt to simulate field conditions is preparation of a well-defined starting surface. The low solubility of elemental sulfur in aqueous solutions limits the ability of acid cleaning methods to remove preexisting elemental sulfur. As a means of removing elemental sulfur that may exist on the sulfide mineral surface prior to the laboratory oxidation experiment, a pretreatment step was added to the mineral cleaning procedures outlined above. Crushed mineral samples were placed in 10 mL of carbon disulfide (Aldrich, 99+%) for approximately 1 h and then rinsed twice with 5-mL aliquots of carbon disulfide. Due to the extremely high vapor pressure of carbon disulfide (48 kPa (360 Torr) at 25 °C) (*25*), little, if any, residual carbon disulfide is expected to remain at the mineral surface when the sample is left exposed to the atmosphere for several minutes after this final mineral preparation step.

TABLE 1. Determination of Elemental Sulfur from Arseopyrite Oxidized under Various Conditions

experimental conditions	arseno-pyrite reacted, g	length of oxidation, days	elemental S extracted, mg
oxygen-purged solution	1.130	13	1.590
air-purged solution	1.132	13	0.666
128 ppm ferric iron with N_2-purge	0.328	6	0.715
255 ppm ferric iron with N_2-purge	0.331	6	1.390
509 ppm ferric iron with N_2-purge	0.329	6	2.242
solution extraction of 509 ppm ferric iron experiment	0.329	6	0.002
extraction of "clean" FeAsS before pretreatment in CS_2	0.212		~0.1

TABLE 2. Elemental Sulfur Extractions from Various Sulfide Minerals Reacted for 6 Days in 509 ppm Fe^{3+} at pH = 1.0 and 42 °C

mineral	amt reacted, g	elemental S extracted, mg
pyrite	0.346	0.779
marcasite	0.351	2.137
chaclopyrite	0.352	3.635
chalcocite	0.354	0.197

Sulfur Extraction from Oxidized Mineral Surfaces. Because the sulfide mineral samples were oxidized in sulfuric acid solutions that simulate acid mine drainage conditions, the extraction process was designed to avoid drying the mineral material and exposing the samples to a different chemical environment before analysis. Although the mineral material is exposed to atmospheric oxygen during extraction, previous work has demonstrated that the rate of dry oxidation of pyrite is negligible up to temperatures of 150 °C (*26*). For the purposes of most laboratory experiments relevant to the conditions of acid mine drainage, oxidation of the mineral exposed to atmospheric oxygen during the extraction process will not be significant. At the end of each oxidation experiment, most of the sulfuric acid solution was carefully decanted, leaving as much of the solution as necessary to avoid losing any mineral material. Perchloroethylene (25 mL) was added to the reaction flask that contained the mineral sample and the remaining aqueous reaction solution. The denser perchloroethylene, which displaces the remaining aqueous phase at the bottom of the unstirred flask, was left in contact with the mineral overnight (8−16 h) at room temperature. After completion of the extraction, the liquid contents of the reaction flask were poured into a separatory funnel, and an aliquot of the bottom perchloroethylene layer was drawn off for analysis. If necessary, serial dilutions with perchloroethylene were performed to bring the concentration of the sample within the linear range of the standard solutions.

Aqueous Phase Extraction. To test whether a significant amount of elemental sulfur remains in the aqueous phase,

