



Air pollution abatement by process gas chromatography
by Terrill Edward Applebury

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

A process gas chromatograph has been developed for the purpose of monitoring the effluent from a Kraft mill recovery furnace. The instrument will analyze in widely varying concentrations of H_2S , SO_2 , CH_3SH and higher order sulfur compounds. It is insensitive to the fixed gases and water vapor and performs its analysis in about ten minutes.

The instrument employs a bromine microcoulometric detection cell and is sensitive to H_2S in as low a concentration as 0.1 ppm and CH_3SH and SO_2 as low as 0.5 ppm. A central control panel has been built to allow operation from a position remote from the stack. Also included is a system which will allow computer evaluation of the data. It is even possible to have on-line evaluation by the computer.

The instrument has worked successfully on a furnace effluent in periods of 24 hours but has not been tried on a recovery furnace.

It has also run on a prepared sample for periods as long as seven days with no maintenance or personal attention necessary.

AIR POLLUTION ABATEMENT
BY PROCESS GAS CHROMATOGRAPHY

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Chemical Engineering

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ABSTRACT

A process gas chromatograph has been developed for the purpose of monitoring the effluent from a Kraft mill recovery furnace. The instrument will analyze in widely varying concentrations of H_2S , SO_2 , CH_3SH and higher order sulfur compounds. It is insensitive to the fixed gases and water vapor and performs its analysis in about ten minutes.

The instrument employs a bromine microcoulometric detection cell and is sensitive to H_2S in as low a concentration as 0.1 ppm and CH_3SH and SO_2 as low as 0.5 ppm. A central control panel has been built to allow operation from a position remote from the stack. Also included is a system which will allow computer evaluation of the data. It is even possible to have on-line evaluation by the computer.

The instrument has worked successfully on a furnace effluent in periods of 24 hours but has not been tried on a recovery furnace. It has also run on a prepared sample for periods as long as seven days with no maintenance or personal attention necessary.

INTRODUCTION

The Kraft process, by which more than 60% of all wood pulp made in the United States is manufactured, creates an air pollution problem by releasing methyl mercaptan, hydrogen sulfide, sulfur dioxide, and other sulfur-containing gases. The two primary sources of these gases are the relief and blow gas stack and the recovery furnace stack. The pollution due to the relief and blow gas has been controlled by collecting and burning these gases. Air pollution abatement on the recovery furnace stack poses a much larger and more complex problem.

This problem is made complex by three factors. First is the large volume of gases emitted by the furnace, making any scrubbing or burning operation very costly and difficult. Second is the many modes of furnace operation, and third is the fact that these gases are used in a direct-contact evaporator, an operation which causes the formation of the hydrogen sulfide.

There are several pollution abatement techniques currently being used. Examples of these are: black liquor oxidation to convert Na_2S to Na_2SO_4 , a more stable compound, prior to the direct contact evaporator and thus reduce the amount of sulfur gases formed, scrubbing the stack gases to remove odorous gases, and operating the recovery furnace under controlled conditions.

Before the effectiveness of these methods can be accurately known and before their effectiveness can be optimized, a method of measuring the sulfur emission from the recovery furnace stack must be developed. This monitoring can be done with standard wet chemical methods. There are several methods mentioned in the literature (7). The problem with most of these methods is that they are sensitive to only one or possibly two of the component sulfur gases. Some of these methods are rendered ineffective because of interaction reactions between the sulfur gases and because of the easy oxidation of these gases. Also, there are problems from the many impurities contained in the stack gases.

These wet chemical methods have one other very serious drawback in becoming an effective monitoring method. This is the time delay necessary between the sample is taken and the time it is analyzed. Because of this, it becomes very difficult to make accurate correlations between emission data and running conditions.

It is felt that process gas chromatography can be a much more effective monitor. It lends itself to automation and thus requires a minimum of man hours. By proper selection of detector and column it can be made sensitive to only desired compounds. It performs its analyses in about ten minutes.

For these reasons we have developed a process gas chromatograph for the purpose of monitoring the sulfur emission of a Kraft mill recovery furnace.

With such an instrument it should be possible to operate the recovery furnace at minimum sulfur emission. It might also be possible to take advantage of favorable weather conditions for increased throughput. It will also be possible to check and optimize the effectiveness of any pollution abatement method being used.

In any event, the first step necessary in solving the Kraft mill pollution problem is the development of an instrument such as this.

RESEARCH OBJECTIVES

Our objective was to develop a process gas chromatograph with the following characteristics:

1. analyze for the concentration of SO_2 , H_2S , CH_3SH , and other sulfur gases
2. insensitive to fixed gases and water vapor
3. withstand plant conditions
4. require a minimum of maintenance
5. perform automatic analyses in less than ten minutes
6. require a minimum of man hours for efficient operation

This chromatograph was designed specifically for operation on the recovery furnace stack of a Kraft pulping mill.

SELECTION AND DEVELOPMENT OF DETECTOR

SELECTION

Walther and Amberg (16) report the following data for the sulfur concentration ranges expected from the Kraft mill recovery furnace effluent:

TABLE I. EXPECTED CONCENTRATIONS

H ₂ S	14-1140 ppm (volume)
CH ₃ SH	0-489 ppm
SO ₂	4-798 ppm

Adams (4) reported the following information on maximum sensitivity to H₂S and CH₃SH of various standard chromatograph detectors:

TABLE II. DETECTOR SENSITIVITY

	H ₂ S (ppm, vol.)	CH ₃ SH (ppm, vol.)
Flame Ionization	---	1
Electron Capture	80	2
Thermal Conductivity	500	500
Thermonic Emission	25	10

It is obvious that none of these detectors are satisfactory because either they are not sensitive to all compounds or their maximum sensitivity lies above that necessary for full-time analysis.

Walther and Amberg (16) reported using a thermal conductivity detector sensitive to 10 ppm on all three sulfur gases. The same article, however, reported testing this chromatograph on a recovery furnace stack and finding both CH_3SH and SO_2 in concentrations below minimum detectability at least part of the time. This, then, does not provide the ultimate answer.

For these reasons we decided to use a coulometric detector. Adams (2) reports sensitivity on this cell as low as 10 ppb on H_2S and CH_3SH , and 50 ppb on SO_2 .

DEVELOPMENT

Studies were begun using a system employing a transistorized microcoulometer and a bromine microtitration cell as recommended by Adams (2). Our detector cell had a different physical design (Figure 1) but employed the same theoretical functions.

After initial experiments we found it very difficult to obtain reproducible results from day to day. The cell was also extremely sensitive to any vibration. Replacement of the recommended Hg-HgBr reference electrode with a commercial calomel (Hg-HgCl) electrode eliminated most of this problem. This also reduced the background noise level by a substantial amount.

To make the cell applicable to continuous process chromatography, it was necessary to make the cell run continuously. This

meant regenerating the titrating solution periodically (adding small amounts of new solution) because of possible contamination and evaporation of the titrating solution. Figure 1 shows the cell arrangement used to do this. The liquid level in the cell was controlled by adjusting the height of the exit tube. The titrating solution was pumped into the cell using a small syringe pump (Table VI).

