

SELECTED METHODS FOR DISSOLVED IRON (II, III) AND DISSOLVED SULFIDE (-II)
DETERMINATIONS IN GEOTHERMAL WATERS

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CONVERSION FACTORS AND ABBREVIATIONS

The metric system of units is used in this report. For readers who prefer inch-pound units, the conversion factors for the terms used in this report are listed as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
cm (centimeter)	0.3937	in (inch)
mL (milliliter)	0.03382	fl oz (fluid ounce)
L (liter)	0.2642	gal (gallon)
g (gram)	0.03520	oz (ounce)

Explanation of abbreviations:

M (Molar, moles per liter)
mg/L (milligrams per liter)
 μ m (micrometer)
nm (nanometer)
 μ g/L (micrograms per liter)

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ABSTRACT

Dissolved sulfide (-II) and dissolved iron (II, III) were determined in geothermal well water samples collected at Cerro Prieto, Mexico. Most samples consisted of liquid and gas (two phases) at the instant of collection; and a subset of samples, referred to as "flashed" samples, consisted of pressurized steam samples which were allowed to condense.

Sulfide was determined by sulfide-specific-ion electrode; Fe(II) and Fe(III) plus Fe(II) were determined spectrophotometrically. The precision and accuracy of the methods were evaluated for these high-silica waters with replicate analyses, spike recoveries, and an alternate method. Direct current (d.c.) argon plasma emission spectrometry was the alternate method used for Fe(III)-plus-Fe(II) analyses.

Mean dissolved iron concentrations ranged from 20.2 to 334 $\mu\text{g/L}$ as Fe(II) and 26.8 to 904 $\mu\text{g/L}$ as Fe(III) plus Fe(II). Mean sulfide concentrations ranged from about 0.01 to 5.3 mg/L (S-II). Generally, higher S(-II) values and larger Fe(II)/Fe(III) ratios were found in the two-phase samples. These findings suggest that the "flashed" samples are at a less reduced state than the two-phase samples.

INTRODUCTION

A set of water samples was collected and preserved at the Cerro Prieto geothermal power production wells in Baja California, Mexico, and analyzed for dissolved Fe(III) plus Fe(II), dissolved Fe(II), and dissolved S(-II). These were companion samples to those analyzed by Ball and Jenne (1983) for 34 elements by direct current (d.c.) argon plasma emission spectrometry and were collected in order to evaluate methods for sampling and determination of the aforementioned species in the power plant effluents.

EXPERIMENTAL METHODS

Sample Collection and Preservation

Samples from the Cerro Prieto geothermal area were collected in January, 1978. Most of the samples from the geothermal wells were drawn off the separator vessel as admixed water and steam under pressure, passed through a coiled condenser tube submerged in an ice and water bath mixture and through a 0.45- μ m filter membrane, then acidified. A selected subset of samples was collected by allowing the pressurized steam to flash through the exit valve of the separator vessel into a 1-L container, where a significant amount of steam was allowed to escape. These (single-phase) samples are subsequently referred to as "flashed" samples. All samples were stored in 250-mL polyethylene bottles.

The samples for dissolved iron were acidified with Ultrex HCl to approximately pH 1. Dissolved S (-II) was fixed with 1 mL of 1 M $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ and 3 mL of 1 M Na_2CO_3 . The Na_2CO_3 was added to raise the pH in order to flocculate the ZnS precipitate and to increase its stability over time.

Dissolved Fe

Dissolved Fe(II) was measured spectrophotometrically using ferrozine as the color reagent. The method of Stookey (1970) was modified slightly in that the ferrozine was dissolved in deionized H_2O instead of HCl.

Ammonium acetate buffer was added to adjust the pH within the range of 4 to 9, a necessity for the quantitative development of the violet Fe(II)-ferrozine complex. Dissolved Fe(III) plus Fe(II) was determined by reducing the Fe(III) present to Fe(II) with $\text{NH}_2\text{OH}\cdot\text{HCl}$ before ferrozine addition. The Fe(III) was obtained by difference. Absorbance was measured at 562 nm using a Bausch and Lomb Spectronic 710 spectrophotometer with a 5-cm cell.