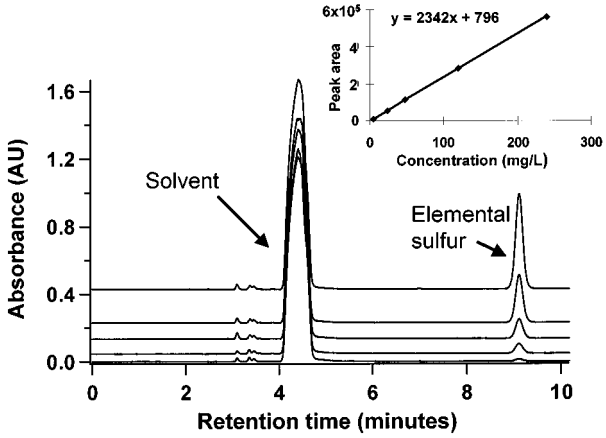

FIGURE 1. Chromatograms of 4.8, 24, 48, 120, and 240 mg/L elemental sulfur standards in perchloroethylene. Eluent was 95:5 methanol: water at a rate of 1.0 mL/min. The large, unchanging peak at approximately 4 min is assigned to the perchloroethylene solvent. The peak at approximately 9 min increases with increasing concentration and is assigned to elemental sulfur. Inset: Calibration of absorbance as a function of elemental sulfur concentration. Each data point represents the measured peak area of a given elemental sulfur concentration. The line represents the best linear fit to the data (r^2 = 0.99999) by the method of least squares.

the sulfuric acid solution from one of the oxidation reactions was analyzed for elemental sulfur content. Forty milliliters of the aqueous oxidation reaction solution were vacuum-filtered through 8 μm quantitative grade filter paper (Whatman). The filter paper was then placed in a beaker containing 50 mL of perchloroethylene for several hours in order to extract any elemental sulfur collected during the filtration.

Results and Discussion

Analysis of Standards. Overlaid chromatograms from a series of standard solutions of elemental sulfur in perchloroethylene are shown in Figure 1. The first small peak just past 3 min is due to acetone residues from glassware that normally was cleaned just prior to use. The largest peak, near 4 min, as well as the minor contaminant peaks at approximately 3.5 min are assigned to the perchloroethylene solvent. Elemental sulfur appears at approximately 9 min. This peak is symmetric with no sign of tailing. No other features were observed over the range of elution times studied (up to 20 min). Because elemental sulfur comes off the column nearly 5 min after the solvent, the analyte is cleanly resolved, enabling quantitative analysis of peak height and area. As shown in Figure 1, the area of the elemental sulfur peak increases with increasing concentration of the standards.

The inset in Figure 1 is the calibration curve for a series of elemental sulfur standards. The points represent the area of the elemental sulfur peak for standard solutions with concentrations of 4.8, 24, 48, 120, and 240 mg/L. The line through the points represents the best linear fit to these data using the method of least squares. The excellent fit to the data ($r^2 = 0.99999$) is an indication of the highly quantitative nature of the HPLC analysis. The relationship between analyte concentration and peak area is linear throughout the investigated range from approximately 5 to 250 mg/L.

The stability of elemental sulfur in perchloroethylene was investigated by observing the change in the chromatograms of a sulfur standard that was stored for a period of weeks. Figure 2 presents the chromatogram of a 240 mg/L elemental sulfur standard after 12 weeks of storage at room temperature. The chromatogram appears identical to those of fresh standards with one sharp peak due to elemental sulfur. Although there is some decomposition of the standards at

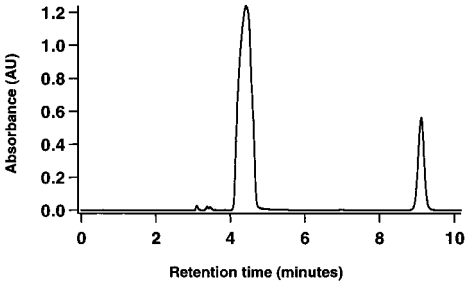

FIGURE 2. Chromatogram of a 240 mg/L elemental sulfur standard after 12 weeks of storage at room temperature. Eluent was 95:5 methanol:water at a rate of 1.0 mL/min.

