



Analysis of gaseous sulfur compounds by process gas chromatography
by Edward I-Sen Wan

A Thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
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Abstract:

A process gas chromatograph for the quantitative determination of gaseous sulfur compounds has been developed and successfully tested on the prepared samples. The instrument is an improved version of the instrument reported by Applebury (4). The sensitivity and precision are increased by replacing the column packing with PORAPAK Q-S material and increasing the titration solution concentration by twenty percent.

A detailed study of the variation of peak size, with sample pumping time, cell adjustment and titrating solution concentration is reported.

The calibration data of hydrogen sulfide, sulfur dioxide and methyl mercaptan are presented at different operating conditions. The study of higher order sulfur compounds, as well as the effects of temperature, carrier gas flow, and steam condensation is also reported.

The instrument can analyze wide concentration ranges of gaseous sulfur compounds (from 0.1 ppm to 1000 ppm by volume), and the analysis may be performed by remote-control at ten minute intervals.

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ANALYSIS OF GASEOUS SULFUR COMPOUNDS

BY PROCESS GAS CHROMATOGRAPHY

by

EDWARD I-SEN WAN

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ABSTRACT

A process gas chromatograph for the quantitative determination of gaseous sulfur compounds has been developed and successfully tested on the prepared samples

The instrument is an improved version of the instrument reported by Applebury (4). The sensitivity and precision are increased by replacing the column packing with PORAPAK Q-S material and increasing the titration solution concentration by twenty percent.

A detailed study of the variation of peak size, with sample pumping time, cell adjustment and titrating solution concentration is reported.

The calibration data of hydrogen sulfide, sulfur dioxide and methyl mercaptan are presented at different operating conditions. The study of higher order sulfur compounds, as well as the effects of temperature, carrier gas flow, and steam condensation is also reported.

The instrument can analyze wide concentration ranges of gaseous sulfur compounds (from 0.1 ppm to 1000 ppm by volume), and the analysis may be performed by remote-control at ten minute intervals.

I. INTRODUCTION.

The Kraft pulp mill has been reported to be a significant contributor to air pollution, and intensive studies are in progress to minimize pollutants from this source. These studies have necessitated the development of analytical techniques capable of obtaining definitive information on the compositions of mill exhaust.

Many gas chromatographic methods for determining gaseous sulfur compounds have been reported in the literature (1, 2, 3), but none of these methods have the capability of continuously monitoring pollutants from pulp mills.

The process gas chromatograph used in this work was originally constructed by Applebury (4), and the instrument described in this thesis is an improved version of that instrument. The sensitivity and precision were increased tenfold by several modifications. These are:

- (1) replacing the column packings with PORAPAK Q-S (100/120 mesh), from Van Waters Assoc. Inc.,
- (2) replacing all tubing and connections with teflon or stainless steel materials,
- (3) replacing the sample valve with a Wesco solenoid valve, model No.A973,
- (4) improving the sampling control box and sample injector,
- (5) increasing the KBr concentration in the titrating solution by twenty percent, and
- (6) increasing the carrier gas flow rate to 200 ml./min.

These modification provided the desired increased sensitivity without loss in resolution.

II. EQUIPMENT AND EXPERIMENTAL PROCEDURES

INSTRUMENTS

The process gas chromatograph consists of an analyzer, a control unit, and a data processing system.

A. Analyzer

The analyzer provides the analysis of the samples. It has a sensitivity of 0.1 ppm to 1 ppm depending on the individual sulfur compound (for a detailed description of the analyzer, the reader is referred to the thesis of Applebury (4)). The schematic diagram of the analyzer is shown in Figure 1.

The detector was a three section bromine coulometric microtitration cell. The position of the sensor electrode was changed so that the capillary tube was perpendicular to the platinum plate of the sensor electrode. The new position is shown in Figure 2. The column packing was replaced with PORAPAK Q-S (100/120 mesh).

B. Control Unit

A control unit governed by a programmed timer mechanism provided remote control of the analysis. The function switch in both the control panel and the microcoulometer permitted either manual or automatic analysis of the sample mixture. A detailed discussion of this unit was described in Applebury's thesis (4).