The absorbances of Fe(III) plus Fe(II) as well as Fe(II) in the sample solutions were compared with the absorbances of a single set of standard solutions. The absorbance of the analyte solution was corrected by subtracting from it the absorbance reading of another aliquot of the sample mixed only with the amount of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ added to the analyte solution.

Dissolved S(-II)

Dissolved sulfide (S(-II)) was determined by the method of Baumann (1974). Each sample was vigorously shaken to suspend the $\text{ZnS-Zn}(\text{OH})_2$ coprecipitate. A 2.50-mL or 5.00-mL aliquot was immediately pipetted into a 25-mL volumetric flask and mixed with 5 mL of alkaline antioxidant reagent (a freshly prepared solution containing 7.2 percent ascorbic acid, 18.6 percent $\text{Na}_2\text{H}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ and 12 percent NaOH). The mixture was diluted to volume, and the flask was stoppered and shaken to dissolve the precipitate.

The EMF of the solution was then measured using an Orion Model 94-16A sulfide-specific-ion electrode in conjunction with an Orion Model 90-02-00 double junction reference electrode and an Orion Model 701 or 801A specific-ion meter. The analyte solutions were purged with nitrogen gas during measurements. The S(-II) concentrations were calculated by comparing sample EMF values with values of S(-II) standards containing appropriate amounts of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ and Na_2CO_3 .

RESULTS AND DISCUSSION

Iron

Iron concentrations obtained range from 20.2 to 834 $\mu\text{g/L}$ Fe(II) and 26.8 to 904 $\mu\text{g/L}$ Fe(III) plus Fe(II) (Table 1). For both the Fe(II) and the Fe(III)-plus-Fe(II) determinations, relative standard deviations of less than 5 percent for duplicates in most cases (Table 1) were typical of the precision obtained with the ferrozine method. Standard deviations for Fe(III) values were calculated by taking the square root of the sum of squares of the standard deviations of Fe(II) and the Fe(III)-plus-Fe(II) determinations.

Spike recoveries were done on 2/5 and 1/5 sample dilutions. Recovery of known additions of Fe(II) or Fe(III) at the 50- $\mu\text{g/L}$ and 100- $\mu\text{g/L}$ levels ranged from 92 to 110 percent (Table 2), with 17 of 20 recoveries between 95 and 105 percent.

At the time of analysis, the samples contained a white floc of amorphous SiO_2 . Initially, sample aliquots were decanted for analysis. However, in some cases removal of the precipitate with a 0.45- μm or 0.1- μm membrane filter was necessary to obtain adequate precision among replicate analyses.

The dissolved Fe values obtained with the spectrophotometric method were only 7.5 to 92 percent of the respective Fe values obtained by d.c. argon plasma emission spectroscopy (Ball and Jenne, 1983) given in Table 3. These differences suggest that previously dissolved Fe may have been incorporated into the white siliceous precipitate as it formed, then measured when some of the precipitate was nebulized in the plasma jet.

The values obtained by d.c. plasma emission spectroscopy were measured using two different cassettes in the emission spectrophotometer during multielement analysis. Cassette 1 and cassette 2 are metal plates with exit slits positioned so as to give optimum optical alignments for determining an individual array of elements. Poor agreement in values for Fe between cassettes can be attributed to either stray light effects with the particular cassette used (Ball and Jenne, 1983) or to variation in the amount of precipitate introduced into the plasma.