Cell specifications are listed in the Appendix in Table IV. The platinum electrodes were made by hammer-welding a platinum wire onto a small platinum plate. The wire was then fused into the end of a soft glass tube. The tube was then filled with mercury and the electrical connection was made by placing a wire into the mercury.

The cell theory is explained in the Dohrman operational manual (3). Very briefly, this theory can be explained as follows: The sulfur gases separated by the column enter the titration cell through the capillary tube inlet. The sulfur ions react with the Br_2 in the electrolyte and change the concentration of the Br_2 in proportion to their quantity. The ion imbalance is immediately sensed by the sensor reference pair of electrodes. The imbalance is the input signal to the microcoulometer's amplifier, which instantly supplies a balancing voltage to the generator electrodes. This balancing voltage generates titrant to restore the electrolyte to its original concentration. The

balancing voltage supplied by the amplifier appears as a current time peak on the recorder chart. The area beneath the peak represents coulombs of electricity required to carry out the titration.

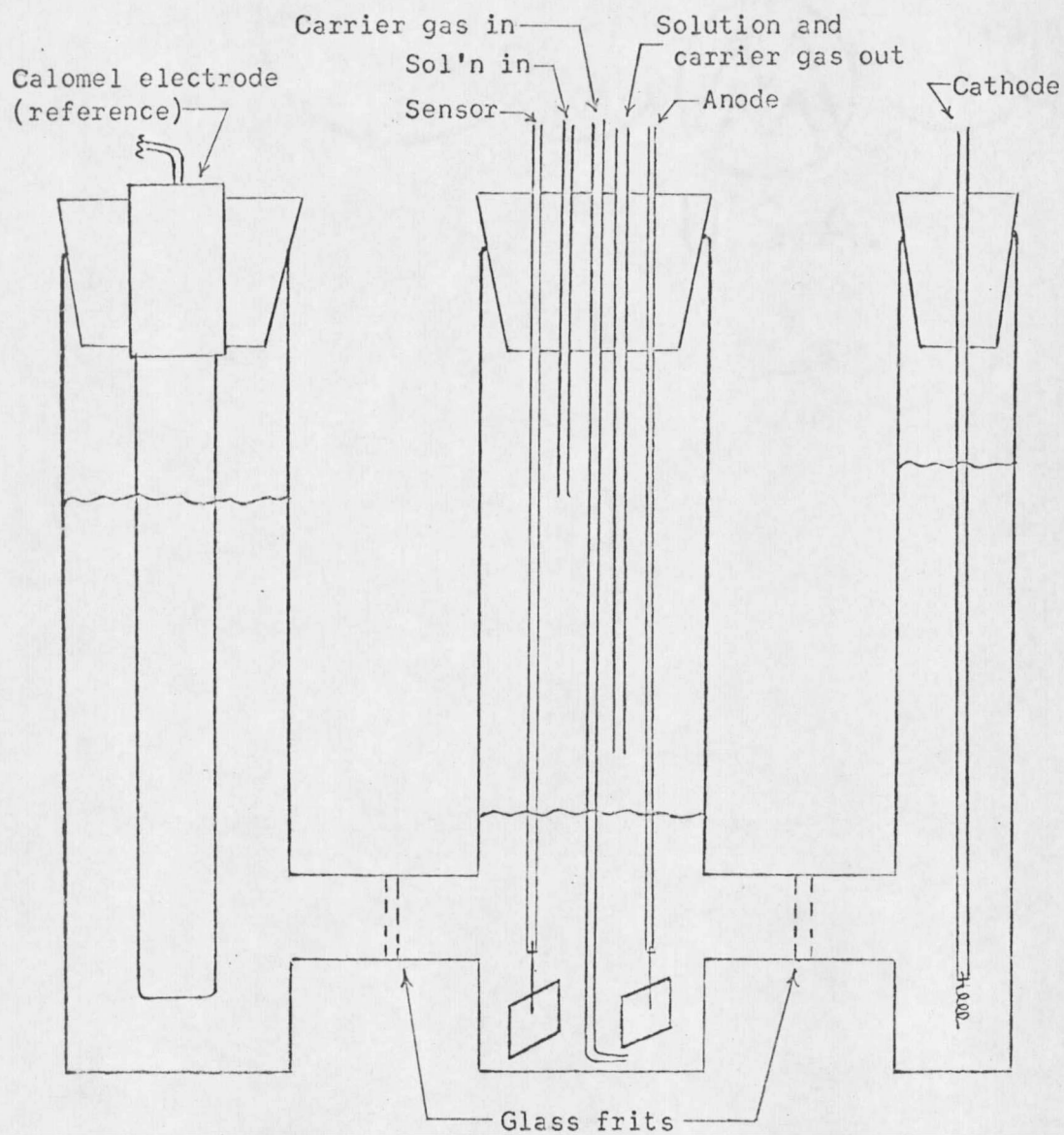


Figure 1. Detection Cell.