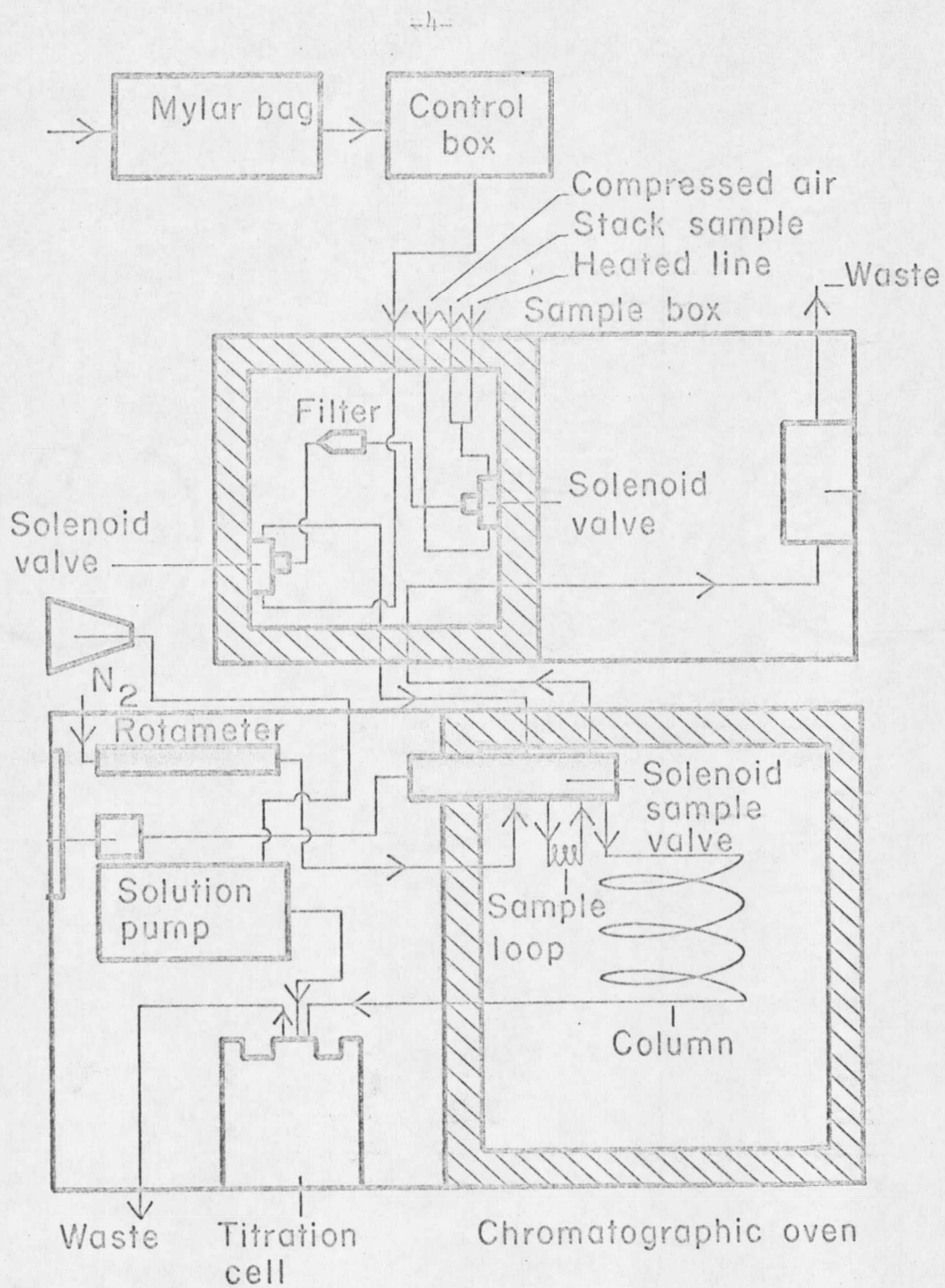


Figure 1. Analyzer

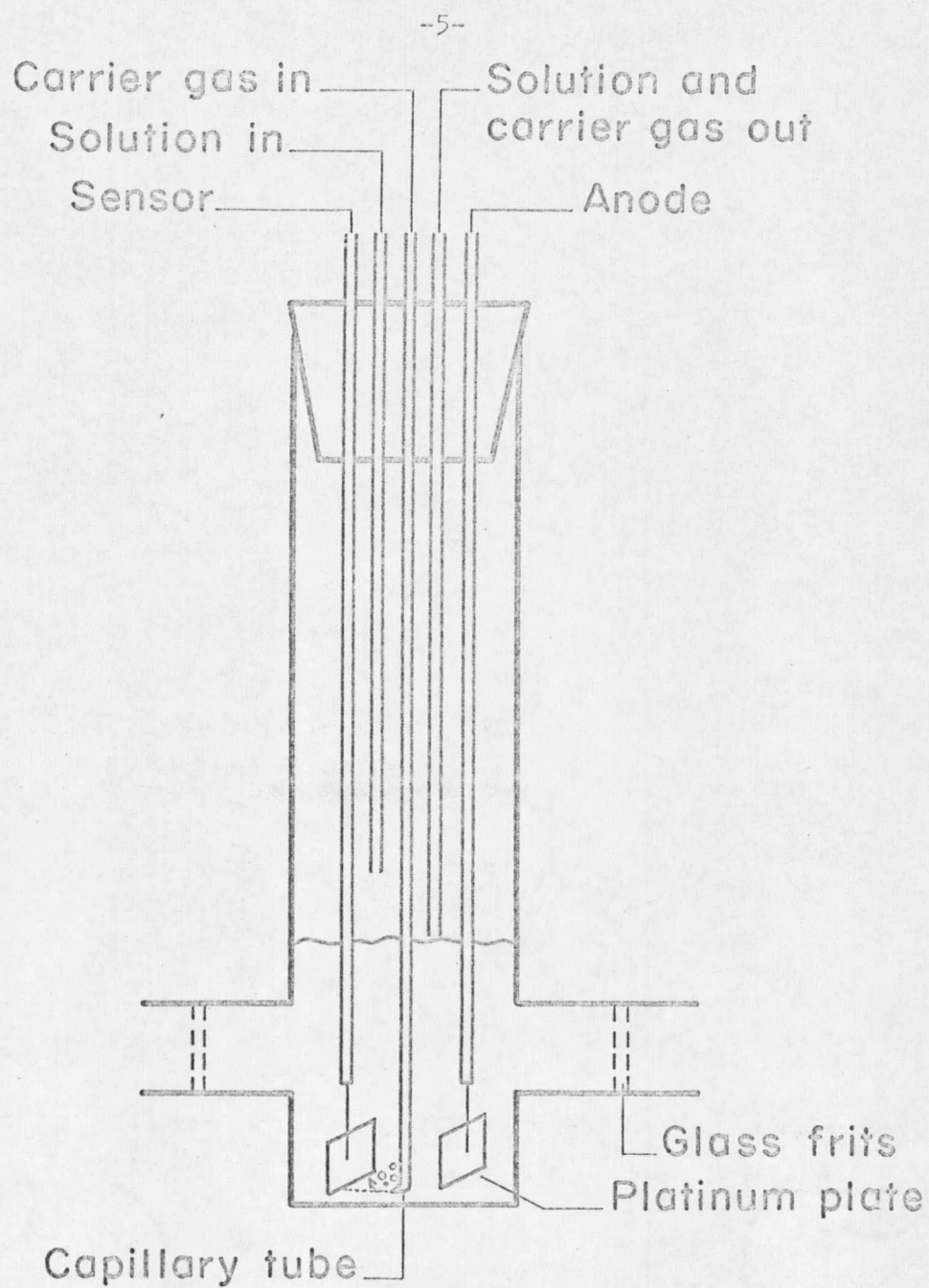


Figure 2. Titration Cell

C. Data Processing System.

The output signal was recorded by a conventional strip chart recorder. The results were found by the cut and weigh method and then compared with the calibration data from a known sample. A schematic diagram of this system is shown in Figure 3.

REAGENT

Gaseous hydrogen sulfide, sulfur dioxide, and methyl mercaptan, (Matheson Company), were used for the preparation of the samples. Pure nitrogen (99.9%), was used for the preparation of the gas standards and for the carrier gas. Compressed air was used to flush out the sample bag. The titration solution was made of reagent grade potassium bromide (Matheson Coleman and Bell), 98% concentrated sulfuric acid (Matheson Company), and distilled water.

PROCEDURE

The standard gas mixtures were prepared by volumetric techniques which involved the use of a wet test meter to measure nitrogen and a gas-tight syringe to measure the pure gases. The standards were prepared in concentrations as shown in Table I. All standard gas mixtures were stored in Mylar bags.

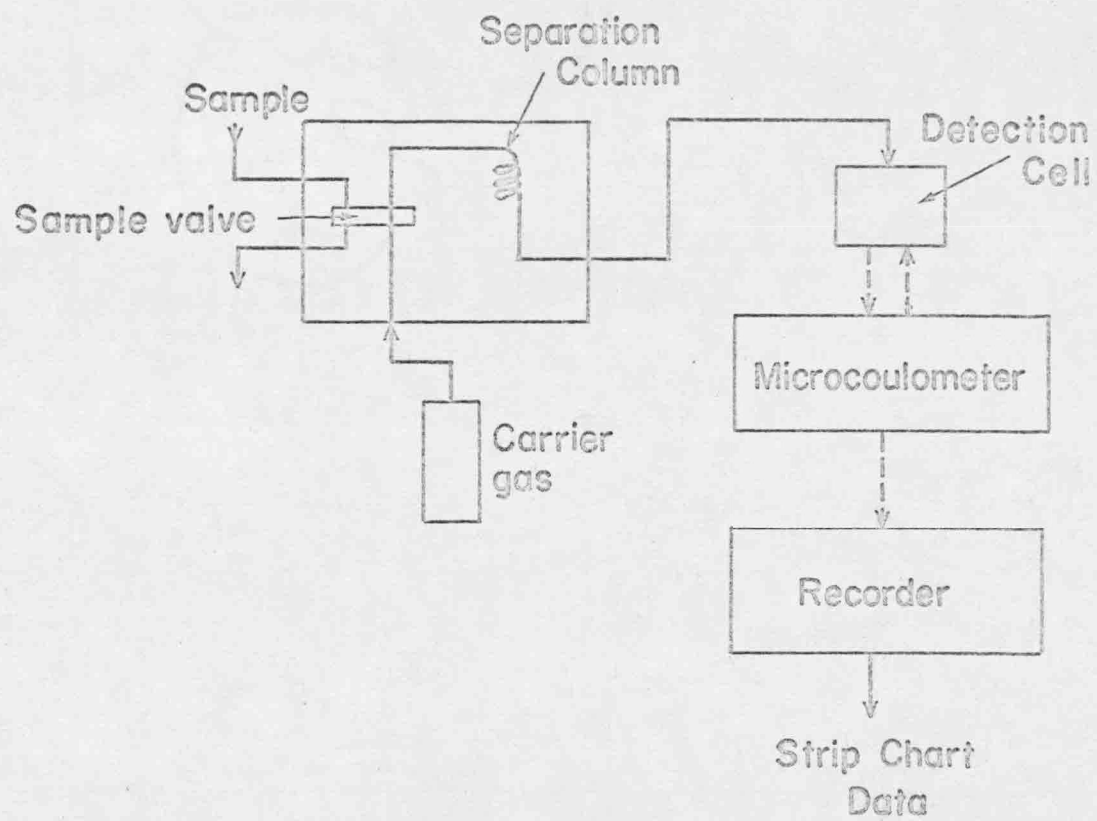


Figure 3. Data Processing System

TABLE I. STANDARD CONCENTRATION

Concentration (ppm by vol.)	Pure Gas	Dilute Nitrogen
*5	2 ml.	1.414 cu.ft.
*10	4 ml.	"
25	10 ml.	"
50	20 ml.	"
75	30 ml.	"
100	40 ml.	"

* The first dilution (20 ppm to 100 ppm) was made in a sample bag. Below this range, the concentration was obtained by multiple dilution.