Dilution of these geothermal waters at the time of sample collection is necessary to prevent the precipitation of amorphous SiO_2 . Iler (1979) stated that the reported solubilities for amorphous SiO_2 are in the range of 70 ppm to more than 150 ppm SiO_2 , and that a 0.01 percent SiO_2 (as monosilicic acid, $\text{Si}(\text{OH})_4$) solution can be prepared when pure amorphous SiO_2 is allowed to equilibrate with water at room temperature. Therefore,

Table 1.--Dissolved Fe(II) and Fe(III) in Cerro Prieto, Mexico, geothermal water samples determined by the ferrozine method.
 $[\sigma = \text{standard deviation}; \text{RSD} = \text{relative standard deviation: } (\sigma/\text{mean}) \times 100]$

Well Number	Fe (III) plus Fe (II)				Fe (II)				Fe (III)			
	Replicates	Mean	σ	RSD Pct.	Replicates	Mean	σ	RSD Pct.	Mean	σ	RSD Pct.	Mean
		----- $\mu\text{g/L}$ -----				----- $\mu\text{g/L}$ -----				----- $\mu\text{g/L}$ -----		----- $\mu\text{g/L}$ -----
M-5	331,327	329	2.8	0.9	324,313	319	7.8	2.4	n.s.			n.s.
M-11	109,113	111	2.8	2.5	104,108	106	2.8	2.7	n.s.			n.s.
M-14	258*,261*	260	2.1	0.8	237*,226*	232	7.8	3.4	28	8.1	29.	28
M-19A	117,127	122	7.1	5.8	96.6,98.0	97.3	0.99	1.0	24.7	7.1	29.	24.7
M-19A#	36.4*,36.0*	36.2	0.28	0.8	26.1*,21.3*	23.7	3.39	14.	12.5	3.40	27.	12.5
M-20#	36.2,41.1*	38.6	3.46	9.0	20.6,19.8*	20.2	0.57	2.8	18.4	3.51	19.	18.4
M-25	329,330	330	0.7	0.2	301,305	303	2.8	0.9	27	2.9	11.	27
M-26	422,425,458*	435	20.0	4.6	413,400,420*	411	10.1	2.5	n.s.			n.s.
M-26#	321,321,322,328*	323	3.4	1.0	203,201,204,202*	202	1.3	0.6	121	3.6	3.0	121
M-29	63.3,63.0	63.2	0.21	0.3	53.9,54.1	54.0	0.14	0.3	9.2	0.25	2.8	9.2
M-30	899,908	904	6.4	0.7	828,839	834	7.8	0.9	70	10.0	14.	70
M-30#	137*,155*	146	12.7	8.7	86.6*,89.0*	85.8	4.53	5.3	60.2	13.5	22.	60.2
M-31(A)	74.9,74.2	74.6	0.49	0.7	69.7,66.9	68.3	1.98	2.9	n.s.			n.s.
M-31(B)	27.9,25.7	26.8	1.56	5.8	24.7,26.2	25.4	1.06	4.2	n.s.			n.s.
M-45	277,282	280	3.5	1.3	246,256	251	7.1	2.8	29	7.9	27.	29
M-51#	149,152*,158*,153*	153	3.7	2.4	118,125*,124*,124*	123	3.2	2.6	30	4.9	16.	30
M-91#	304*,340*,357*	334	27.1	8.1	190*,209*,234*	211	22.1	10.	123	35.0	28.	123

- "Flushed" sample

* - Sample aliquot refiltered just prior to analysis

n.s. - no significant amount of Fe(II) based on t statistic for two means at the 0.05 level

Table 2.--Dissolved Fe(II) and total Fe recovery data for Cerro Prieto, Mexico,
geothermal water samples.

Well		Fe(II)		Total Fe		
Number	Added	Found	Recovered	Added	Found	Recovered
	-----µg/L-----		Percent	-----µg/L-----		Percent
M-5	0	81.3	--	0	85.0	--
	45.1	124	95	52.0	137	100
	90.2	170	98	104	190	101
M-14*	-	56.4	--	0	65.3	--
	50.5	112	110	50.0	116	101
	101	157	100	100	166	101
	0	119	--	0	128	--
	50.5	168	97	50.0	177	98
	126	239	95	125	253	100
M-26**	0	101	--	0	160	--
	51.0	152	100	50.0	207	94
	102	201	98	100	256	96
M-45	0	61.4	--	0	69.2	--
	51.0	111	97	50.0	115	92
	102	163	100	100	167	98

* Sample aliquots refiltered just prior to analysis

** "Flashed" sample

Table 3.--Comparison of two different methods for the determination of dissolved-Fe(III)-plus-Fe(II) concentrations in Cerro Prieto, Mexico, geothermal water samples.