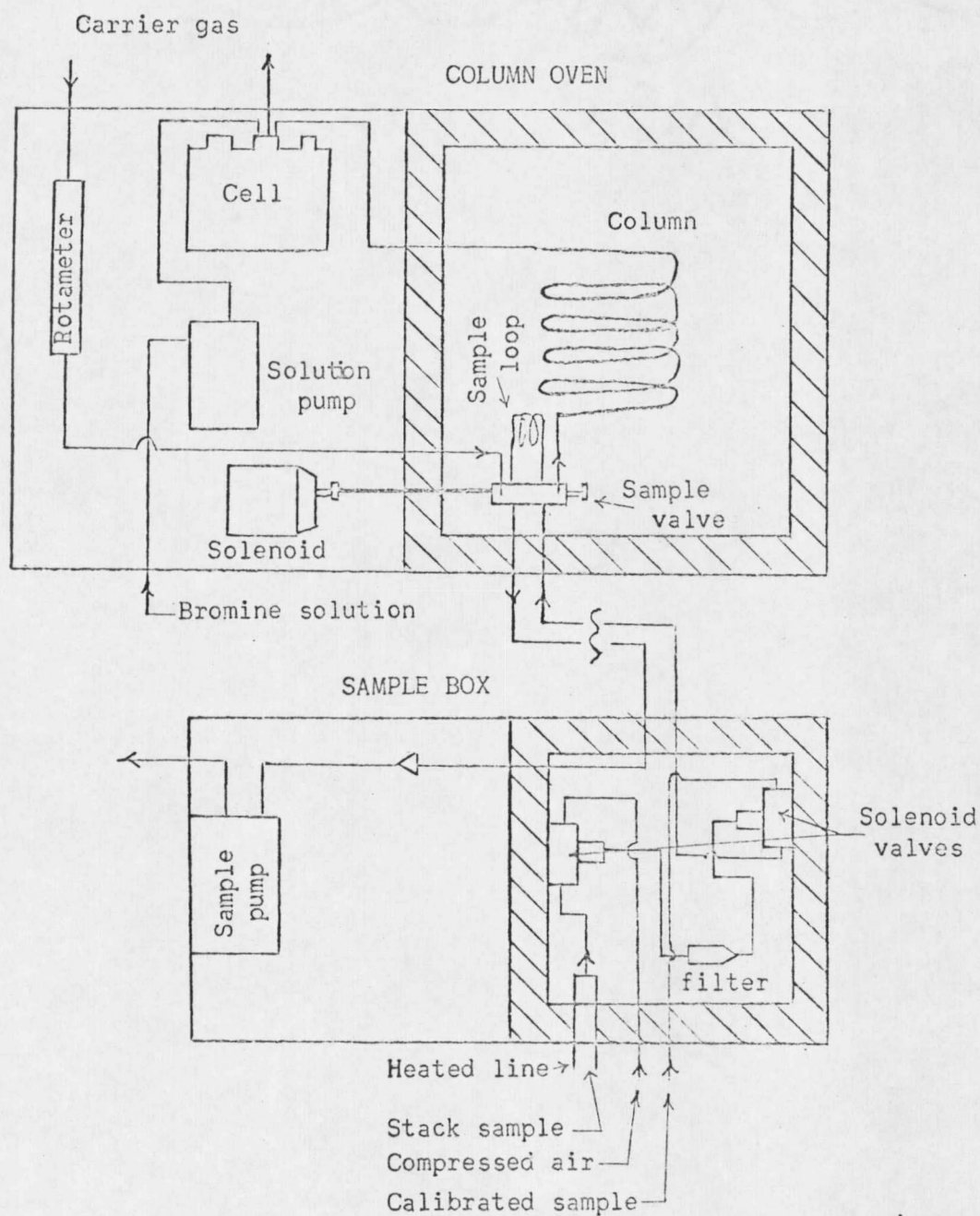


Figure 2. Sampling and Separation Equipment.

CHROMATOGRAPH EQUIPMENT

OVEN

A flow diagram is shown in Figure 2 and pictures in Figures 8 and 9. The oven is heated by means of four 150-watt strip heaters. The temperature is controlled by a temperature controller discussed under "Control Panel".

The sample valve is a Varian-Aerograph "six-way linear gas sampling valve (tube type)". The sample size can be changed by changing the size of the sample loop on this valve. The valve is located in the temperature-controlled oven so that it will maintain a constant sample size. We found this valve to work best with silicone "O" rings. The valve is operated with an electrical solenoid activated by a timer on the control panel. The carrier gas flow is controlled by a rotameter and needle valve.

Also contained in the oven box are the titrating solution pump and the detector cell. The cell is enclosed in a Styrofoam block which provides both an impact cushion and insulation against sudden temperature changes.

All fittings are stainless steel "Swagelok" fittings and the tubing is stainless steel or teflon.

SAMPLING BOX

A flow diagram is shown in Figure 2 and a picture in Figure 10. The box is insulated and is heated by a flat plate heater controlled by a 110-v Powerstat. This is to prevent condensation of water vapor in the sample drawn from the stack. Two three-way solenoid valves are provided to permit introduction of a prepared sample for calibration of the cell and to permit a blow back through the sampling probe in cleaning.

The line to the stack and sampling probe is electrically heated to prevent water vapor condensation. Its temperature is controlled by a 110-v Powerstat. The sampling probe is a porous stainless steel cylinder mounted inside an open-end steel cylinder.

A vacuum pump is provided to draw the sample from the stack. This is controlled by the timer.

CONTROL PANEL

A central control panel is provided so that the chromatograph can be operated from a remote location. The control panel is connected to the chromatograph by two multi-conductor cables, one is shielded for the low voltage instrument signals. A wiring diagram is shown in the Appendix (Figure 5).

The control panel contains a cam timer which allows automatic operation of the chromatograph. Switches are provided to allow manual operation. Mounted on the panel is a pyrometer to indicate the temperature in the column oven, the sample box, the sample line, and the cell.

The temperature is controlled from the control panel. Powerstats are provided to control the temperature of the sample box and the sample line. The oven temperature is controlled by a silicon-controlled rectifier temperature control unit, shown in Figure 6 (13).

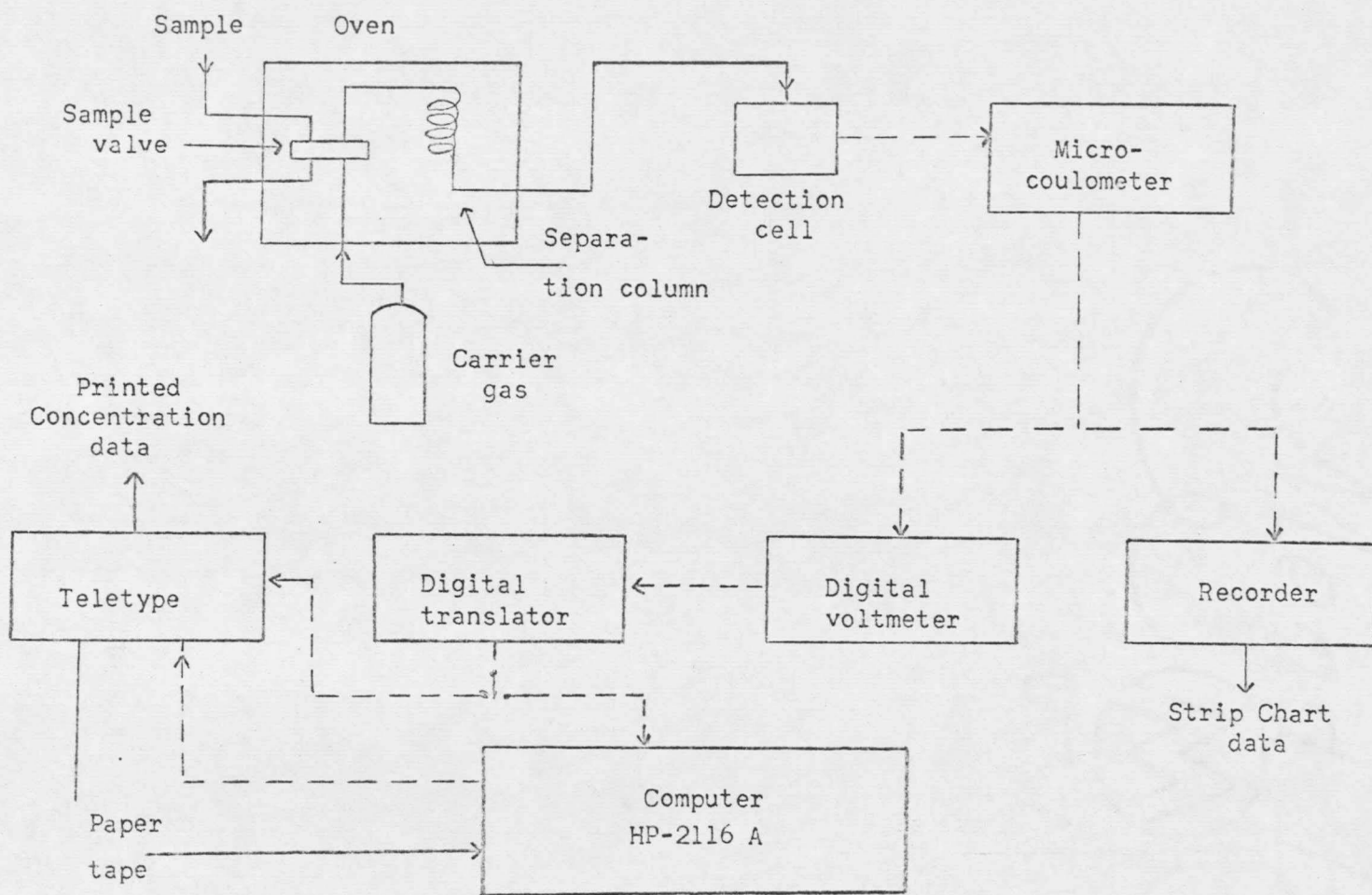
Also provided is a zero suppression unit to allow on-scale operation at the higher range settings. When the computer is used it is necessary to indicate a termination of the data with a negative signal. This unit is in the control panel and is also controlled with the timer.

