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**Gas chromatographic procedure for analysis of drill core
samples for carbon dioxide and volatile sulfur species**

By

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ABSTRACT

A method was developed to analyze gases derived from rock and mineral samples, and this method was used to analyze samples of drill cores from the Casa Grande West porphyry copper deposit near Casa Grande, Arizona. The cores were ground and heated to desorb gaseous constituents, which were analyzed for sulfur compounds and carbon dioxide by gas chromatography.

Carbon disulfide, carbonyl sulfide, sulfur dioxide, and carbon dioxide were desorbed from the dry drill core samples. Hydrogen sulfide and organic sulfur compounds were not detected.

In an experiment designed to simulate natural weathering conditions, the drill cores were moistened with water and incubated for 6 days at 30°C. The same gaseous species of CS₂, COS, SO₂, and CO₂ were produced by these moistened samples, however in different concentrations from the gases produced by ground drill cores analyzed in the dry state. These gases may be useful geochemical indicators of buried porphyry copper deposits.

INTRODUCTION

There is increasing interest in using volatiles emanating from mineral deposits as an exploration guide. Anomalous quantities of volatiles such as sulfur compounds and carbon dioxide may be concentrated in soil gases over or peripheral to a buried deposit. Taylor and others (1982) conducted experiments to determine which gases were given off by various sulfide minerals, and analyzed the gases for sulfur compounds by gas chromatography. They found that CS₂ and COS were the most prevalent types of sulfur gases produced, and that pyrite gave off more sulfur gases than other sulfide minerals.

The purpose of this study was to develop a method for the analysis of gases derived from drill core samples.

The Casa Grande Copper Company provided 17 cores from 9 drill holes in various parts of the Casa Grande West porphyry copper deposit near Casa Grande, Arizona. Most of the cores were taken from the central part of the deposit. Gases in the crushed and heated samples were assumed to be derived from fluid inclusions and oxidation of fresh rock.

Descriptions of the cores and the analytical results are presented in table 1.

EXPERIMENTAL SECTION

General Procedure

Volatile sulfur compounds and carbon dioxide produced by heating the samples were analyzed by gas chromatography. The gas sample was injected by syringe into the entrance port of the gas-sample loop of the first of two closely spaced gas chromatographs. The exit port of the gas-sample loop of the first chromatograph was connected by tygon tubing to the entrance port of the second gas chromatograph. A 10-ml sample volume was necessary to completely fill both sample loops plus the connecting tubing. The sample

Table 1.--Analytical Results

Drill Core No.	Depth, meters	Rock	Description (Casa Grande Copper Company) Alteration	Mineralogy	ppb CS ₂	ppb COS	ppb SO ₂	% CO ₂	% Total S
19	788-791	conglomeritic sandstone and arkose, boulders			ND	ND	1150	0.9	0.004
19	890-892	dacite porphyry	propylitic, chloritic	pyrite	130	420	1140	1.7	0.802
19	901-904	granite	propylitic	pyrite	ND	355	1185	1.0	0.680
24	576-579	arkosic sandstone, pebbles, clay			ND	ND	1240	1.1	0.002
26	787-789	granite	chloritized/granite propylitic	pyrite, chalcopryrite	ND	ND	1530	0.5	0.204
27	967-970	granite	sericitic, potassic	chalcopryrite, pyrite, bornite	106	385	1305	0.7	0.430
27A	770-773	brecciated granite	sericitic, silicic	chrysocolla, hematite	ND	ND	1460	1.2	0.006
34	901-903	granodiorite	sericitic, secondary K-feldspar	chalcopryrite, pyrite	290	510	1445	1.2	1.24
81	699-701	brecciated granite	sericitic, clay	chalcocite	ND	385	1050	0.4	0.430
82	378-380	granite breccia	sericitic gougy matrix	transported limonite	ND	370	1040	0.3	0.012
82	465-467	granite	sericitic		ND	ND	1160	0.3	X
82	509-512	granite	sericitic, silicic	hematite after chalcocite	ND	ND	1060	0.4	0.050
82	575-578	dacite porphyry	sericitic, silicic	chalcocite, chrysocolla, hematite	ND	ND	1040	1.3	0.064
84	831-834	granite	potassic, sericitic	chalcopryrite	153	495	1095	0.6	1.25
116	815-818	granite	propylitic, supergene clay	chrysacolla	ND	ND	1110	0.3	0.012
116	909-912	granite	sericitic, clay, propylitic	chrysacolla	ND	ND	1155	0.4	0.02
116	1046-1049	latite porphyry	chloritized, sericitized plagioclase	pyrite	ND	ND	1115	0.9	0.134

ND = not detected at limit of detection for sulfur compounds (50 ppb)

X = not determined because of interference.

loops and connecting tubing were flushed with air between analyses to remove any traces of residual gases. Laboratory air was analyzed daily to make sure that the laboratory was free of sulfur-gas contamination.

A Varian printer-plotter with four-channel plotting and integrating capability and a remote-control station box was used to start and control the chromatographic runs. The operating conditions for each chromatograph are listed in table 2.