Well Number	Sample Number	Fe(III) plus Fe(II)		
		Ferrozine*	Cassette 1 α	Cassette 2 α
		----- μ g/L-----		
M-5	78WA116	329	710	592
M-11	78WA145	111	282	376
M-19A	78WA118	122	514	378
M-19A+	78WA119	36.2	484	333
M-26	78WA121	435	767	718
M-26+	78WA122	323	632	525
M-29	78WA124	63.2	467	278
M-30	78WA125	904	981	972
M-30+	78WA126	146	700	617
M-31	78WA127	50.7	450	243

+ "Flashed" samples

* Colorimetry

α D.C. argon plasma emission spectrometry

a SiO₂ level of less than 70 mg/L is required to keep SiO₂ dissolved in the monomeric state.

Factors limiting accurate estimation of Fe(II) and Fe(III) levels in the original water are sampling technique and promptness of analysis. During sampling, contamination with either Fe or oxidizing or reducing agents must be prevented. The stability of the Fe(II)/Fe(III) ratio in the acid-preserved samples has been a subject of debate. Shapiro (1966) reported that in HCl-acidified lake water (1 mL concentrated HCl per liter of sample) containing 1.5 mg/L total Fe, the Fe(II) concentration increased from an initial value of almost zero to 0.6 mg/L after 1 week. However, Shapiro (1966) did not specify sample filtration, and the possibility that the sample contained mixed Fe(II)/Fe(III) colloidal precipitates cannot be discounted. The increase of Fe(II) with time which is occasionally observed has been attributed to the photoreduction of Fe(III) in the presence of dissolved organic compounds (McMahon, 1967, 1969; Lewin and Chen, 1973). In filtered lake water (0.22 µm) preserved with HCl, McMahon (1967) found that the Fe(II) level increased from 0.061 to 1.40 mg/L over a 90-minute period with exposure to sunlight while the Fe(II) concentration increased to only 0.10 mg/L in another sample of the same water which had been stored for 90 minutes in the dark. In Table 4, variations in Fe(II) over time are given for geothermal, estuarine, and mine-tailings runoff samples. Generally, slight increases in Fe(II) concentrations in the estuarine and runoff samples were observed. However, runoff sample 76WA141 apparently became contaminated because the increase in Fe(II) concentration was much greater than the other samples. With the two HCl-preserved geothermal water samples containing about 300 mg/L SiO₂, irregular loss in Fe(II) was observed over a 15-month period. These decreases were probably due to co-precipitation of dissolved Fe species with precipitating amorphous SiO₂ and/or oxidation. The several months which elapsed between collection and analysis of these Cerro Prieto samples increases the uncertainty in the amounts of Fe(II) and Fe(III) present at the time of sample collection.

The mean values of dissolved Fe(III) plus Fe(II) of the "flashed" samples were significantly lower than those of the two-phase samples from wells M-19A, M-26 and M-30 (Table 3) with the exception of the d. c. argon plasma results for well M-19A which were approximately equivalent. The shorter time needed to collect the "flashed" samples would minimize the potential for Fe contamination from dissolution of corrosion products and scaling at the well head. Therefore, this source of Fe contamination would be more likely to affect the condensed samples.

The "flashed" samples from wells M-19A, M-26 and M-30 had lower Fe(II)/Fe(III) ratios than the two-phase samples (Table 5), indicating that the flashed samples were at a less reduced state than their two-phase counterparts. This suggests that some oxidation of Fe(II) to Fe(III) occurs during the collection of "flashed" samples.