The instrument automatically samples and analyses the standard mixtures, and records the response on a strip chart as a chromatogram.

The quantitative measurement of the elution time and peak area identify the compound and its concentration.

The cut and weigh method was used for quantitative measurement of the peak area. The accuracy was 5%.

III. RESULTS AND DISCUSSION

VARIATION OF PEAK SIZE

Early experimental results indicated an irregularity of the response and it was difficult to obtain reproducible data. Figure 4 is an example of an early result.

The size of the first peak was smaller than the rest, and the from the second to the sixth, the response gradually increased. After that, the response was stable. This abnormal behavior has been studied and several parameters were found that directly affect the peak size. The parameters were: sample time, cell adjustment, and titration solution concentration.

A. Pumping Time

Because the prepared mixture is not directly injected into the chromatographic column, the quantity of sample pumped was sometimes insufficient to have a full response.

Figure 4 shows that the small response of the first run of the analysis was due to insufficient sampling time. This has been improved by increasing the pumping time to one minute. The dotted line in Figure 4 shows the improved response.

B. Cell Adjustment

The microtitration cell is designed to operate at a constant titration ion concentration which is determined by the bias set control

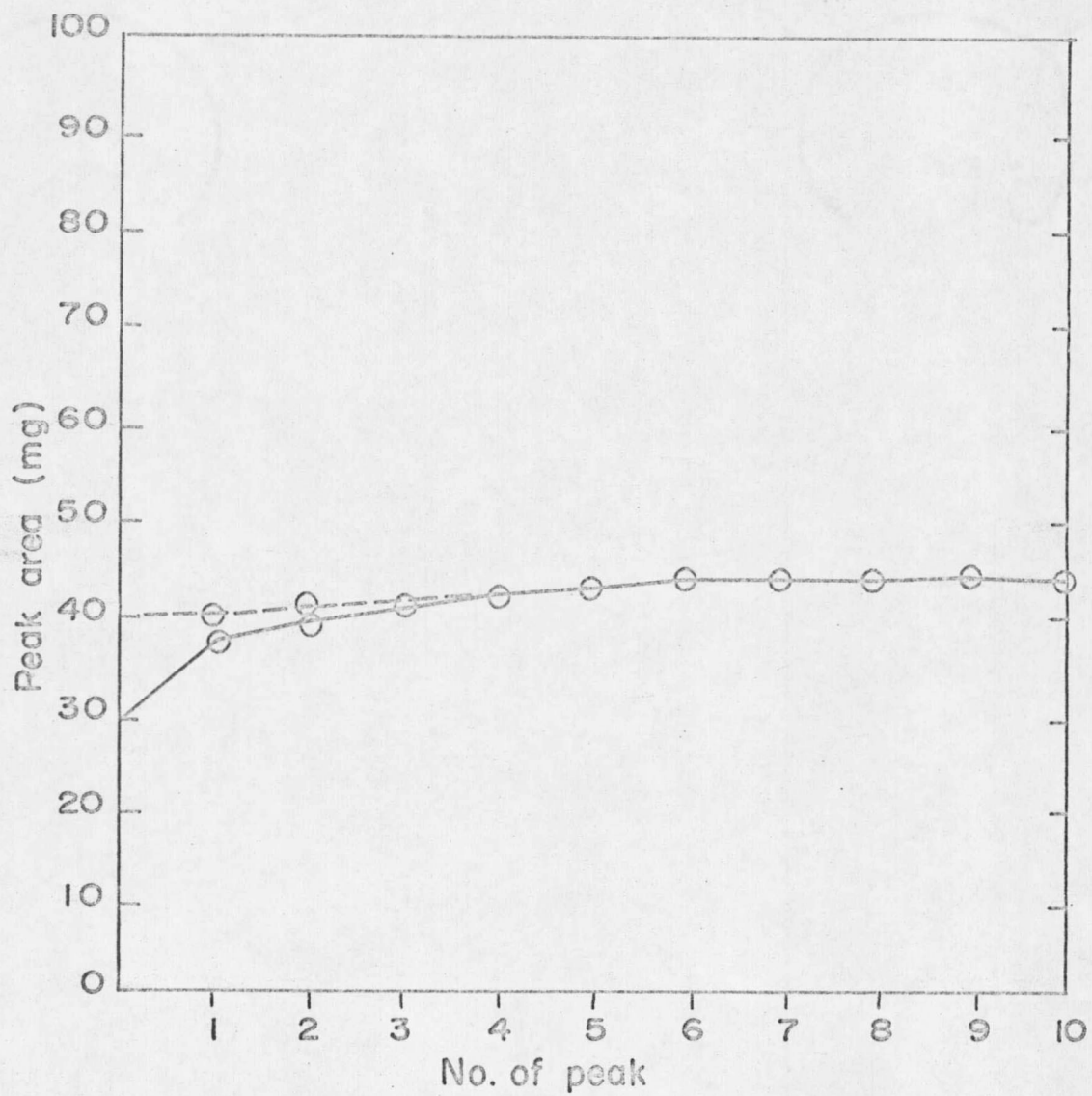


Figure 4. Variation of peak size during the continuous course of analysis.

of the microcoulometer. The titration ions are Br^-/Br_2 . A shift in titrant ion concentration within the titration cell is detected by the reference sensor electrodes. The EMF between these electrodes is a direct function of the titrant ion concentration (activity) upon the surface of the platinum electrode. After each analysis, the generator pair re-establishes the titrant to its original concentration and the system is again in equilibrium. The titration solution is replaced by periodically pumping a small amount of electrolyte (i.e. 20% of total electrolyte in the titration cell) into the cell after each analysis.

It was found that the equilibrium time for the fresh electrolyte solution was on the order of three to ten minutes. There are three parameters which affect this equilibrium time. They are: (1) the location of the sensor electrode, (2) the sample residence time in the solution, and (3) the regeneration solution rate.

The electrodes were placed so that the sensor electrode was directly in front of the gas inlet capillary. The more perpendicular the position of the sensor electrode to the capillary, the less time required for equilibrium. Also, the more perpendicular the position of the sensor electrode to the capillary, the less tailing of the sample peak.

The gas sample was emitted from the capillary tube and reacted in the titration solution. The equilibrium time depended upon the solution reaction time, which in turn was a function of gas flow rate. The greater the gas flow rate, the smaller the sample residence time and hence,

less reaction time was needed. The regeneration rate not only determined the equilibrium time, but also effected the shape of the peak and the location of the baseline. If the regeneration rate was not properly adjusted, there was an excess or deficiency of titration ion in the cell. An excess of Br^- ion produced a shallow overshoot and a deficiency produced a lengthy tail as the cell equilibrated.

For proper operation it was necessary that the sensor electrode, the carrier gas flow, and the regeneration rate be adjusted so that the peak had no overshoot or tailing.

Experience showed that the following conditions produce satisfactory results: (1) the capillary tube perpendicular to the sensor electrode, (2) the carrier gas flow rate at 200 ml./min., and (3) the regeneration rate at 3 cc/cycle.

C. Titrate solution concentration

Several concentrations were investigated since a change in the titration solution concentration effected the cell operation. Table II shows the cases investigated and the results.