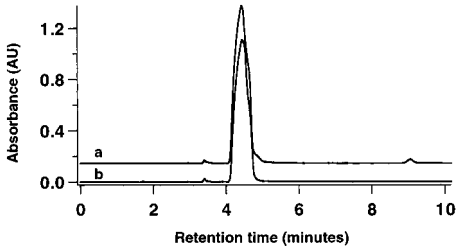

FIGURE 3. Chromatograms of an arsenopyrite sample that had been cleaned in ethanol and HCl (a) and one that received an additional pretreatment in carbon disulfide (b). Eluent was 95:5 methanol: water at a rate of 1.0 mL/min. No residual surface products were detected on the pretreated sample.

longer storage times (>12 weeks), elemental sulfur appears to be stable in perchloroethylene for periods of weeks.

Evaluation of Carbon Disulfide Pretreatment. An arsenopyrite sample that was ultrasonically cleaned in ethanol and treated with 50% HCl, but not oxidized in a sulfuric acid solution, was analyzed in order to investigate the state of the mineral surface prior to any laboratory oxidation experiment. The resulting chromatogram is presented in Figure 3a, and the analysis is summarized in Table 1. Clearly, significant amounts of elemental sulfur (approximately 0.1 mg) are present on the mineral surface prior to the laboratory oxidation experiment as indicated by the peak that appears just past 9 min. This observation implies that either elemental sulfur existed on the mineral surface before it came into contact with the perchloroethylene or the extraction process itself resulted in the formation of elemental sulfur. To distinguish between these two possibilities, an arsenopyrite sample was pretreated in carbon disulfide before analysis by HPLC. Because of the extremely high solubility of elemental sulfur in carbon disulfide, this process should remove any elemental sulfur on the mineral surface. As shown in Figure 3b, the sample that was pretreated in carbon disulfide showed no sign of elemental sulfur after extraction in perchloroethylene. The absence of elemental sulfur in this case implies that the mineral is not further oxidized in perchloroethylene and no elemental sulfur is created during the extraction process. Furthermore, the pretreatment in carbon disulfide to remove residual elemental sulfur creates a chemically clean starting surface for laboratory experiments.

Extraction of Oxidized Minerals. The chromatogram of the elemental sulfur extracted from an arsenopyrite sample that was oxidized in an oxygen-saturated sulfuric acid solution (pH = 1, 42 °C) for 13 days is presented in Figure 4. The only peak observed in addition to the solvent peak at about 4 min is the rather large peak just past 9 min. This retention time correlates precisely with the retention time of the elemental sulfur in the standards. The narrow width and symmetry of the peak again suggest this peak is due only to elemental sulfur. Additionally, no other peaks were observed at times of up to 20 min. To confirm that the dissolved substance in

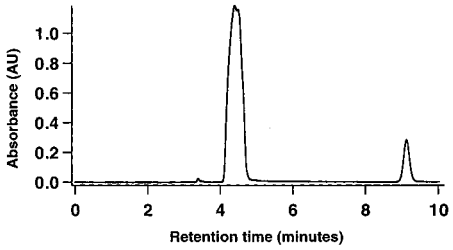

FIGURE 4. Example of a chromatogram of elemental sulfur extracted from an oxidized mineral. Eluent was 95:5 methanol:water at a rate of 1.0 mL/min. The arsenopyrite had been exposed to an oxygen-saturated sulfuric acid solution (pH = 1) for 13 days. Elemental sulfur was extracted into perchloroethylene overnight.

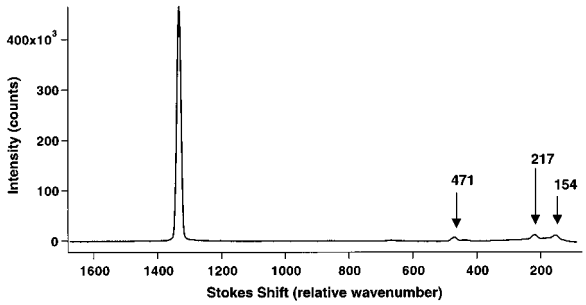

FIGURE 5. Raman spectrum of the evaporative residue of the perchloroethylene extraction of an arsenopyrite sample. The spectrum is the compilation of 20 individual exposures of 2 min at a laser power of ~50 mW. The arsenopyrite had been previously oxidized in 1000 ppm ferric iron (pH = 1) for 4 days. The largest peak at 1333 cm^{-1} is due to the diamond substrate on which the sample was analyzed. The only other visible lines at 471, 217, and 154 cm^{-1} are assigned to elemental sulfur.