Table 4. Variations in Fe(II) concentration ($\mu\text{g/L}$) in samples preserved with HCl^{a}

Sample Number	pH*			
Geothermal samples (Yellowstone National Park, September 1975)				
Filter pore size: 0.1 μm				
		<u>January</u>	<u>August</u>	<u>December</u>
75WA183	1.10	2340	2410	1960, 1990
75WA184	1.05	3040	2060	720, 740
Estuarine samples (San Francisco Bay, September 1976)				
Filter pore size: 0.2 μm				
			<u>October</u>	<u>December</u>
76WA202	1.05		5,11	11
76WA208	1.00		<0.5,<0.8 ^b	3
76WA209	1.00		3,3	16
76WA213	1.15		<0.5,<0.8 ^b	2
Mine-tailings runoff samples (Missouri, June 1976)				
Filter pore size: 0.1 μm				
			<u>August</u>	<u>December</u>
76WA119	1.25		66,000	65,700;67,900
76WA128	1.20		2	9
76WA129	1.15		11	22
76WA130	1.20		48	58
76WA141	1.10		210,270	544
76WA146	1.10		100	120
76WA149	1.10		260	273
76WA155	0.95		100	117
76WA156	1.10		120	135

* pH of HCl -preserved samples (2 ml conc. acid/250 ml sample)

^a All analyses done in 1976

^b Below detection levels given

Sulfide Species

S(-II) values in the geothermal samples ranged from 0.01 to 5.3 mg/L (Table 5). Six of the eight "flashed" samples had S(-II) levels between 0.11 and 0.39 mg/L. These lower S(-II) levels are consistent with the lower Fe(II)/Fe(III) ratios of less than 2.0 (Table 5) found for the "flashed" samples, as compared to the two-phase samples for wells M-19A and M-30. The "flashed" samples may have lost S(-II) because of partial oxidation or H₂S exsolution during sampling. However, the 5.3 mg/L S(-II) mean concentration, found in the "flashed" sample of well M-26, was anomalously high and inconsistent with its low Fe(II)/Fe(III) ratio. A "flashed" sample from well M-51 had a mean concentration of 1.24 mg/L S(-II), more than most of the other "flashed" samples but consistent with the Fe(II)/Fe(III) ratio. The low S(-II) levels in the "flashed" samples from wells M-20 and M-91 corresponded to the lower Fe(II)/Fe(III) ratios for these samples.

Relative standard deviations of 5.2 percent or less are typical of the precision obtained for S(-II) determinations (Table 5). Inhomogeneity of the agitated sample at the time of subsampling may be a source of error whenever poor precision is encountered. Carbonates, formed as a result of sample preservation with Na₂CO₃, may armor some of the ZnS and Zn(OH)₂ (Jenne, 1977) thereby slowing dissolution of the precipitated sulfide in the alkaline antioxidant reagent.

Recovery studies were performed routinely during analysis, using spike additions (~40, ~200, and ~400 µg/L) of a S(-II) standard prepared in the alkaline antioxidant reagent.

Ninety to 111 percent of the added S(-II) was recovered from the 1/5 and 1/10 sample dilutions (Table 6). The mean recovery was 98.1 percent and the standard deviation was 5.8 percent. Recovery values < 95 percent might suggest that there is oxidation of S(-II) during measurement yielding low readings. Recoveries > 105 percent could indicate that more of the S(-II) armored by the insoluble carbonates are released for measurement during re-equilibration of the electrodes after standard addition.

Time stability of S(-II) fixed with Zn(C₂H₃O₂)₂ and Na₂CO₃ is dependent on pH, dissolved-solids content, and the amount of S(-II) present (Vivit and others, 1984). At a S(-II) level of 0.5 mg/L, 98 percent of the S(-II) added to 0.04 M NaOH (pH ~9) was recovered after 7 months. In contrast, only 56 percent of the S(-II) fixed in a distilled water matrix (pH ~6) was recovered after 7 months. In an artificial estuarine water (salinity = 27.5 parts per thousand, pH ~6), the S(-II) recovered after 7 months was 83 percent whereas in an artificial river water (pH ~6) only 68 percent was recovered after the same storage period.