TABLE II. SOLUTION CONCENTRATION INVESTIGATION

	Composition	Response/Concentration		
		H ₂ S	SO ₂	CH ₃ SH
Case 1	7.2g KB _r + 6 ml.H ₂ SO ₄ + 1 liter H ₂ O	0.51	0.20	0.70
Case 2	8.64gKB _r + 6 ml.H ₂ SO ₄ + 1 liter H ₂ O	0.60	0.26	0.85
Case 3	7.2g KB _r + 7.2ml.H ₂ SO ₄ + 1 liter H ₂ O	0.63	0.28	0.90
Case 4	8.64gKB _r + 7.2ml.H ₂ SO ₄ + 1 liter H ₂ O	0.69	0.31	1.00

The above data indicates that the higher concentration level gave the higher sensitivities. Therefore, we operated the titration cell with the concentration level of Case 4.

CALIBRATION DATA

After the steady state response had been found, replicated bags of standard samples were prepared and analyzed. A calibration curve was obtained for standards of pure H₂S, SO₂, and CH₃SH, and a linear response was shown. Then a mixture of H₂S, SO₂, and CH₃SH was prepared to investigate the possible reactions between the compounds. The experimental results indicated that, in the first four hours, the mixture had the same response as each compound prepared separately. However, after four hours, the results showed that the SO₂ and H₂S reacted slowly with each other. Therefore the response of these two was slightly decreased, as shown in Figure 5. In addition, a random concentration sample was prepared and used to compare with the pure compound's response. This study revealed that the responses were almost the same during the first four hours of

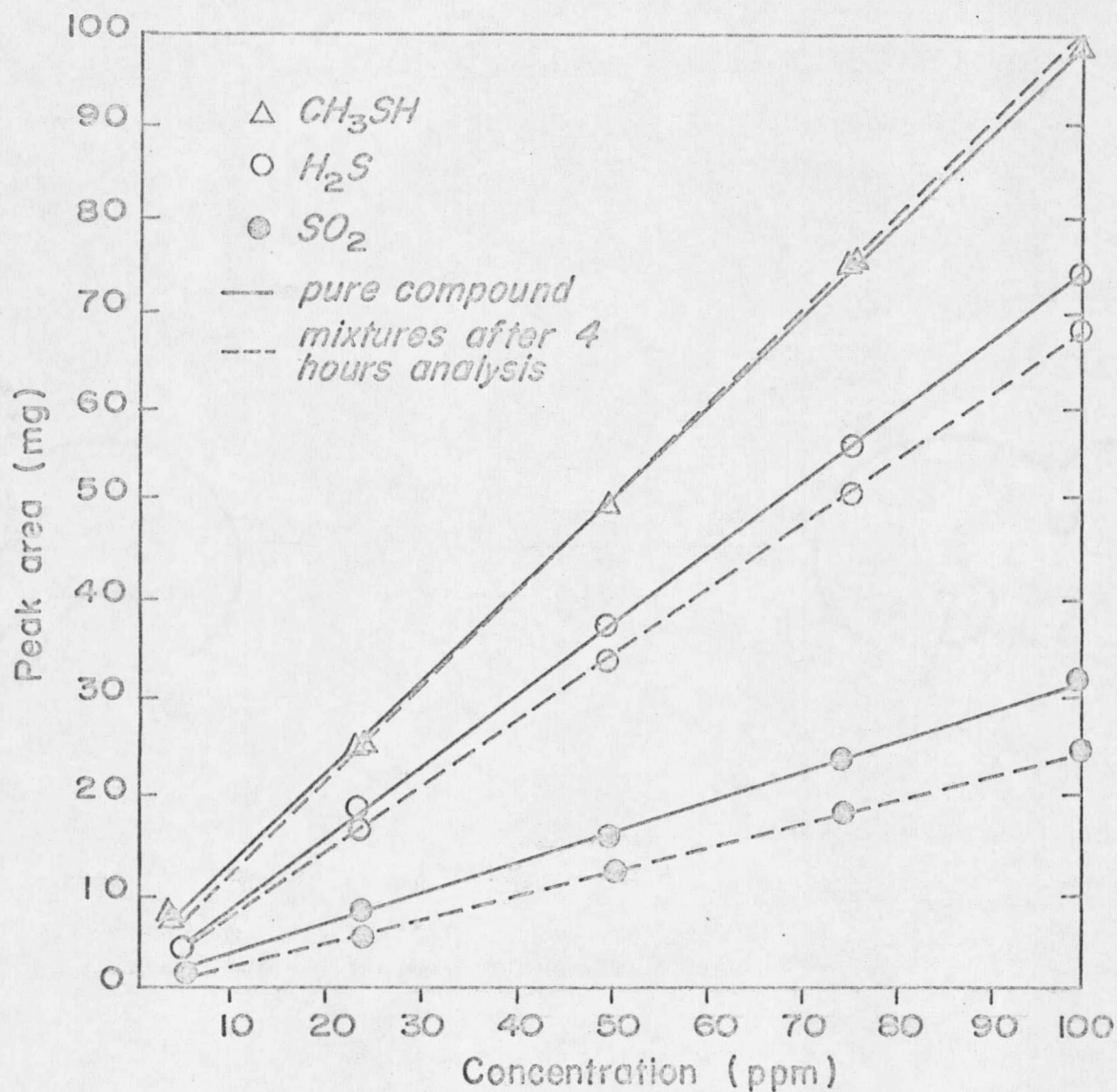


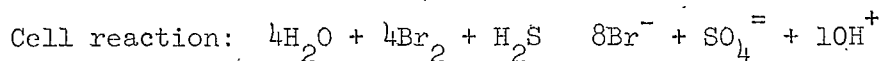
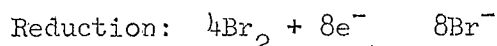
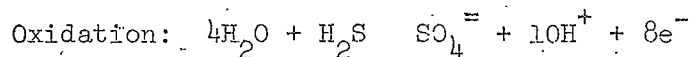
Figure 5. Comparison of mixture and pure component's response after 4 hours analysis at column temperature = 90°C . Carrier gas flow = 200 ml/min. Bias set = 725 mv. Range 2. $1/4'' \times 6'$ PORAPAK Q-S column.

analysis. Consequently, the calibration data can only be taken during the first four hours.

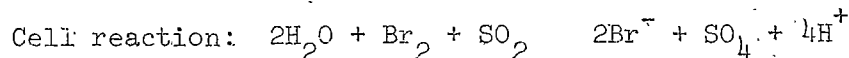
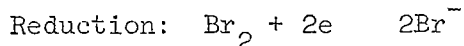
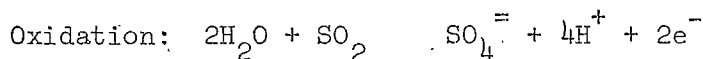
The calibration data for all three compounds at different operating conditions are listed on Table III, Table IV, Table V, Table VI and Table VII. Table VIII shows the minimum detectable concentration.

Theoretically, the response of either H_2S or CH_3SH should be four times greater than SO_2 , because of the difference in electron requirement for the electrochemical reactions. This is shown in the following equations.

A. H_2S



B. SO_2



Similarly, the methyl mercaptan has the same electron change required as in the H_2S reaction. The calibration curve of the mixture prepared for 5 ppm, 10 ppm, 25 ppm, 50 ppm, 75 ppm and 100 ppm is shown in

TABLE III. CALIBRATION DATA OF PREPARED MIXTURE AT TEMPERATURE=90°C,
CARRIER GAS FLOW=150 ml/min BIAS SET=725 mv AND RANGE=2.