DATA SYSTEM

The primary data output device is a strip chart recorder. Quantitative results are found by measuring the peak areas and comparing calibration data taken from known samples.

We have built, but have not yet thoroughly tested, an alternate method of recording data. This system employs a digital voltmeter which converts the output signal from the microcoulometer to a binary

signal. This signal passes through a digital translator which changes the signal to an ASCII code which, in turn, is the input to a teletype. The teletype records the data on punched paper tape. The tape serves as an input to a computer (Hewlett Packard 2116A) which is programmed to calculate and print out the peak areas. We also have the capability of by-passing the teletype with a direct input to the computer. This data will then be compared (manually or by the computer) to calibration data to obtain the concentration data. A schematic diagram of this system is shown in Figure 3.



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Figure 3. Data System.

EXPERIMENTAL PROCEDURE

SAMPLE MAKING

Bag: Samples were made by injecting known amounts of N_2 and the component gases into a plastic bag. The N_2 was measured with a wet test meter and the component gases were measured with a gas-tight syringe. The bag is made of a Mylar-Dacron laminate. This was necessary in order to prevent adsorption of the sulfur onto the bag. N_2 was used to prevent oxidation of the sulfur.

Samples of 10 ppm and higher were reproducible to an accuracy of 10%. Very little work was done with lower concentration samples. There was evidence that some sulfur was left in the bags after flushing, making the low concentration samples less accurate. Some sample decay was noticed on samples of less than 1 ppm after a period of 24 hours.

Manifold: Initial attempts at making samples of a known concentration were directed toward building a gas manifold to produce a continuous stream of known concentration. The apparatus constructed is shown in Figure 4.

The total flow was measured by means of a calibrated pitot tube at the vertical end of the manifold. Component gases (H_2S , CH_3SH , SO_2) were measured by metering them through small orifices. Pressure drops across these orifices were used for a flow rate calibration.

The orifices used to meter the component gases were the backbone of the apparatus and also the source of all the trouble. These orifices were made by two techniques. The first technique was to pack asbestos into small glass tubes. This was a fairly simple procedure and it was not too difficult to obtain a certain range of pressure drop. The problem was that they did not remain constant for more than an hour or two.

The second method of making orifices consisted of placing a small amount of soft glass in the end of a small piece of pyrex tubing and fusing the two together in a flame. When the tube cooled it formed a very small crack in the end of the tube. This method worked rather well and the orifices can be made for a given pressure drop range by varying the amount of soft glass used. The main problem with this type of orifice was that they broke very easily. Sometimes even the gas pressure was enough to do this.

These orifices remained constant on a day-to-day basis but at any given time varied in a certain flow rate range. For example, a rotameter used for calibration may vary up to 4% for a given orifice and pressure drop during a minute time span. The amount of this variation was characteristic of each particular orifice and thus the problem can be eliminated with an improved orifice-making technique.

Associated with the orifice problem and possibly the cause or at least partial cause for the instability mentioned was the problem of measuring the component gas flow rates. The first method used to do this was the standard soap bubble method. After using this for quite some time, it was realized that the gases were reacting with the soap solution giving rise to, at times, a high fluctuation in measured flow rates.

When this problem was discovered, we turned to a low flow rotameter. With this it was possible to measure flow rates in the range desired (± 1 ml/min). A plugging problem was encountered with this and thus a full evaluation of this method has not been made.

Generally speaking, this method was much less satisfactory than the bag method.

TEST RUNS

Prepared Sample: The longest runs were made using a prepared sample. Sample concentration of 10 ppm H_2S , 20 ppm CH_3SH , and 150 ppm SO_2 were used. The purpose of these runs was to uncover potential maintenance problems.

Burner: Three runs were made taking samples from the effluent of a ceramic kiln. The kiln burned natural gas as a fuel and was also burning the non-condensables from a large distillation column. The

column was distilling a crude Kraft turpentine rich in entrained sulfur. It was hoped that the kiln effluent would contain measurable amounts of sulfur compounds.

Data Analysis: Peak areas were measured using a planimeter. The areas were then put on an arbitrary basis (chart scale 10 mv and range 100) so that they could be compared. For example, an area taken at a scale of 5, range 200, was recorded as (area $\div$ 4). Or an area taken at scale 10, range 50, was recorded as (area $\times$ 2).

For quantitative results, calibration data was compared to the experimental data.

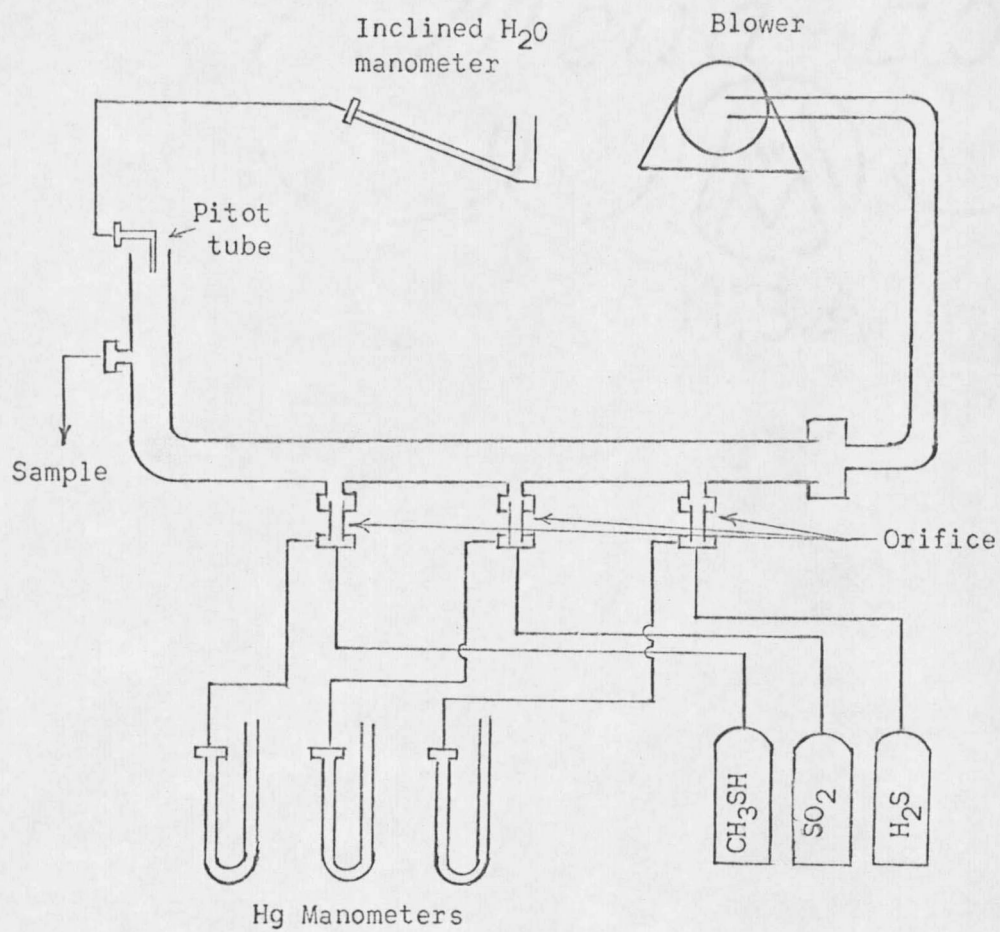


Figure 4. Gas Manifold.