For the level of Zn(C₂H₃O₂)₂ used to preserve the matrix-time-study samples (1.64-mL of 1 M Zn(C₂H₃O₂)₂ solution per 125 mL sample) and for the range of 0.04 to 2.2 mg/L S(-II) in distilled water, less than 90 percent of S(-II) was found after one week at all S(-II) concentrations except the ~0.5 mg/L level. Generally, < 90 percent of the original S(-II) concentration is found after storage if the sample pH is ~9. The actual levels of S(-II) in the Cerro Prieto samples at the time of collection could have been higher as determinations were done several months later.

Table 5.--Dissolved sulfide in Cerro Prieto, Mexico, geothermal water samples determined by sulfide-specific-ion electrode.

Well Number	Replicate values -----mg/L S(-II)-----	Mean	σ	RSD Pct.	Fe(II)/Fe(III)**
M-5	1.90,2.39,2.59	2.29	0.355	15.	n.s.
M-8	2.21,2.26	2.24	0.035	1.6	n.a.
M-11	2.61,2.06,2.35,2.76,2.96,2.83	2.60	0.335	13.	n.s.
M-14	4.88,4.46,5.66	5.00	0.609	12.	8.3
M-19A	2.62,2.73	2.68	0.078	2.9	3.9
M-19A*	0.176,0.170	0.173	0.0042	2.5	1.9
M-20*	0.254,0.264	0.259	0.007	2.7	1.1
M-21	3.73,3.70	3.72	0.021	0.6	n.a.
M-25	3.53,3.54	3.54	0.007	0.2	0.9
M-26	4.07,4.49,2.59,5.01	4.04	1.040	26.	n.s.
M-26*	5.4,5.2	5.3	0.14	2.7	1.7
M-27*	0.417,0.400	0.408	0.0120	2.9	n.a.
M-29	0.738,0.758	0.743	0.0141	1.9	5.9
M-30	2.24,2.01,2.35,2.68,2.80,3.26, 2.90,3.14	2.67	0.441	17.	7.6
M-30*	0.110,0.113	0.112	0.0021	1.9	1.4
M-31	3.55,3.82	3.68	0.191	5.2	n.s.
M-35	0.424,0.395	0.410	0.0205	5.0	n.a.
M-42*	0.213,0.208	0.210	0.0035	1.7	n.a.
M-45	2.78,3.33,3.16,3.28	3.14	0.249	7.9	8.7
M-51*	1.26,1.21	1.24	0.035	2.9	4.1
M-91*	0.363,0.412	0.388	0.0346	8.9	1.7
SpF-31	0.0141,0.0137	0.0139	0.00028	2.0	n.a.

* --"Flashed" sample

** --Ratio calculated from Table 1 mean values

n.s.--No significant amount of Fe(III) present (see Table 1) which results in some high Fe(II)/Fe(III) value, since the small amount of Fe(III) cannot be differentiated from Fe(II).

n.a.--No sample available for iron analysis

Table 6.--Sulfide recovery data for Cerro Prieto, Mexico geothermal water samples.

Well Number	Sample Volume* -----mL-----	Volume After Spike -----	Added -----µg/L-----	Found	Recovered Percent
M-5	2.50	--	0	190	102
	--	25.5	195	385	102
	2.50	--	0	259	--
	--	26.0	392	621	95
	2.50	--	0	239	--
	--	25.5	392	598	94
M-8	2.50	--	0	221	--
	--	25.5	198	446	96
M-11	2.50	--	0	262	--
	--	25.5	198	446	96
	2.50	--	0	235	--
	--	25.5	195	439	107
	2.50	--	0	295	--
	--	26.0	377	674	104
	5.0	--	0	361	--
	--	25.5	198	574	111
	2.50	--	0	488	--
M-14	--	26.0	383	853	100
	2.50	--	0	446	--
	--	26.0	392	796	94
	2.50	--	0	566	--
	--	26.0	392	911	94
	2.50	--	0	274	--
M-19A	--	25.25	100	364	93
	2.50	--	0	17.6	--
M-19A**	--	25.1	38.9	55.7	98

* Diluted to 25.0 mL

** "Flashed" sample

Table 6.--Sulfide recovery data for Cerro Prieto, Mexico geothermal water samples
(continued).