A. Hydrogen sulfide

Concentration(ppm)	Response (peak area in mg)					Avg. Response
5	5.4	5.2	5.5	5.3	5.1	5.3
10	9.8	10.0	9.7	9.9	10.2	9.9
25	24.1	24.3	23.8	24.2	23.6	23.9
50	48.2	49.2	49.9	50.3	48.9	49.3
75	73.0	73.9	75.4	74.9	75.9	74.3
100	99.4	98.6	99.3	99.7	100.3	99.4

B. Sulfur dioxide

5	2.5	2.6	2.7	2.3	2.5	2.5
10	5.7	5.8	5.4	5.5	5.4	5.6
25	9.5	9.4	9.8	9.9	9.7	9.7
50	19.4	20.0	20.7	20.8	20.5	20.3
75	28.0	29.8	29.7	29.0	28.9	29.0
100	40.9	39.3	41.4	41.1	40.6	40.7

C. Methyl mercaptan

5	9.1	9.3	9.8	8.7	8.4	8.9
10	16.9	16.6	15.9	16.5	17.0	16.6
25	35.9	34.0	35.7	35.2	34.4	35.0
50	64.6	66.3	64.9	66.8	66.4	65.8
75	95.2	98.5	97.1	96.0	95.4	96.4
100	126.2	122.5	120.5	121.7	125.6	123.3

TABLE IV. CALIBRATION DATA OF PREPARED MIXTURE AT TEMPERATURE=80°C,
CARRIER GAS FLOW=200 ml/min, BIAS SET=725 mv AND RANGE=2.

A. Hydrogen sulfide

Concentration(ppm)	Response (peak area in mg)					Avg. Response
5	7.2	7.4	7.0	6.9	6.7	7.0
10	13.2	12.6	13.4	13.1	13.5	13.2
25	28.5	27.0	28.3	27.9	27.3	27.8
50	51.3	52.6	51.5	53.0	52.7	52.2
75	76.2	78.2	77.1	76.3	75.5	76.6
100	100.2	97.3	95.7	96.6	99.8	97.9

B. Sulfur dioxide

5	2.3	2.4	2.5	2.2	2.3	2.3
10	5.0	5.2	4.9	5.0	4.8	5.0
25	8.3	8.2	8.4	8.3	8.3	8.3
50	16.5	17.5	17.1	17.7	16.9	17.1
75	23.6	25.2	25.1	24.6	24.5	24.6
100	34.2	32.9	34.7	34.5	34.0	34.1

C. Methyl mercaptan

5	9.2	8.7	9.1	8.9	8.6	8.9
10	16.6	16.4	15.6	16.1	16.7	16.3
25	34.2	34.4	34.0	33.5	32.9	33.8
50	59.5	61.0	59.8	61.5	61.1	60.5
75	87.4	89.9	88.6	88.2	86.8	88.1
100	114.3	118.8	108.4	109.9	113.8	111.4

TABLE V. CALIBRATION DATA OF PREPARED MIXTURE AT TEMPERATURE=80°C,
CARRIER GAS FLOW=200 ml/min, BIAS SET=725 mv AND RANGE=2.

A. Hydrogen sulfide

Concentration(ppm)	Response (peak area in mg)					Avg. Response
5	5.1	4.8	5.1	5.0	4.9	4.9
10	8.9	9.1	9.0	9.1	9.2	9.1
25	21.0	21.2	20.7	20.9	20.9	20.9
50	41.3	42.2	42.7	42.9	41.9	42.2
75	61.4	62.2	63.8	63.5	63.1	63.0
100	82.8	82.1	82.4	82.7	83.6	82.8

B. Sulfur dioxide

5	1.9	2.0	1.8	2.1	1.9	1.9
10	4.4	4.5	4.3	4.2	4.2	4.3
25	7.4	7.3	7.7	7.6	7.5	7.5
50	15.0	15.5	16.1	16.0	15.5	15.6
75	21.7	23.1	22.5	23.0	22.4	22.5
100	31.7	32.1	31.9	32.1	31.5	31.5

C. Methyl mercaptan

5	7.2	7.4	7.0	6.9	6.7	7.0
10	13.4	13.2	12.6	13.1	13.5	13.2
25	28.5	27.0	28.3	27.9	27.3	27.8
50	51.3	52.6	51.5	53.0	52.7	52.2
75	76.0	78.2	77.1	76.3	75.5	76.6
100	100.2	97.3	95.7	96.6	99.8	97.9

TABLE VI. CALIBRATION DATA OF PREPARED MIXTURE AT TEMPERATURE=100°C,
CARRIER GAS FLOW=200 ml/min, BIAS SET=725 mv AND RANGE=2.

A. Hydrogen sulfide

Concentration(ppm)	Response (peak area in mg)					Avg. Response
5	3.1	3.0	2.8	3.0	3.1	3.0
10	5.9	6.0	5.8	6.0	6.2	6.0
25	15.2	15.4	15.1	15.1	14.9	15.1
50	31.7	32.4	32.9	33.1	32.3	32.5
75	49.2	49.8	51.2	50.9	50.5	50.3
100	67.8	67.4	67.5	67.7	68.4	67.7

B. Sulfur dioxide

5	1.5	1.6	1.6	1.4	1.5	1.5
10	3.7	3.8	3.6	3.8	3.5	3.7
25	6.4	6.5	6.6	6.6	6.5	6.5
50	13.7	14.0	14.5	14.4	14.1	14.1
75	19.7	21.0	20.9	20.4	20.2	20.5
100	29.2	28.0	29.5	29.3	29.0	29.0

C. Methyl mercaptan

5	5.1	5.2	4.9	4.8	4.7	4.9
10	10.2	10.0	9.6	9.9	10.3	10.0
25	22.8	21.6	22.6	22.3	21.7	22.2
50	43.1	44.2	43.2	44.5	44.3	43.8
75	64.6	66.5	65.6	64.4	64.2	65.0
100	85.9	83.8	83.0	83.3	85.8	84.3

TABLE VII. CALIBRATION DATA OF PREPARED MIXTURE AT TEMPERATURE=90°C,
CARRIER GAS FLOW=250 ml/min, BIAS SET=725 mv AND RANGE=2.

A. Hydrogen sulfide

Concentration(ppm)	Response (peak area in mg)					Avg. Response
5	2.8	2.0	2.9	2.7	2.5	2.7
10	5.0	5.2	5.1	5.2	5.1	5.1
25	13.1	13.3	12.9	13.0	12.8	13.0
50	24.8	25.4	25.0	25.3	25.4	25.3
75	37.6	38.1	39.1	39.0	38.7	38.5
100	51.2	50.8	51.3	51.9	51.4	51.3

B. Sulfur dioxide

5	1.3	1.4	1.5	1.3	1.2	1.3
10	3.1	3.2	3.0	3.1	3.0	3.1
25	5.3	5.4	5.8	5.2	5.0	5.4
50	10.6	11.0	11.3	11.5	11.2	11.3
75	15.4	16.4	16.9	16.0	15.9	16.1
100	22.5	21.7	22.8	22.7	22.4	22.3

C. Methyl mercaptan

5	5.3	5.5	5.2	5.1	5.0	5.2
10	9.9	9.8	9.3	9.7	9.9	9.7
25	21.1	20.0	20.9	20.0	20.2	20.5
50	38.0	38.9	38.1	39.2	39.0	38.6
75	56.8	57.9	57.1	56.6	55.6	56.8
100	74.2	73.1	70.9	71.6	74.0	72.7

TABLE VIII. MINIMUM DETECTABLE CONCENTRATIONS

H_2S	0.05 ppm
SO_2	0.1 ppm
CH_3SH	0.05 ppm

Figure 6. As seen in this figure, the response of H_2S was not four times greater than SO_2 . Instead, it was 2.5 times greater than SO_2 . The smaller response of both H_2S and CH_3SH was three times greater than SO_2 . The smaller response of both H_2S and CH_3SH is due to the incomplete reaction of these compounds in the titration solution. All three compounds show the linear response. In the low concentration range, the absorption in the column was noticeable; especially for the SO_2 . Therefore, the response was less than expected for the low concentration region of the calibration curve. The order of elution was H_2S , SO_2 , and CH_3SH .