RESULTS

The stated objective of this research was to develop a process gas chromatograph capable of analyzing recovery furnace effluent. Most of the effort and time was spent on the construction and debugging of the equipment. We have arrived at an instrument which will analyze for H_2S , SO_2 , and CH_3SH in the concentration range expected. The equipment is not without flaws but it does show a great deal of promise.

A test run was not made on recovery furnace stack gases but we have tried the equipment on some burner effluent as explained in the "Experimental Procedure" section of this thesis. The data collected from these runs is shown in Table III. Generally speaking, all three runs went very well. No problems were encountered with the equipment and everything performed as designed. These runs each lasted about 24 hours.

We also made extended runs on prepared samples for as long as ten days. These runs went well for about seven days with no adjustments necessary other than to replenish carrier gas and the sample bag. At the end of seven days a very noticeable decrease in peak sizes began to appear. This was particularly pronounced on the SO_2 peak. Accompanying this peak size decay was a rapidly increasing noise level. During these runs, no mechanical difficulty was encountered with the possible exception of the sample valve. The valve

worked as designed mechanically but evidence indicates that it may have been leaking, a problem which is discussed in the following section.

Data were obtained to indicate the minimum detectible concentrations of the sulfur gases. These data are shown in Table IV.

Data were also taken in an effort to calibrate the instrument for quantitative analysis (Table V). These data were used to the data reported in Table III.

TABLE III. BURNER EFFLUENT DATA

Run No.	I	II	III
	(b)	(c)	(d)
Crude Turpentine Source	Potlatch	Snowflake	Waldorf
Column Packing	Porapak Q	Porapak Q	Porapak Q
Column Size	1/4" x 6'	1/4" x 6'	1/4" x 6'
Sample Size	40 ml	40 ml	40 ml
Bias	790	790	790
Column Temperature	90°C	90°C	90°C
Carrier Gas Flow Rate (Rotameter Reading (e))	4.5	4.5	4.5

Maximum Concentration Detected (ppm volume)

H ₂ S	20	10	trace
SO ₂	30 (200) (a)	1	trace
CH ₃ SH	1	1	ND

"Normal" Concentration Range (ppm volume)

H ₂ S	1 to 5	ND to 0.5	ND
SO ₂	0.5 to 1	trace to 1	trace
CH ₃ SH	ND to 0.5	ND to trace	ND

- (a) occurred during an upset
 (b) Potlatch Forest Industries, Lewiston, Idaho
 (c) Southwest Forest Industries, Snowflake, Arizona
 (d) Hoerner-Waldorf Paper Products Co., Missoula, Montana
 (e) Matheson Model 602
 ND Not Detectible

TABLE IV. MINIMUM DETECTIBLE CONCENTRATIONS

H ₂ S	- - - - -	0.1 ppm
CH ₃ SH	- - - - -	0.5 ppm
SO ₂	- - - - -	0.5 ppm

Run Data:

40 ml sample

Porapak Q column, 1/4" x 6'

Flow -- 4.5

Temperature -- 90°C

TABLE V. CALIBRATION DATA

	<u>Concentration (ppm)</u>	<u>Peak Area</u>
H_2S	1000	4.4
	100	1.7
	50	0.7
	10	0.3
	1	0.03
	0.5	0.01
	0.1	trace
SO_2	1000	7.0
	500	3.0
	100	1.3
	50	1.2
	10	0.20
	1	0.13
	0.5	trace

TABLE V. (continued)

	<u>Concentration (ppm)</u>	<u>Peak Area</u>
CH ₃ SH	1000	10.0
	100	3.0
	50	1.5
	10	0.4
	1	0.05
	0.5	trace

Run Data:

40 ml sample

Porapak Q column, 1/4" x 6'

Flow -- 4.5

Temperature -- 90°C

DISCUSSION OF RESULTS

TRIAL RUNS

The trial runs on the burner were made essentially to "feel out" the equipment and get an idea about whether or not it would really do what it was designed to do. The data collected show that the equipment does work and that varying sulfur gas concentrations in the burner effluent can be detected even to the point of detecting an upset in the burner operation.

It should not be concluded from this that the instrument will work as flawlessly on a recovery furnace stack. Several factors are expected to be different. The first is a much wider range of concentrations. It is not known exactly what ranges the present system will handle, but indications are that it should handle a range of about 0.1 to 500 ppm without modification. Another factor is sample purity. There may be impurities in the sample which will contaminate the titrating solution and render the cell inoperable. Also, the presence of higher order sulfur compounds might have an effect on the operation of the instrument. The exact effect of these factors and others cannot be found until an extended trial run can be made on recovery furnace stack gases.

The trial runs made using a prepared sample were intended to point out any maintenance problems. The equipment was relatively maintenance-free. The main problem encountered during these runs

was the decreasing peak size. This problem will be discussed in connection with the calibration data.

MINIMUM DETECTIBILITY

The data shown in Table IV are intended to show only the general order of magnitude and must not be assumed to be more accurate than that. Minimum detectibility is defined as the concentration of a sample which yields a peak twice as large as the background noise.

Whether or not this sensitivity is high enough will not be known until the instrument has undergone its first on-line trial. The reported sensitivity is substantially lower than that reported by Adams (2). It must be realized, however, that Adams obtained his data by direct injection into the cell rather than by passing the sample through a column, as we did.

One way to increase the sensitivity, if it becomes necessary, is to reduce the noise level, thus allowing operation at lower attenuation. This would involve a change in the cell design. This noise level is affected by such things as electrode design, material, and position. Of these, only electrode position has been investigated. It was found that the cell operates at a lower noise level when the carrier gas injector is pointed away from the sensor electrode.

Two types of carrier gas injectors were tried. The first was a tube with a porous tip providing gas dispersion in all directions. The second, and more satisfactory, type was a capillary tube injector. This type of injection allowed cell operation at a substantially reduced noise level.

Other factors which probably affect the noise level but which have not yet been investigated are the volume of titrating solution in the cell, the solution concentration, and the amount of titrating solution added for regeneration during each cycle.