Standards for sulfur compounds were prepared in permeation ovens by diluting the sulfur gases that diffused from permeation tubes with different pressures of helium (O'Keefe and Ortman, 1966; Stevens et al., 1969). Standards of CO_2 were obtained from commercial aerosol bottles. Reproducibility of standards was ± 10 percent for CO_2 and ± 20 -25 percent for sulfur compounds. Standard curves were prepared by plotting instrumental integrated-peak areas versus different concentrations of gas standards, and these standard curves were used to determine the concentration of gases in the samples.

Operating conditions

In developing the analytical method, three operating conditions were evaluated: the optimum reaction tube temperature of the Hall detector; the optimum mesh size for the ground sample; and the optimum heating temperature and duration of heating for the samples.

I. Determination of optimum reaction tube temperature: The operating manual for the Hall detector states that 800 to 850°C is the best temperature for oxidation of gaseous sulfur compounds to SO_2 (Tracor, 1980). Gluck (1982) found that the optimum reaction temperature was 800°C for diethyldisulfide, but stated that higher temperatures might be necessary for other sulfur species. To establish the optimum reaction tube temperature for gases in this study, sulfur compounds from permeation tubes were run at reaction temperatures from 850 to 1000 degrees centigrade. The Hall reaction tube temperature was allowed to stabilize at each temperature for 24 hours before running the standards. From this study, 900°C was determined to be the optimum reaction temperature (figure 1).

II. Determination of optimum sample mesh size: In this experiment the optimum mesh size and heating temperature were determined. One-gram samples of ground pyrite were placed in 40 ml glass vials with screw-caps that had teflon-lined silicone septa. The vials were placed in a brass heating block and the block was heated on a hot plate for 30 minutes. Samples were run in triplicate for pyrite at -30+80 mesh (between 0.18 and 0.60 mm) and -80+150 mesh (between 0.10 and 0.18 mm) sizes, and for temperatures of 60°C and 90°C.

The ground pyrite produced large quantities of gas on heating. Gas within the vial was removed with a syringe and diluted with ambient air to 2.5 percent of the original concentration, in order to avoid contamination of the gas chromatographic columns, detectors, and connecting tubing. The gas sample was injected into the gas-sample loops of the gas chromatographs, following the procedure described above.

Table 2.--Operating conditions for gas chromatographs

	<u>Chromatograph I</u>	<u>Chromatograph II</u>
Brand and Model ^{1/}	Carle 8500	Tracor 560/700A
Gases analyzed	CO ₂	CS ₂ , COS, H ₂ S, SO ₂ and organic-sulfur compounds
Detector	Thermistor Detector	Hall Electrolytic Conductivity Detector, operated in the sulfur mode
Lower limit of detection	0.03 percent CO ₂ (volume/volume) ²	50 ppb for sulfur compounds (volume/volume)
Column	Concentric stainless steel outer column: 6 ft x 1/4 in activated molecular sieve; inner column: 6 ft x 1/8 in Porapak mixture (Alltech Associates, Deerfield, IL)	30 in x 1/8 in Teflon Packed with 18 in of acetone-washed 80/100 mesh Porapak QS (Supelpak-S) (Supelco, Inc., Bellefonte, PA)
Carrier gas	Helium at 90 ml/min	Ultra-high-purity helium at 60 ml/min Hall detector: Methanol flow rate = 0.5 ml/min Ultra-high purity air flow rate = 35 ml/min
Temperature	Column: 70°C Detector: "Low" mode	5 minutes hold at 50°C, programmed to 150°C at 30°C/min. Hold at 150°C for 7 minutes

^{1/}Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS.