the perchloroethylene was indeed elemental sulfur, the evaporative residue of an extract aliquot was examined. Several milliliters of the perchloroethylene solution were left in an open container, and the perchloroethylene was allowed to evaporate. The crystalline residue was collected and analyzed by Raman spectroscopy. The resulting spectrum, the summation of 20 individual exposures of 2 min each, is shown in Figure 5. The largest peak at 1333 cm^{-1} is due to the diamond substrate (*27*) that the sample was placed on for analysis. The only other observable peaks at 471, 217, and 154 cm^{-1} can be assigned to the three most intense lines of elemental sulfur (*12*). No additional features were seen in the Raman spectrum.

Because the extraction and HPLC analysis are performed ex situ at the completion of the laboratory experiments, the method of analysis is the same irrespective of the nature of the oxidation experiment. The results of extractions from a variety of arsenopyrite samples are listed in Table 1. Significant amounts of elemental sulfur were found on all the samples exposed to oxidizing conditions. The amount of elemental sulfur found on these arsenopyrite samples varies as would be expected from a qualitative estimate of the extent of reaction; the quantity of elemental sulfur increases with increasing concentration of Fe^{3+} or in going from an air-saturated to an oxygen-saturated solution. As suggested by these observed differences in the amount of elemental sulfur formed under different oxidative conditions, the method provides quantitative data that could be used in the study of chemical speciation on sulfide mineral surfaces.

Efficiency of Extraction Process. As a check of the efficiency of the extraction process, sequential extractions of one sample were performed on 0.63 g of crushed arsenopyrite that were oxidized in 1000 ppm ferric iron for 3 days. Figure 6 presents the chromatogram for each of the extractions.

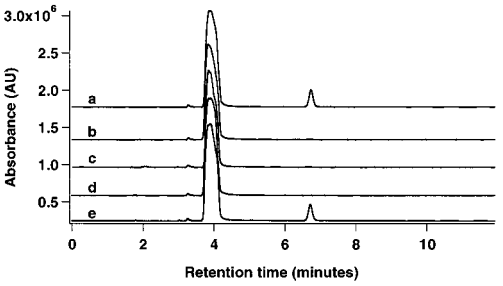

FIGURE 6. Chromatograms of sequential extractions of elemental sulfur with perchloroethylene. The peak at 6.7 min corresponds to elemental sulfur extracted from oxidized arsenopyrite after (a) 4 h, (b) an additional 6 h, (c) an additional 12 h, and (d) an additional 2 h while being gently stirred. Fresh perchloroethylene was used for each sequential extraction. A 58 mg/L elemental sulfur standard (e) is shown for comparison. Eluent was 95:5 methanol:water at a rate of 1.0 mL/min.

After 4 h in perchloroethylene (Figure 6a), an elemental sulfur concentration approximately equal to a 58 mg/L sulfur standard (Figure 6e) was obtained. Although the retention time for elemental sulfur (6.7 min) has shifted to shorter times relative to earlier experiments due to aging of the column, the retention time of the sample (Figure 6a) is the same as that of the standard (Figure 6e). After the initial extraction, the first extract solution was poured off, and a fresh aliquot of perchloroethylene was added. At the completion of an additional 6 h of extraction in the fresh perchloroethylene, the chromatogram in Figure 6b was obtained. A small amount of elemental sulfur, corresponding to approximately 10% of the original extraction, was measured. A third repetition of the process, for an additional 12 h of exposure to a fresh aliquot of perchloroethylene, resulted in an elemental sulfur peak that is barely above the detection limit (Figure 6c). Finally, the perchloroethylene was replaced again, and the solution was gently stirred with a magnetic stir bar for 2 h. Elemental sulfur was not detected in this final extraction (Figure 6d).