Another means of increasing the sensitivity is to increase the sample size. The data shown in Table IV were taken with a 40-ml sample. There is no indication that this size is a maximum. The size limit comes as a result of having to run at higher concentrations. This is a variable which will have to be adjusted after preliminary sampling on the recovery furnace stack gas.

Another factor which is particularly important at low concentrations is the column. The column (Porapak Q) absorbs a small amount of the sulfur gases, thus reducing the amount of the component reaching the cell and therefore reducing the sensitivity.

This effect is particularly noticeable with SO_2 . Peak size can be changed greatly by varying the time interval between samples; the shorter the interval the greater the peak size for a given con-

centration. This suggests the same type of absorption problem which causes the tail on a peak.

CALIBRATION DATA

It must be emphasized that there is insufficient data here from which to draw any major conclusions. The data show several things that would not be expected from a theoretical standpoint. The first point is that the 100 ppm peaks are much more than 1/10 the area of the 1000 ppm peak. This suggests that there is incomplete reaction of the sulfur in the cell when the amount is large. This conclusion is backed by the fact that the 1000 ppm H_2S peak is smaller than either the SO_2 or CH_3SH peaks. This might be expected since the H_2S comes out of the column in a much sharper peak than either SO_2 or CH_3SH and thus less is absorbed.

This same type of inconsistent data are found at lower concentrations. The reasons are probably different. Possibly there are some residual sulfur compounds left in the sample bag when the sample is changed. This becomes more and more significant as the sample becomes more dilute, explaining why there is a less than proportionate decrease in peak size when compared to the decrease in sample concentration.

On an hour-to-hour basis, the data is reproducible to about 10% even when the sample is remade. On a day-to-day basis there is a

completely different story. Variability on a given sample concentration can run as high as 50%.

Another malfunction is encountered only after extended steady use (five to six days) of the chromatograph. At this time a very marked decrease in the SO_2 peak size for a given sample concentration can be noted. The same thing occurs with the other peaks but the magnitude of change is much less.

These are the two major problems yet unsolved. We offer no solutions but can only point to some potential trouble spots which could be the cause of these malfunctions. The first is the column. We have already discussed its high SO_2 absorbtivity. This effect is even more pronounced after extended steady use. Thus, the column appears as though it might be the major contributor to these problems. Two directions of investigation are suggested. First, improvement of the existing column. This might be done by eliminating the fines from the packing. Another method which might improve the column is a method known as "silanizing" (11). The second solution to this problem might be to find a better packing material, several of which have been recommended (12, 16).

Brief studies of the problem show the absorption to be less at lower column temperatures and higher carrier gas flow rates. An attempt was made, without success, to reduce absorption by using wet

carrier gas. This was done by passing the gas through a water bath. It was hoped that the water molecules would occupy some of the absorption sights, thus reducing the sulfur absorption.

A second possible source of the above-mentioned malfunctions is the electrodes. Some type of contamination occurring on the surface of the sensor electrode could conceivably cause the problems. Possibly a different electrode material might be more suitable to the reaction and ions involved.

The third source is the Br^- concentration of the titration solution. It is difficult to say what the exact effect of changing concentration might be, but it would definitely cause problems. The change is probably a result of evaporation caused by the carrier gas bubbling through the solution. New solution was added periodically to prevent this, but possibly the amount added was not enough to prevent a gradual change.

Another possible malfunction which might contribute to the reproducibility of the data is the sample valve. It is very difficult to keep the valve from leaking when operated under a vacuum (valve before pump). If it were leaking, it would help to explain the decreasing peak size. The problem was solved somewhat by operating under pressure (valve after pump). Final design, however,

requires that the sample valve be placed in the line before the pump. This design is necessary because of the possibility of water vapor condensing in the pump and because of possible sample contamination in the pump. Therefore, this problem must be eliminated by another method.

This non-reproducibility remains the major problem in establishing a reliable instrument. We do not know exactly what the problem is, but feel certain that it is a solvable one.

SUMMARY

The equipment developed thus far is mechanically sound, with the possible exception of the sample valve, and will run unattended for long periods of time. It will analyze for H_2S , SO_2 , and CH_3SH in widely varying concentrations and in the anticipated concentration range. This applies to both prepared samples and furnace effluent.

The major problem remaining to be solved is that of reliability. At times it is very difficult to attain reproducible data. This problem must be solved even before a meaningful test can be made on a recovery furnace.

RECOMMENDATIONS FOR FUTURE STUDY

Future study with this instrument should be pointed in two directions. The first is to obtain an instrument which will give highly reproducible data. The second is to reduce the background noise level allowing greater sensitivity.

With these goals in mind, I make the following recommendations:

1. investigate electrode design and material
2. if necessary, investigate a different cell design
3. investigate the following cell variables:
titrating solution concentration, titrating solution volume, and amount of solution added for regeneration during each cycle
4. investigate sample size
5. improve column by improving present packing, or finding a more effective column packing material
6. improve the sample valve design to eliminate leaking
7. improve the sample-making technique.

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APPENDIX

CELL OPERATION

This section is intended to be an aid to someone who might be trying to operate the chromatograph. Following is a list of several cell variables, their qualitative effect on cell operation, and their normal operating ranges. It should be noted that this discussion applies only to the chromatograph in use in this study.

Bias: An increase in bias decreases cell response, thus decreasing overshoot when it occurs.

Decreasing the bias will help eliminate the tail on a peak. Normal operation is about 790, depending on sample concentration and the condition of the titration solution.

Carrier gas flow: Increased flow rate gives a sharper, higher peak. Noise level seems better at flow rates between about 150 and 200 cc/min. Normal operation is at about 300 cc/min (4.5 on rotameter). This flow rate is dictated by the column.

Regeneration: The cell operates well at a regeneration rate of 3 ml/cycle.

Liquid Level: Normal operation has been about 40 ml of solution in the titrating compartment.

Solution Concentration: Normal operation is with a solution containing 0.72 g KBr and 6 ml H_2SO_4 per liter of H_2O .

TABLE VI. EQUIPMENT LIST

<u>Article</u>	<u>Specifications</u>	<u>Source</u>
Control Panel		
Multiple-conductor cable	200' 11 pairs conductors individually shielded	Belden
	200' 25 conductors, not paired, not shielded	Belden
Connectors	26 contact and 22 contact	Amphenol
Switches	Toggle 2-pole single throw	Cutler-Hammer
Panel lights	125 v, 1/3 watt	Lee Craft
Pyrometer	Iron-constantan 0-400 C	Assembler Products, Inc.
Timer	Cam timer - 12 switch	Industrial Timer Corp.
Data System		
Digital translator	-----	Electronics Research Lab Montana State Univ.
Digital voltmeter	-----	Hewlett-Packard
Recorder	Model SR	Sargent
Teletype	Model 33 TZ	Teletype Corp.