COLUMN TEMPERATURE EFFECT

From quantitative studies, the results show that the higher the column temperature, the lower the response. Also, it was found that samples at lower concentrations had less temperature effect than those at higher concentrations.

A comparison of the three compounds shows that SO_2 is the least affected by the temperature, and CH_3SH is the most affected. The temperature effect on all three compounds at a constant carrier gas flow (200 ml./min.) is shown in Figure 7.

A column temperature also affects the peak shape and retention time. The higher the temperature, the sharper the peak and the shorter the retention time. A plot of retention time versus temperature is shown in Figure 8.

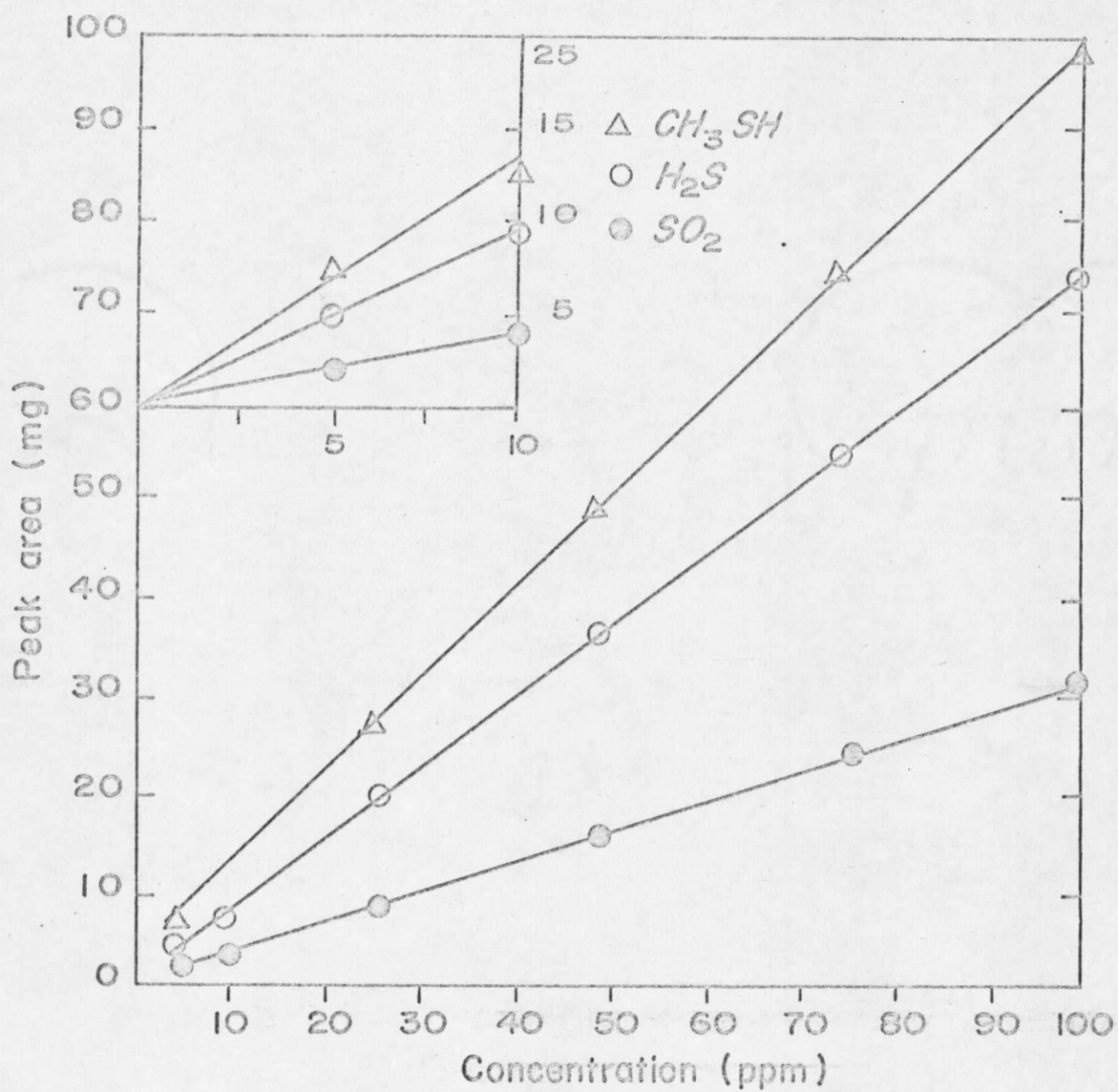


Figure 6. Direct Calibration Curve of H_2S , SO_2 , CH_3SH .

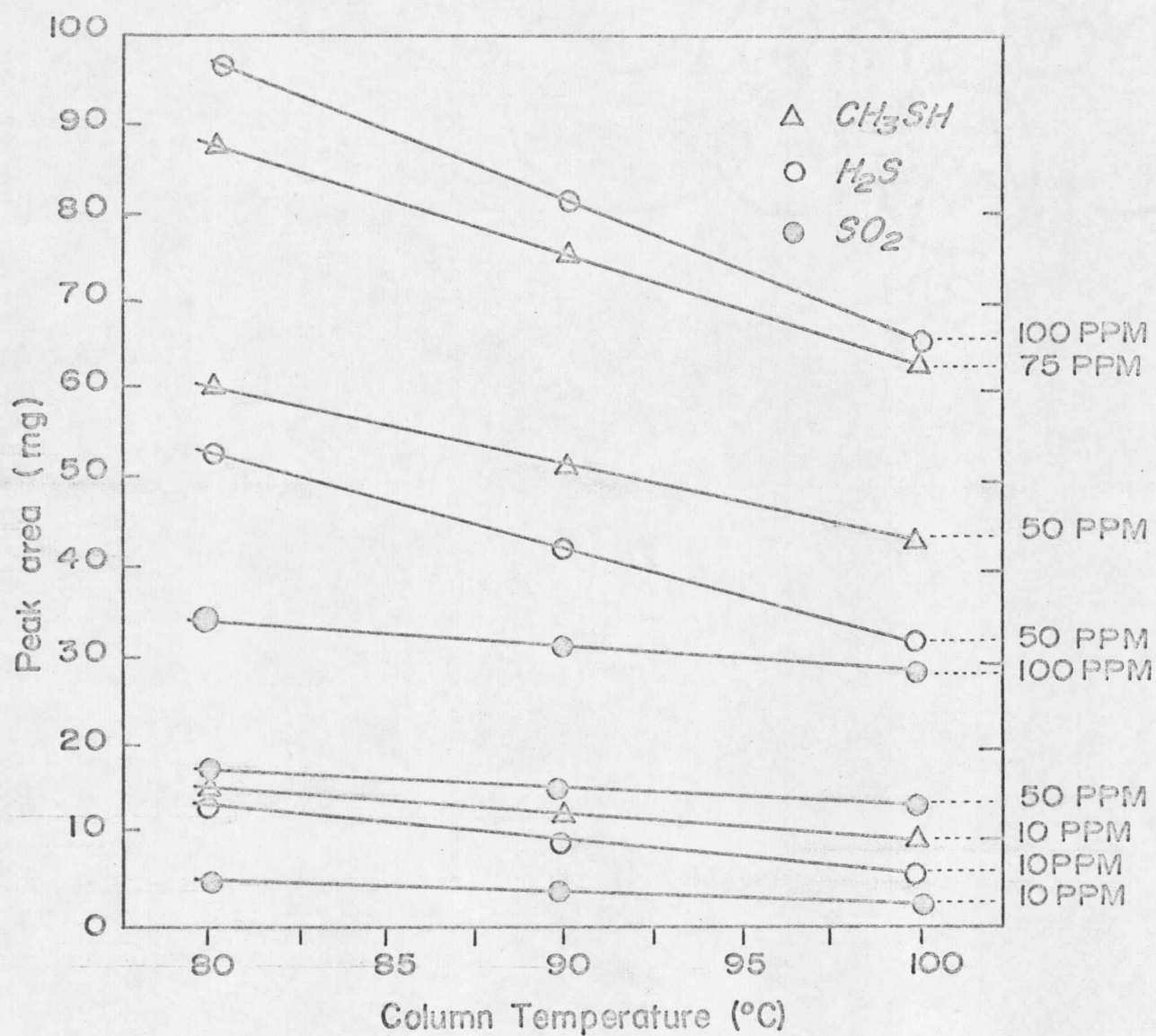


Figure 7. Column temperature affects the Chromatographic Response.