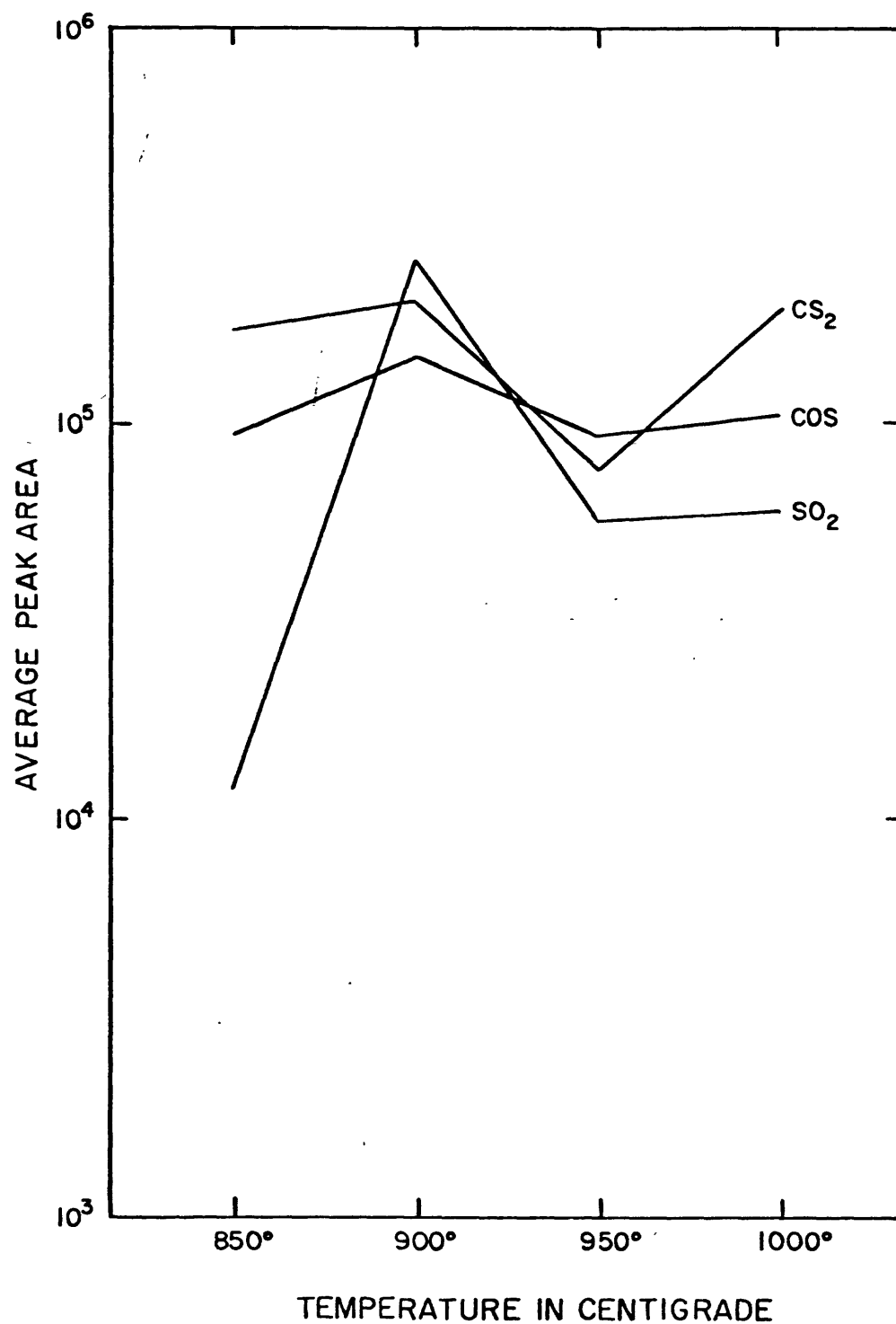


Figure 1.--Optimal reactor tube temperature.

Results of this experiment showed that (1) peak height was greater for the -80+150 mesh samples at each temperature, and (2) peak height increased for both mesh sizes when the temperature was raised from 60° to 90°C (figure 2).

III. Determination of optimum heating temperature and duration of heating: in this experiment, 1.0 gram of pyrite, ground and sieved to -80+150 mesh, was placed in the 40 ml vials and heated in the brass heating block at different temperatures and for different periods of time. Samples were run in duplicate at 40°, 60°, and 80°C, for 15, 30, and 45 minutes at each temperature. Gases removed from the vials were diluted to 2.5 percent of their original concentration with air, to avoid contamination of the gas chromatographs. Total sulfur gas content for the duplicate runs is compared to heating time and temperature in figures 3a-3c. Results of this experiment indicated that (1) reproducibility improved with increasing incubation time at every temperature, and (2) peak height increased with increasing temperature, as was also observed in experiment II. Because reproducibility improved with increasing incubation time, and because incubation for periods up to 1 1/2 hours did not affect the sulfur gas content measured for the pyrite samples, a heating time of 1 hour \pm 10 minutes at 80°C was selected for incubation of the ground drill core samples.

Reactions between gases in vials

In addition to evaluating the operating conditions for the analytical method, it was necessary to verify that the gases withdrawn from the heated vials were actually derived from the samples and were not products of gases reacting with each other or with air inside the vials.

Empty vials were filled with COS and CS₂ permeation gas standards, using a pump as shown in figure 4. Four vials were left at room temperature and four vials were heated for one hour at 80°C after covering the needle holes in the septa with silicone glue. Gas samples were removed from the vials for analysis by injecting 10 ml of air and removing 10 ml of mixed air and gas sample. Concentrations of COS and CS₂ in the samples from the unheated and heated vials were compared to concentrations of COS and CS₂ in standards injected directly into the gas chromatograph (table 3).

The only gases detected in the vials were COS and CS₂. Sulfur dioxide, which might be produced by the oxidation of CS₂, was not detected in either the unheated or heated vials. The decreased concentration of both COS and CS₂ in the vials compared with the standards is due to dilution by the air injected into the vials for removal of the gas sample. The air injection does not affect the precision of the vial sampling technique.