TABLE VI (continued)

<u>Article</u>	<u>Specifications</u>	<u>Source</u>
Detector		
Cell frits	10 mm; porosity E	Ace Glass, Inc.
Microcoulometer	Model C-200 A	Dohrman
Platinum electrodes	-----	Englehard Industries
Reference electrode	Calomel (fiber tip)	Coleman
Oven		
Fittings	Swagelok (stainless steel)	Swagelok
Heaters	150 watt (strip heater)	Chromalux
Column	Porapak Q; 1/4" x 6'	Waters Assoc., Inc.
Column and sample loop tubing	1/4" Teflon	Varian Aerograph
Rotameter	Model No. 602	Matheson
Solution pump	"Mini Pump"	Van Waters & Rogers
Sample valve	6-way linear (tube type)	Varian Aerograph
Solenoid	-----	Dormeyer
Tubing	1/6" stainless steel	-----

TABLE VI (continued)

<u>Article</u>	<u>Specifications</u>	<u>Source</u>
Sample-making apparatus bags	Mylar-Dacron laminate	Schjeldahl Company
Sealant tape	Schjeldahl Type GT-400	Schjeldahl Company
Syringes	Gas-tight	Hamilton
Wet test meter	-----	Precision Scientific Co.
Rotameter	Model No. 610	Matheson
Gas	H ₂ S, SO ₂ , CH ₃ SH	Matheson
Sample Box Filter	Aluminum filter holder	Gelman
Sample probe	Porous stainless steel cylinder	Pall Trinity Micro Corp.
Sample line	Stainless steel tubing, electrically heated	Deckoron
Valves	3-way solenoid valves	Asco

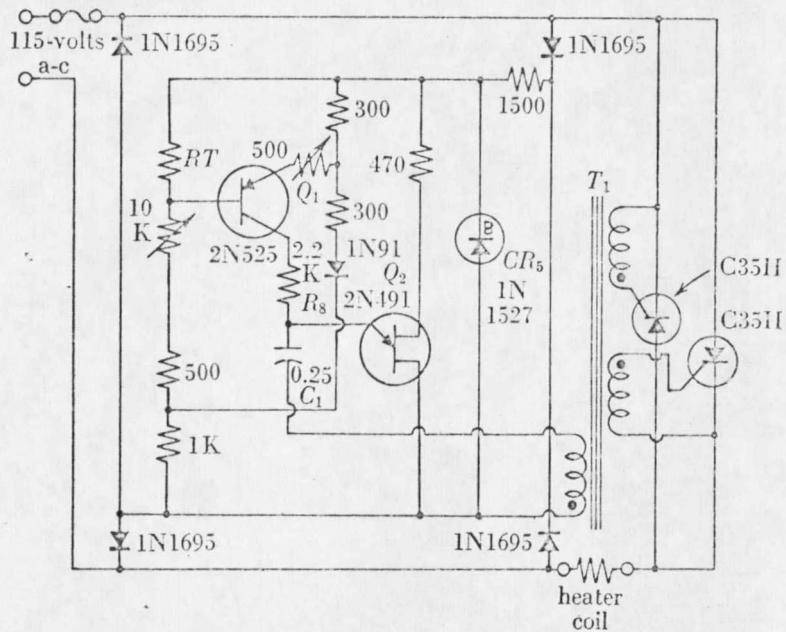


Figure 6. Silicon-controlled-rectifier Temperature Control. (13).