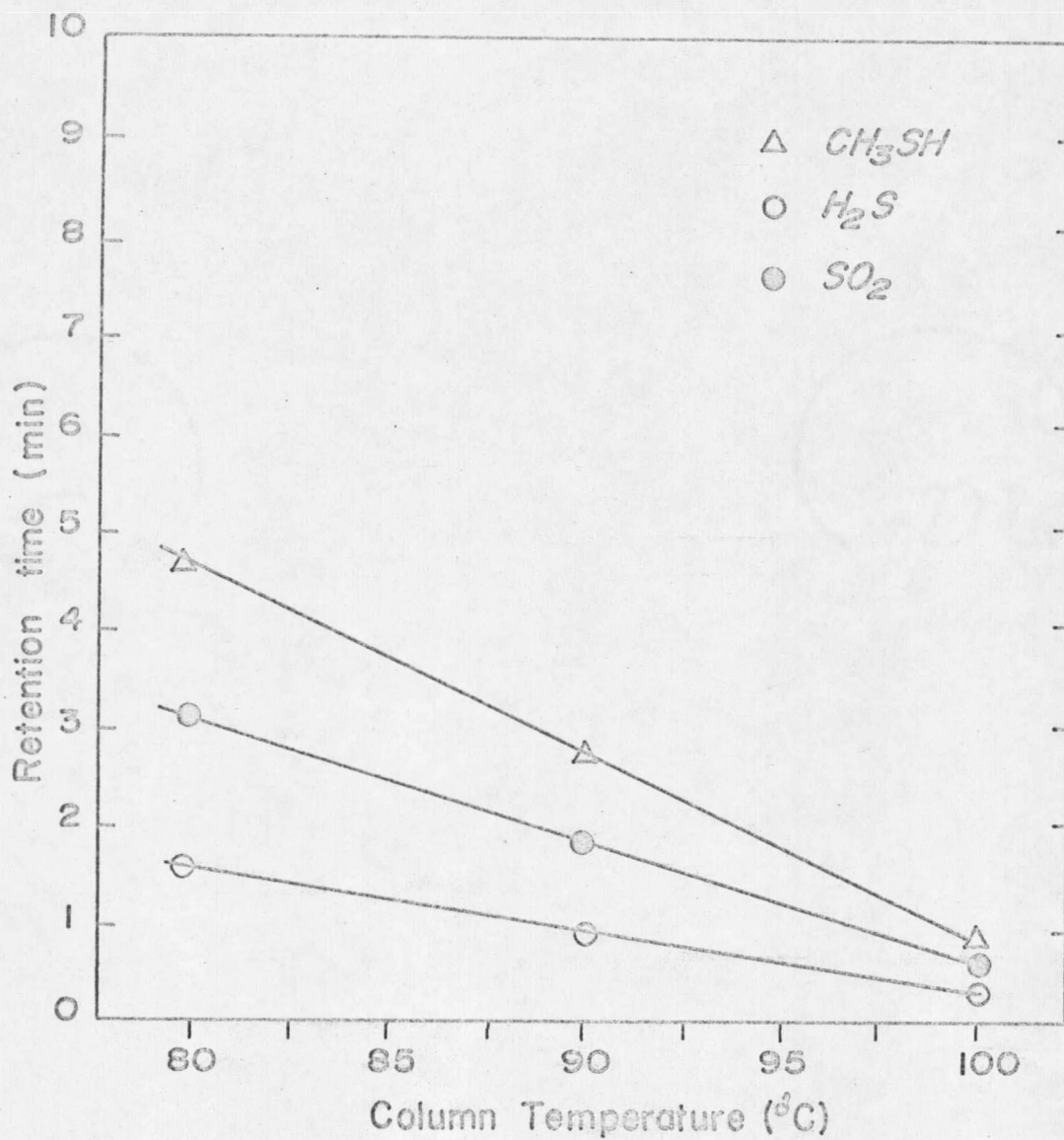


Figure 8. Column temperature affects the retention time at barrier gas flow = 200 ml./min. Bias set = 725 mv. Range = 2. 1/4" x 6' PORAPAK Q-S column.

CARRIER GAS FLOW EFFECT

The change of the carrier gas flow rate affects the peak shape, peak size, and elution time. It was noticed that the higher the carrier gas flow, the greater the random noise. The highest carrier gas flow without noticeable noise was 200 ml./min. At this condition, the noise level was estimated to be 1% of full scale. A diagram relating the carrier gas flow to the response of each compound at constant temperature is shown in Figure 9. The slope shows that the response of all three compounds decreased with increasing flow rate. Also, both the response of SO_2 and CH_3SH show a linear decreasing relationship, while H_2S shows a nonlinear relationship. The effect of carrier gas flow on retention time is shown in Figure 10. It shows that the retention time approaches a definite value at higher flow rates.

STEAM CONDENSATION TEST

The water-gas streams from pulping processes are saturated with water at elevated temperatures. The condensation of this water vapor inside the sample box and sampling tube may cause a corrosion problem. In order to prevent condensation during the analysis process, both the sampling tube and the sample box were insulated and maintained at a temperature of 100°C . A trial run using steam as the sample was studied. The results showed no chromatographic peak appeared on the strip chart recorder and that the instrument continued to perform satisfactorily after the test. Although the condensation of steam in the cell could