Analysis of the drill cores

Drill core samples from the Casa Grande copper deposit were ground and sieved to -80+150 mesh. Twenty grams of the ground and sieved material were placed in a capped 40 ml vial and heated at 80°C for 1 hour. Because there were lower concentrations of sulfide minerals in the drill cores, a smaller volume of gas was produced by the core samples than by pyrite alone. For analysis of the head space gas (gas in the space over the samples in the vials), 10 ml of air was injected by syringe through the teflon septum, and

Table 3.--Comparison of concentration of COS and CS₂
in gas reaction experiments

[COS = 885 ppb (parts per billion) and CS₂ = 100 ppb]

Method	COS ppb measured	CS ₂ ppb measured
Direct Injection	1020	100
	750	90
	960	110
	860	115
	820	100
-	882	103
X	882	103
S	± 108	± 10
Unheated Vial	850	95
	700	100
	760	90
	780	95
-	772	95
X	772	95
S	± 62	± 4
Heated Vial	720	90
	760	110
	860	95
	750	95
-	773	98
X	773	98
S	± 61	± 9

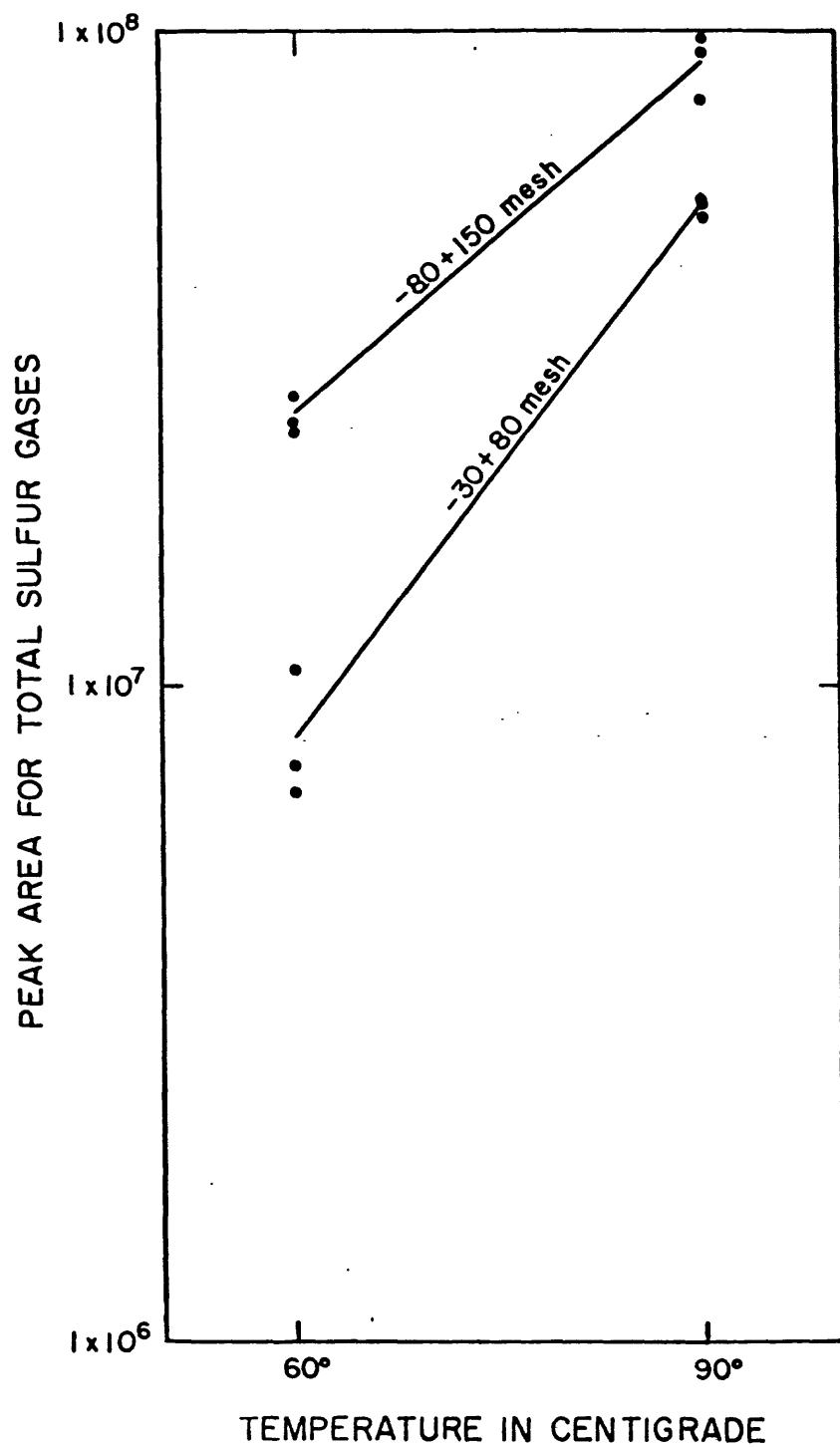


Figure 2.--Sample mesh size for pyrite.