Although elemental sulfur was detected in the third extraction after 10 h of exposure to perchloroethylene (4 h in the first extraction and six in the second), it is possible that this small amount is due to residual perchloroethylene solution remaining with the mineral after the first two extractions. Consequently, an overnight extraction (8−16 h) appears to be sufficient to complete a quantitative extraction. Additionally, the insignificant amount of elemental sulfur extracted when the solution was stirred suggests that agitation of the solution is not necessary.

As another test of the extraction efficiency, the polished face of an arsenopyrite crystal that had been oxidized in a 1000 ppm ferric iron solution for 3 days was examined by Raman spectroscopy before and after extraction with perchloroethylene. Figure 7a illustrates the Raman spectrum of the arsenopyrite before extraction. In addition to the features at approximately 400, 330, 303, 194, 167, and 127 cm^{-1} that can be assigned to arsenopyrite (*9*), intense, sharp lines at 468, 432, 218, and 151 cm^{-1} are present. These lines correspond with the vibrational frequencies of elemental sulfur. After extraction (Figure 7b), only the arsenopyrite phonons are observed. Based on the noise level in this spectrum, one can conclude that the amount of elemental sulfur remaining on the mineral surface is less than 1% of the amount on the surface before extraction.

The extraction method employed here primarily detects elemental sulfur bound to the mineral surface. To check whether elemental sulfur might remain suspended in the aqueous phase of the oxidation solutions, the 509 ppm Fe^{3+} solution in contact with arsenopyrite was also extracted with

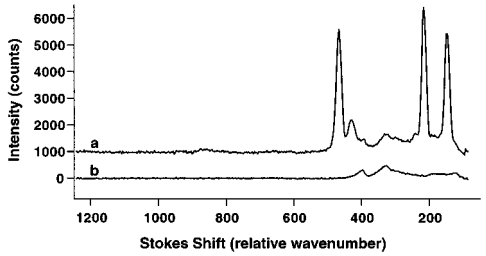

FIGURE 7. Raman spectra of the polished face of an oxidized arsenopyrite crystal before (a) and after (b) extraction in perchloroethylene overnight. The sample was previously oxidized in 1000 ppm ferric iron solution (pH = 1) for 3 days. Elemental sulfur present before extraction, as noted by the intense peaks at 468, 432, 218, and 151 cm^{-1}, is not observed in the spectrum taken after extraction. The spectra are the compilation of 12 individual exposures of 5 min at a laser power of ~50 mW.

perchloroethylene as described above. The results are summarized in Table 1. Analysis of the solid precipitate collected from the filtration of the reaction solution revealed that the sulfuric acid solution contained no more than 0.002 mg of elemental sulfur or less than 0.1% of the amount extracted from the mineral surface of this particular sample. These findings suggest that the elemental sulfur found at the mineral surface can be taken as a close (99+%) approximation to the total amount of elemental sulfur. Routine analysis of the aqueous reaction solutions in addition to the mineral surfaces should not be necessary in most cases.

General Applicability. Finally, extractions and HPLC analyses were performed on a variety of other oxidized sulfide minerals in order to further test the general applicability of the method. Table 2 summarizes the results of elemental sulfur measurements of pyrite, marcasite, chalcopyrite, and chalcocite samples oxidized in 509 ppm Fe^{3+} for 6 days. Elemental sulfur was found on all the sulfide mineral surfaces; however, the quantities varied greatly from mineral to mineral. These results offer a tantalizing glimpse of the quantifying power and broad applicability of the method.

Acknowledgments

This work was supported by grants from the Environmental Protection Agency (R 826189) and the National Science Foundation (CHE 9807598). The authors also wish to acknowledge Dr. Jillian Banfield for many helpful discussions.

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Received for review April 7, 2000. Revised manuscript received August 15, 2000. Accepted August 15, 2000.

ES0011663