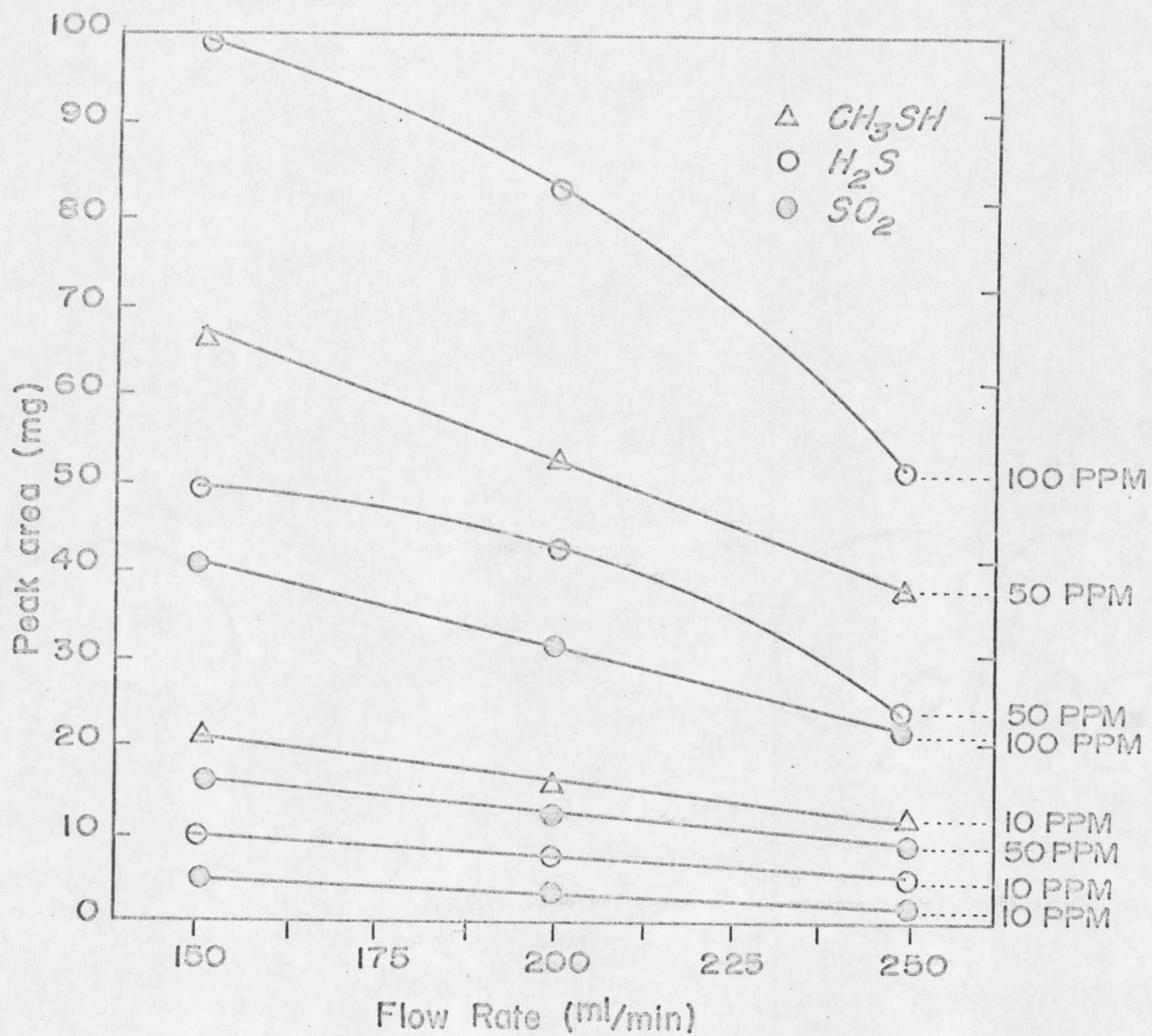


Figure 9. Carrier gas flow affects the chromatographic response.

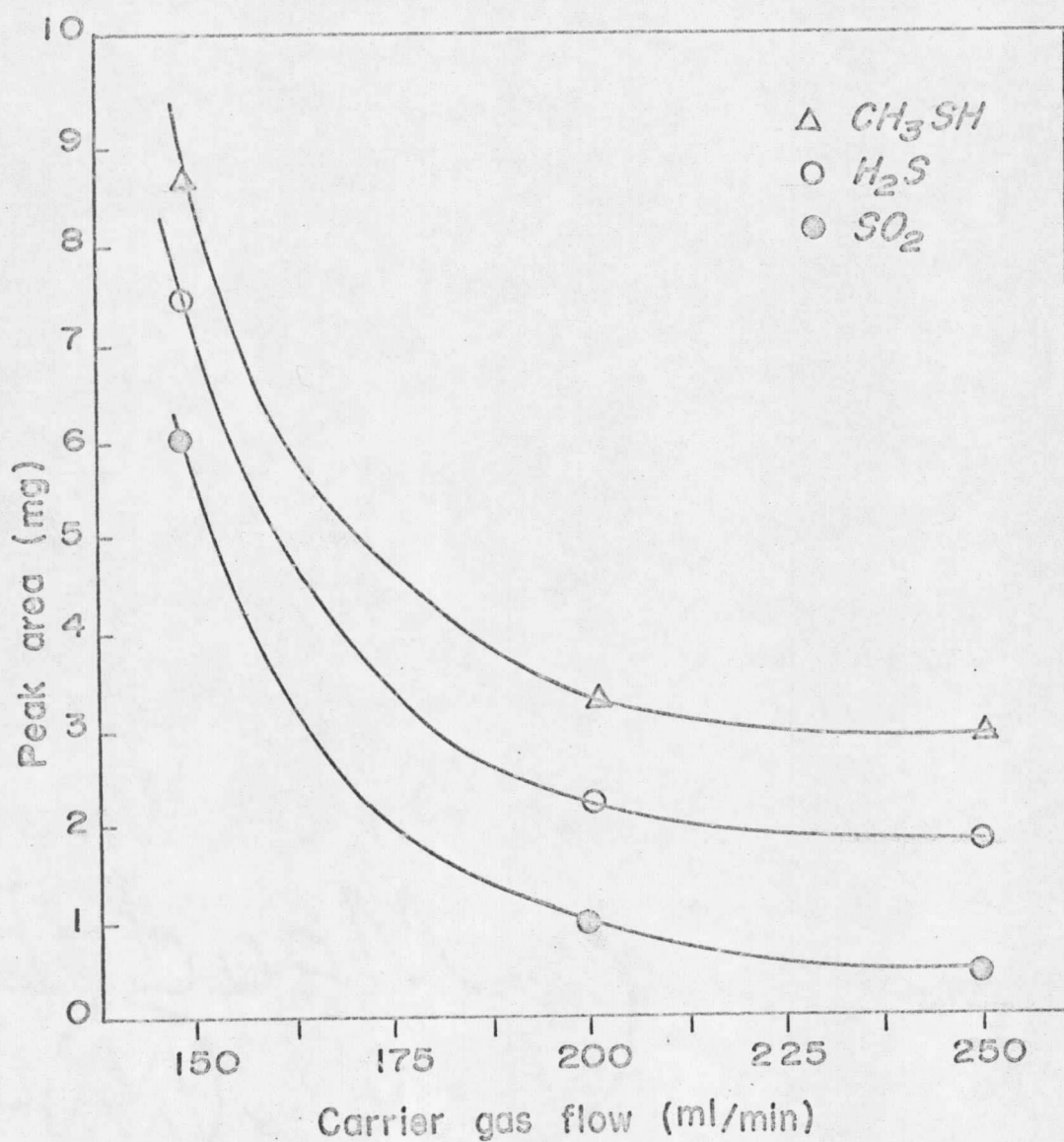


Figure 10. Carrier gas flow affects retention time.

possibly change the titration solution, the experimental results indicated that the effect was negligible.

HIGHER ORDER SULFUR COMPOUNDS

The higher order sulfur compounds including dimethyl sulfide and dimethyl disulfide were studied. These two compounds exist as liquids at room temperature. Therefore, the standard samples were prepared by dissolving the compound in acetone, and then injecting it into the Mylar bag. The sample bag was then heated gradually by a steam heater. The qualitative analysis of these compounds showed that both compounds have broad chromatographic peaks. The retention time for dimethyl sulfide was four minutes and for dimethyl disulfide was 10.5 minutes. No calibration curves were obtained.

SUGGESTED OPERATING CONDITIONS

It was found that the following operating conditions produced satisfactory results:

Column: 1/4" x 6' PORAPAK Q-S 100/120 mesh.

Titration solution: 8.64 mg. KBr_2 added to the 14.4 ml. conc.
sulfuric acid and 1 liter of distilled water.

Column temperature: 90°C

Sampling tube temperature: 100°C

Sample box temperature: 100°C

Carrier Gas flow: 200 ml./min.

Bias set; 725.mv.

Range; 2

Recommended regular maintenance:

1. Clean the titration cell once a month.
2. Clean the Dyna pump every six months.
3. Check the solenoid sample valve every six months to see if the silicon rubber O-rings are broken.
4. Check the battery in the recorder and control system.

IV. CONCLUSION

Results presented show that the improved instrument gives reliable calibration data under simulated plant conditions.

The instrument performed successfully without major mechanical troubles for a period of ten months. An unknown sample can be analyzed within fifteen minutes. The retention time identifies the compound and the response indicates the concentration of the compound.

The average deviation is estimated as 12%. The deviations are caused by errors in sampling and in the data handling method.

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