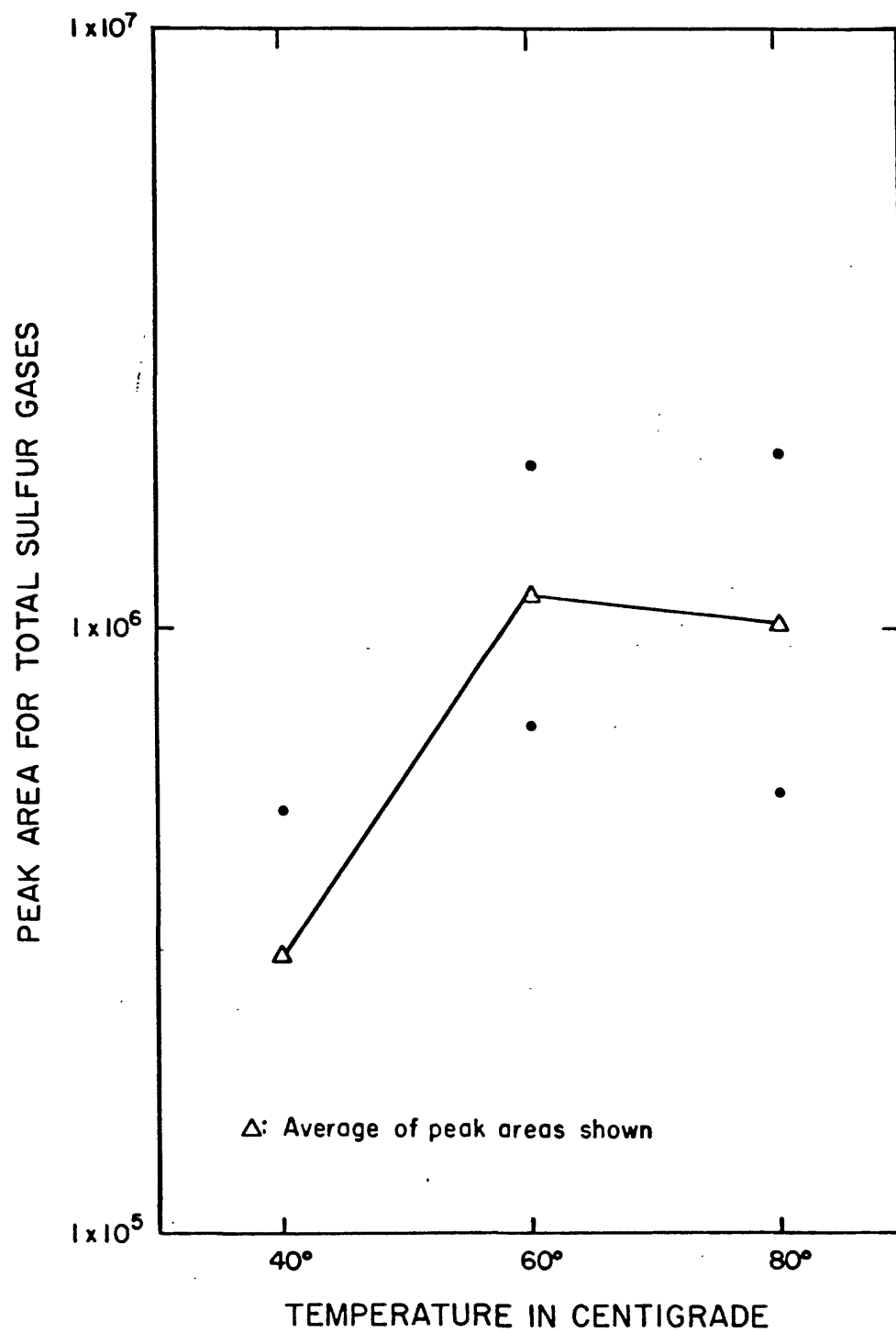


Figure 3a.--Peak areas versus heating temperature -15 minutes.