Well Number	Sample Volume* -----mL-----	Volume After Spike -----	Added -----µg/L-----	Found -----	Recovered Percent
M-20**	5.00	--	0	50.8	--
	--	25.1	39.2	87.3	94
M-21	5.00	--	0	747	--
	--	26.0	379	1093	99
M-25	5.00	--	0	705	--
	--	26.0	389	1089	106
M-26	2.50	--	0	406	--
	--	26.0	383	778	101
	2.50	--	0	359	--
	--	26.0	392	715	94
M-26**	5.00	--	0	1.1	--
	--	25.1	39.2	38.0	94
M-27**	5.00	--	0	83.3	--
	--	25.25	97	175	95
M-29	5.00	--	0	148	--
	--	25.25	97	237	93
M-30	2.50	--	0	274	--
	--	25.25	100	364	109
	2.50	--	0	235	--
	--	25.5	195	439	107
	2.50	--	0	280	--
	--	26.0	377	648	100
	2.50	--	0	290	--
	--	26.0	392	649	94
	2.50	--	0	314	--
	--	26.0	392	670	94
	5.00	--	0	417	--
	--	25.5	198	629	111

Table 6.--Sulfide recovery data for Cerro Prieto, Mexico geothermal water samples
(continued).

Well Number	Sample Volume* -----mL-----	Volume After Spike -----	Added -----µg/L-----	Found	Recovered Percent
M-30**	5.00	--	0	22.0	--
	--	25.25	100	117	96
	5.00	--	0	23.5	--
	--	25.25	100	115	92
	5.00	--	0	22.9	--
	--	25.1	40.2	62.1	98
M-31	2.50	--	0	355	--
	--	26.0	383	720	99
M-35	5.00	--	0	79.1	--
	--	25.25	100	168	90
M-42**	5.00	--	0	42.6	--
	--	25.1	39.2	77.8	90
M-45	2.50	--	0	278	--
	--	25.5	192	478	107
	2.50	--	0	333	--
	--	26.0	377	695	99
	2.50	--	0	316	--
	--	26.0	392	660	91
	2.50	--	0	328	--
	--	26.0	392	685	94
M-51**	2.50	--	0	126	--
	--	25.5	192	315	100
M-91**	2.50	--	0	36.3	--
	--	25.5	38.9	72.6	93
SpF-31	2.50	--	0	1.4	--
	--	25.1	38.9	39.2	97

In subsequent analyses of both Cerro Prieto and freshwater samples, NaOH instead of Na_2CO_3 was used with $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ to stabilize the ZnS precipitate. This was done to avoid coprecipitation of insoluble carbonates. However, a solid residue remained undissolved in the alkaline antioxidant reagent after analysis. Auger spectroscopy was used to determine the elemental composition of the freshwater residue which remained in the analyte solution after analysis (Vivit and others, 1984). The solid was found to consist primarily of Mg, O, and Si, a composition which suggests that the residue is a magnesium silicate. Sulfur was not detected in the solid residue.

CONCLUSIONS

The mean concentrations for dissolved iron in water samples from Cerro Prieto geothermal wells in this study range from 20.2 to 834 $\mu\text{g/L}$ as Fe(II) and 26.8 to 904 $\mu\text{g/L}$ as Fe(III) plus Fe(II). Mean sulfide concentrations range from approximately 0.01 to 5.3 mg/L S(-II). Generally, the higher S(-II) concentrations and the higher Fe(II)/Fe(III) ratios were found in the two-phase samples. This suggests that the "flashed" samples are at a less reduced state than the two-phase samples.

Prompt laboratory analyses are needed whenever field analyses are impractical or undesirable. This study indicates that changes are needed in sample preservation techniques to obtain more accurate values for dissolved species of Fe in these waters. The results obtained in this study also indicate a need to modify S(-II) preservation techniques. The use of NaOH rather than Na_2CO_3 should notably reduce the amount of carbonate precipitate that may armor the ZnS precipitate and hinder the dissolution of ZnS in the analytical step. Solid residues, possibly silicates, are still present when NaOH is used, but these solids apparently do not affect the analysis for S(-II).

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