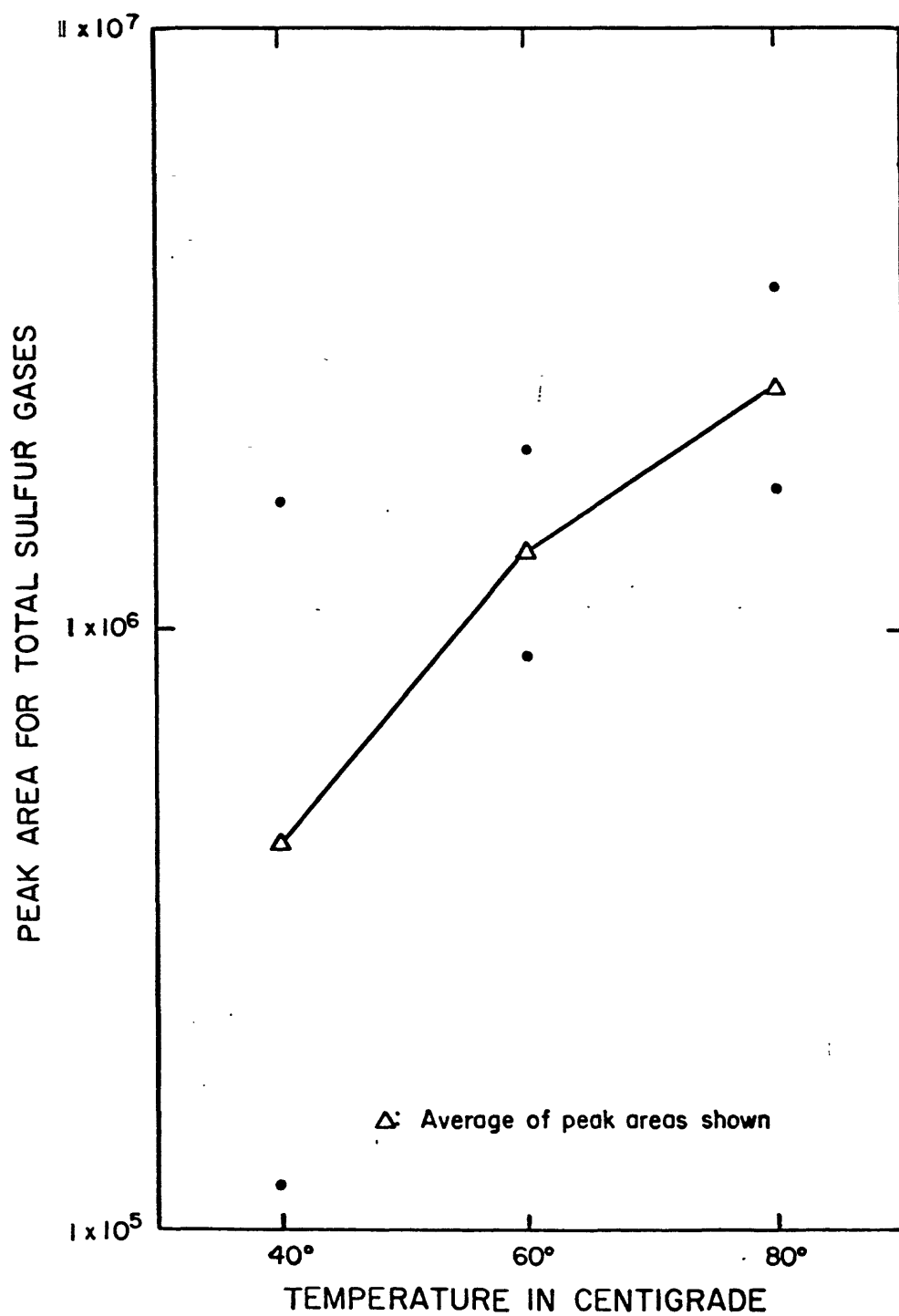


Figure 3b.--Peak areas versus heating temperature -30 minutes.

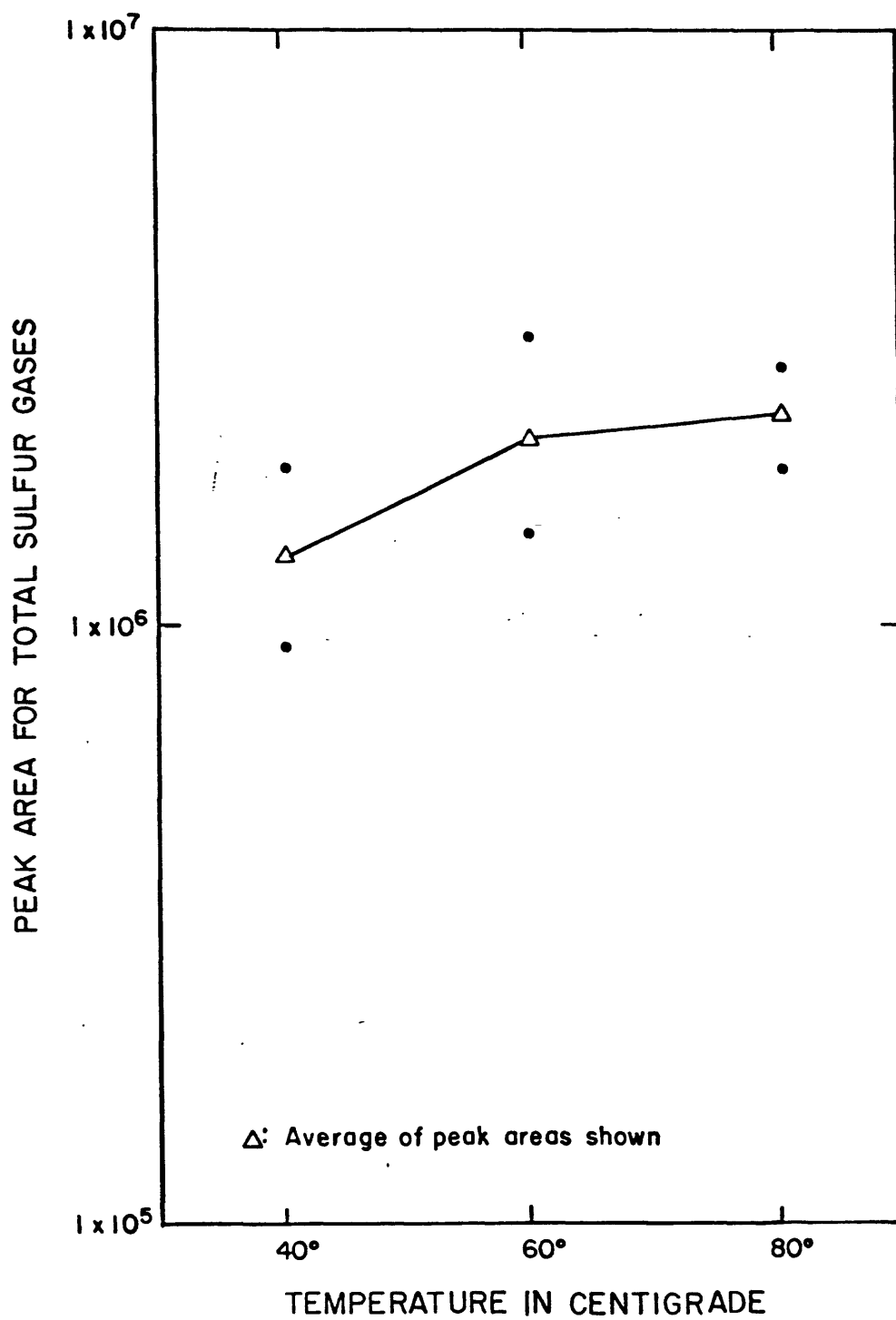


Figure 3c.--Peak areas versus heating temperature -45 minutes.

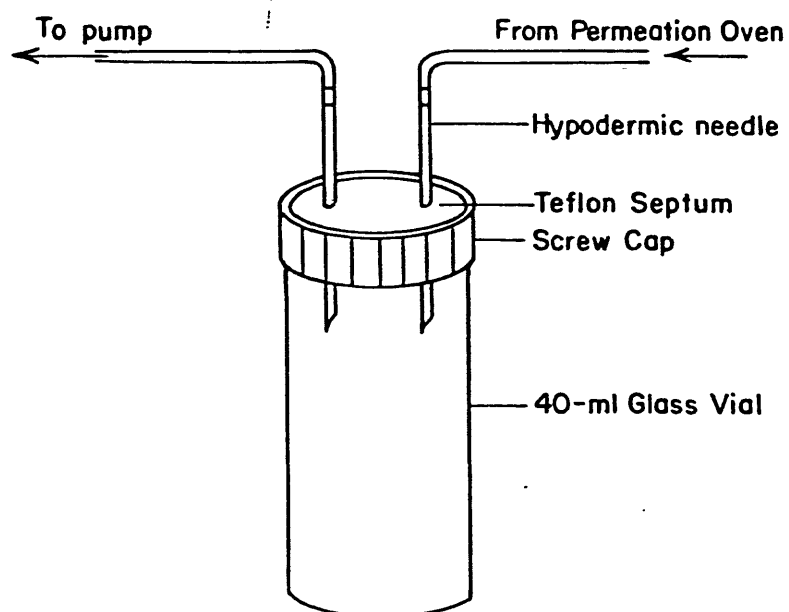


Figure 4.--Method of filling vials with permeation gas standards.

10 ml of mixed air and head space gas was removed from the vial and injected into the gas chromatographs.

Analytical results from the samples were compared to results obtained by analyses of gas standards, and concentrations of volatile constituents of the head space gas over the ground samples were calculated. No dilution factor was calculated for the addition of air to the vials containing the ground drill core samples. Duplicate samples were run for each ground drill core and the results were averaged. All averaged results for the drill core samples were within ± 20 percent of the measured results.

The ground cores were also analyzed for total solid phase sulfur content (Leco Corporation, 1963).

Results of all the analyses are summarized in table 1.

RESULTS

All of the samples that contained carbon disulfide also contained carbonyl sulfide. However, carbonyl sulfide also occurred in samples that did not contain carbon disulfide. The correlation coefficient for CS_2 and COS was 0.71, which indicates that CS_2 and COS are closely related, probably due to oxidation of CS_2 to COS.

Sulfur dioxide and carbon dioxide were present in all samples, but concentrations of the two compounds were not related (correlation coefficient = 0.05). Sulfur dioxide was not related to either CS_2 or COS (correlation coefficients were 0.31 and -0.03, respectively). Hydrogen sulfide was not detected in any drill core sample. The absence of H_2S in these samples is similar to the results of Taylor and others (1982). Organic sulfur compounds were not detected in any of the drill core samples.

Total concentration of gaseous sulfur derived from COS, CS_2 , and SO_2 was closely related to the total solid-phase sulfur content of the drill cores. The correlation coefficient between sulfur from the total volatile sulfur species and total solid sulfur was 0.86. Correlation coefficients between total solid sulfur and specific sulfur gases were CS_2 --0.86, COS--0.84, and SO_2 --0.15.

Comparison of gases produced under dry and moist conditions

Samples of drill cores were moistened with water and heated in an incubator before analysis in an effort to simulate conditions in the natural weathering process and promote the production of gases from sulfide minerals. For this experiment, 10 grams of ground drill cores were placed in 40-ml vials and moistened with 2 ml of demineralized water. The vials were capped, placed in an incubator, and heated at 30°C for 6 days. Gas samples were removed from the vials by adding 10 ml of air and removing 10 ml of mixed air and gas sample for analysis. Because only half the quantity of ground drill-core samples was used in the moistened experiment as was used in the dry experiment, the concentrations of gases measured in the moistened experiment were multiplied by 2 for comparison with the dry runs. In addition, gas from vials containing 2 ml of demineralized water alone was analyzed for CO_2 to determine background concentrations of CO_2 that might degas from the water;

only atmospheric CO_2 was present in the gas in these vials. Results of the chromatographic analyses of the moistened samples are presented in table 4.

Ground drill core samples in these experiments produced the same volatile compounds under moist conditions as they did when dry, although the concentrations of the gases differed between the moist and dry samples. In general, the CO_2 content of gases derived from the moistened drill cores was considerably higher than from the dry samples. The correlation coefficient between CO_2 concentrations of moist and dry samples was 0.67. The correlation coefficient between CO_2 concentrations and total solid-phase sulfur content of the drill cores rose from 0.29 for CO_2 and total sulfur in dry cores to 0.56 for CO_2 and total sulfur in moist cores. More CO_2 was produced from the moist than from the dry ground drill cores, probably as a result of SO_2 reacting with water to form H_2SO_4 , which attacked carbonate material in the cores.

Most of the drill core samples that produced COS and CS_2 when dry also produced COS and CS_2 when moist. Quantities of COS were significantly higher for the moistened samples, probably due to oxidation of the sulfide minerals. Quantities of SO_2 , on the other hand, were lower or not detected in most of the moistened samples, probably due to the reaction of SO_2 with water to form sulfuric acid.

Whether they were moist or dry, the same samples produced the majority of the sulfur gases and CO_2 that were measured here. The correlation coefficient between the total gaseous sulfur compounds produced by the moist samples and the total solid-phase sulfur content of the samples was 0.79.

CONCLUSIONS

A method for the analysis of gases in rock samples was developed and applied to gases derived from drill cores from the Casa Grande porphyry copper deposit. Temperatures from 40 to 90°C and mesh sizes of -30+80 and -80+150 were studied in the development of the method. Higher temperatures and a finer mesh size yielded the highest and most reproducible results. Carbon disulfide, carbonyl sulfide, sulfur dioxide, and carbon dioxide were the only gases detected from drill core samples from the deposit. These volatiles were closely related to total solid-phase sulfur content of the drill cores. No hydrogen sulfide or organic sulfur compounds were detected.

When the drill cores were moistened with water and incubated at 30°C for 6 days, the same gases COS, CS_2 , SO_2 , and CO_2 were produced, however, in different concentrations from gases produced by the cores that were analyzed in the dry state. Carbon dioxide concentrations were much higher, whereas sulfur dioxide concentrations were much lower than in the drill cores that were analyzed in the dry state. This is probably because SO_2 reacted with the water to form H_2SO_4 , which in turn reacted with carbonate material in the drill cores to produce CO_2 . The ratio of COS to CS_2 concentrations was much higher in the moist samples than in the dry samples. This higher ratio of COS to CS_2 for moist samples may indicate that COS is more prevalent than CS_2 over a weathering sulfide deposit.

The analytical method developed in this study can be used for the analysis of gases derived from rock and mineral samples. Results of this study indicate that CS_2 , COS, SO_2 , and CO_2 are the most prevalent volatile

Table 4.--Results of analyses of moistened drill cores
[ppb = parts per billion]

Drill core number	Depth, meters	COS (ppb)	CS ₂ (ppb)	SO ₂ (ppb)	CO ₂ (percent)
19	788-791				3.4
19	890-892				5.4
19	901-904	1200		1080	2.8
24	576-579				2.2
26	787-789			940	1.4
27	967-970	1140		1118	2.0
27A	770-773			930	1.8
34	901-903	1400	120	1080	5.6
81	699-701	1000		1716	0.4
82	378-380	1080		1515	1.4
82	465-467				1.0
82	509-512				2.2
82	575-578			1020	1.2
84	831-834	3720	560		2.2
116	815-818				1.6
116	909-912			910	1.6
116	1046-1049			900	3.0

compounds degassed from drill core samples from the Casa Grande deposit, regardless of whether the core samples were analyzed in the dry state or under conditions simulating natural weathering. Therefore, these compounds may be useful geochemical indicators over this and other porphyry copper deposits.

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