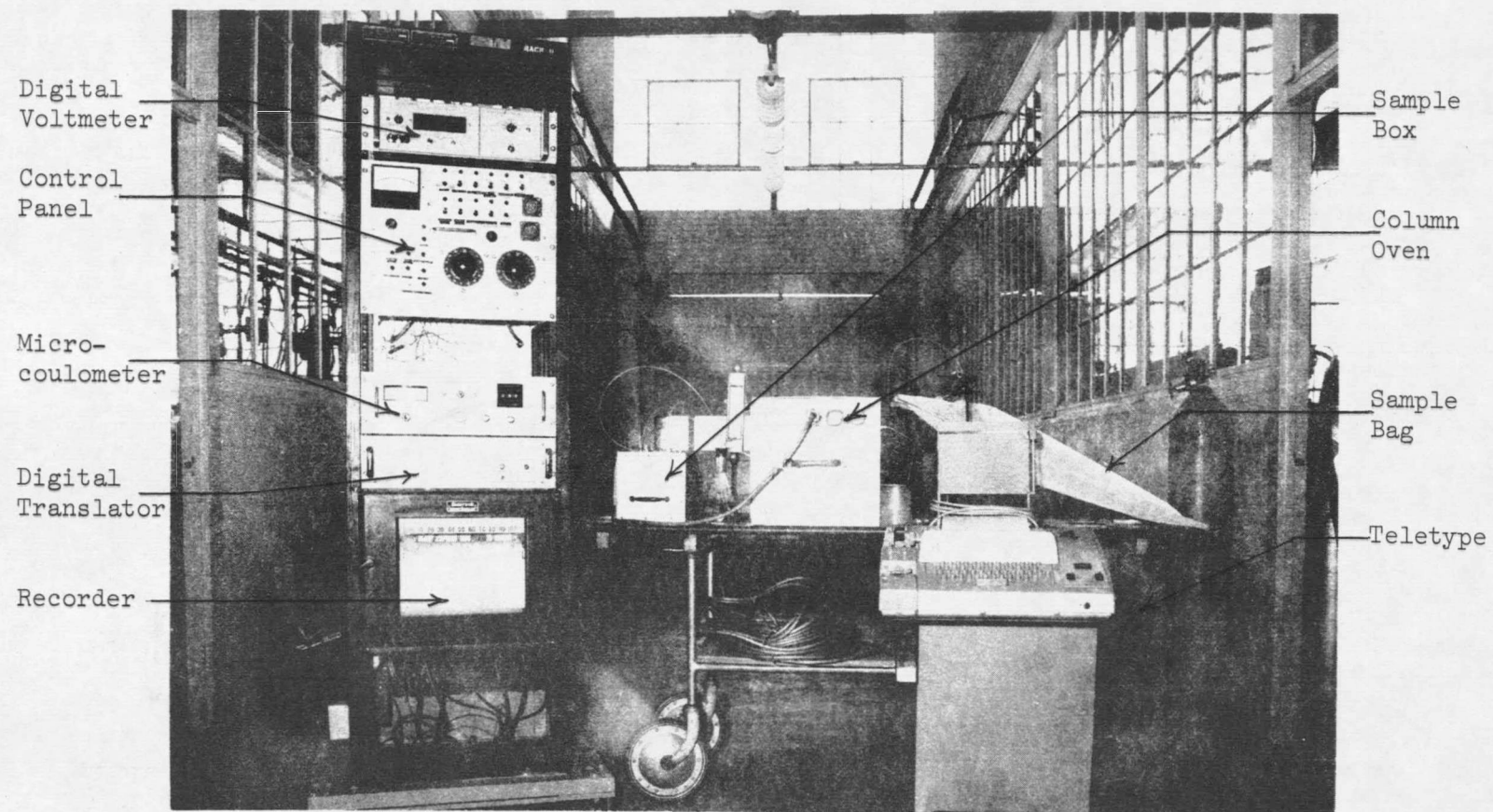


Figure 7. Process Gas Chromatograph

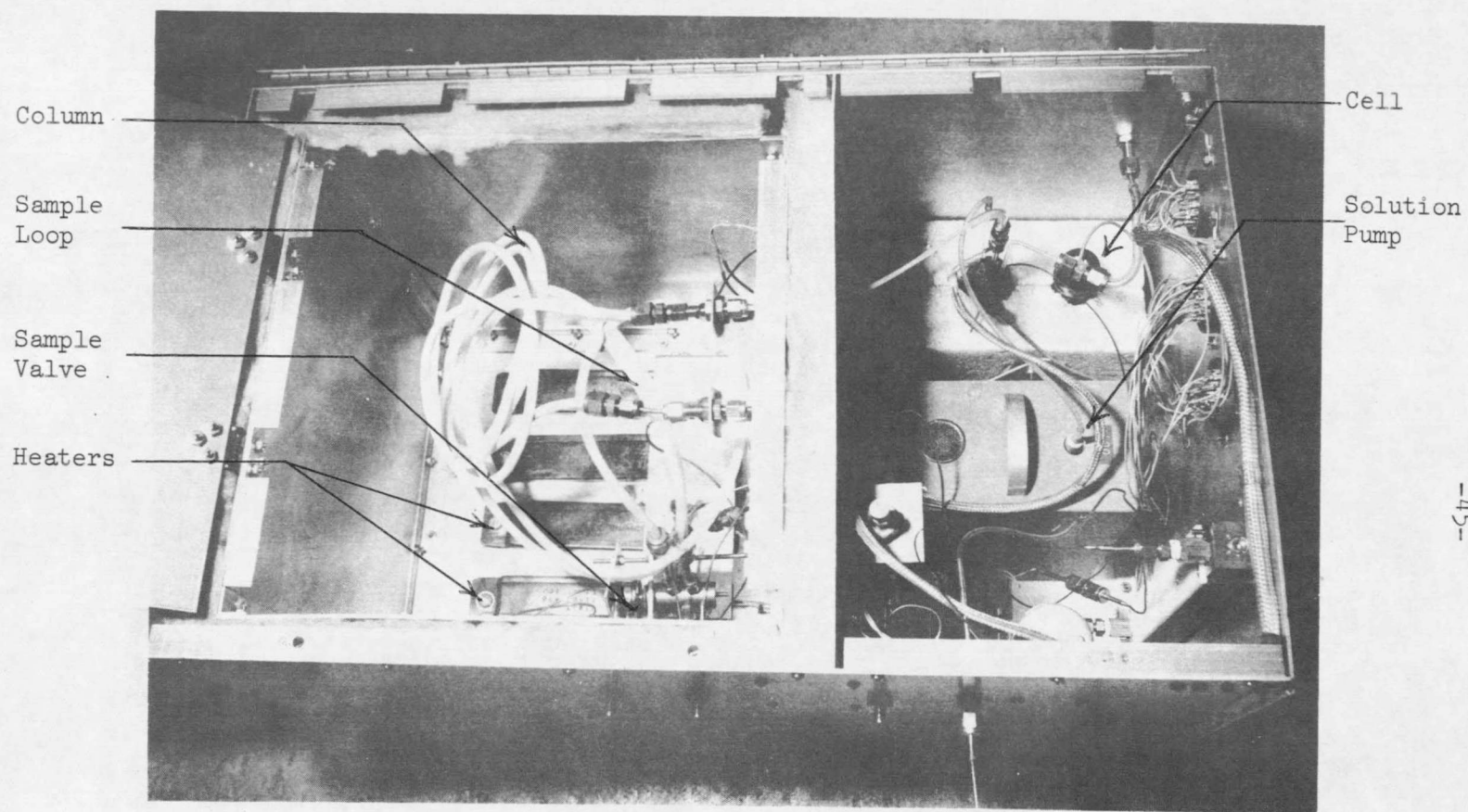
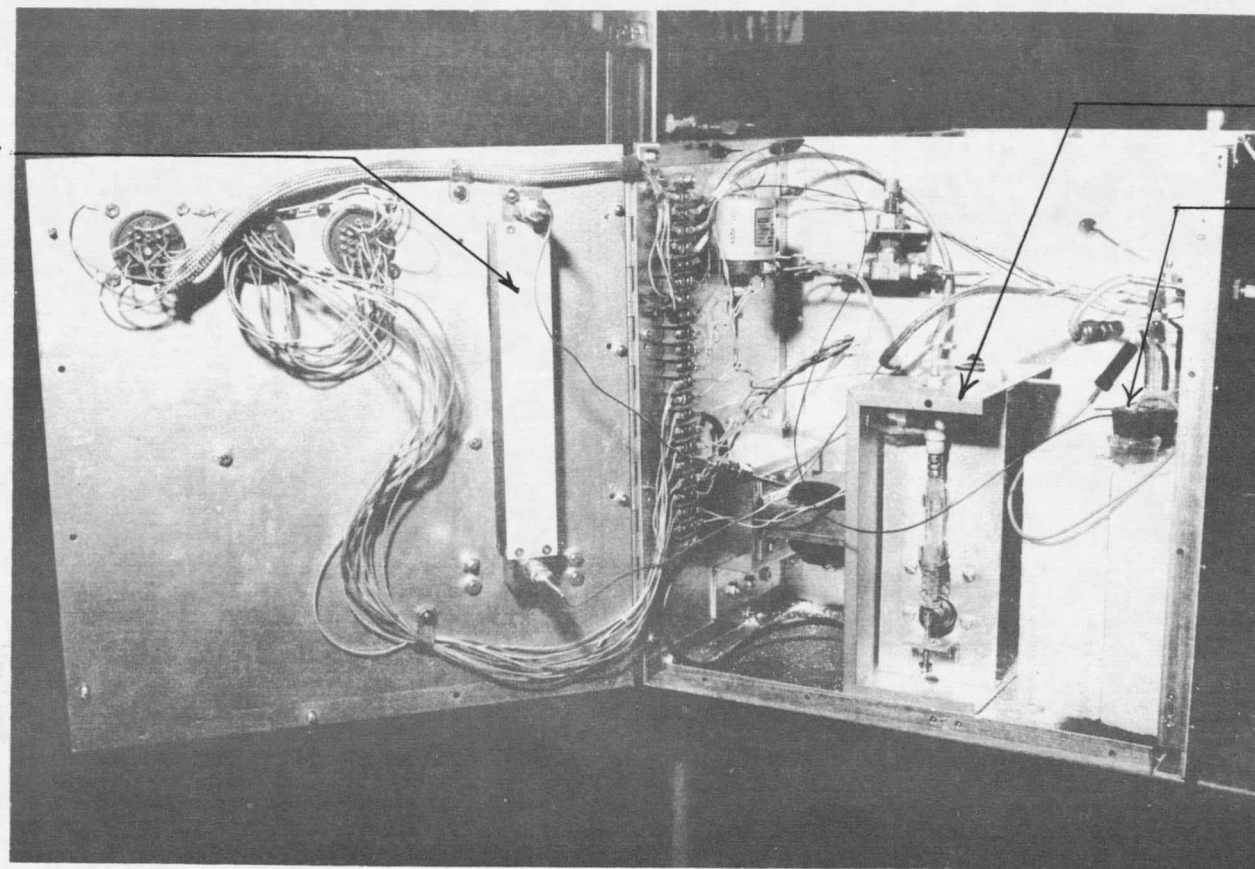


Figure 8. Column Oven (top)

Rotameter

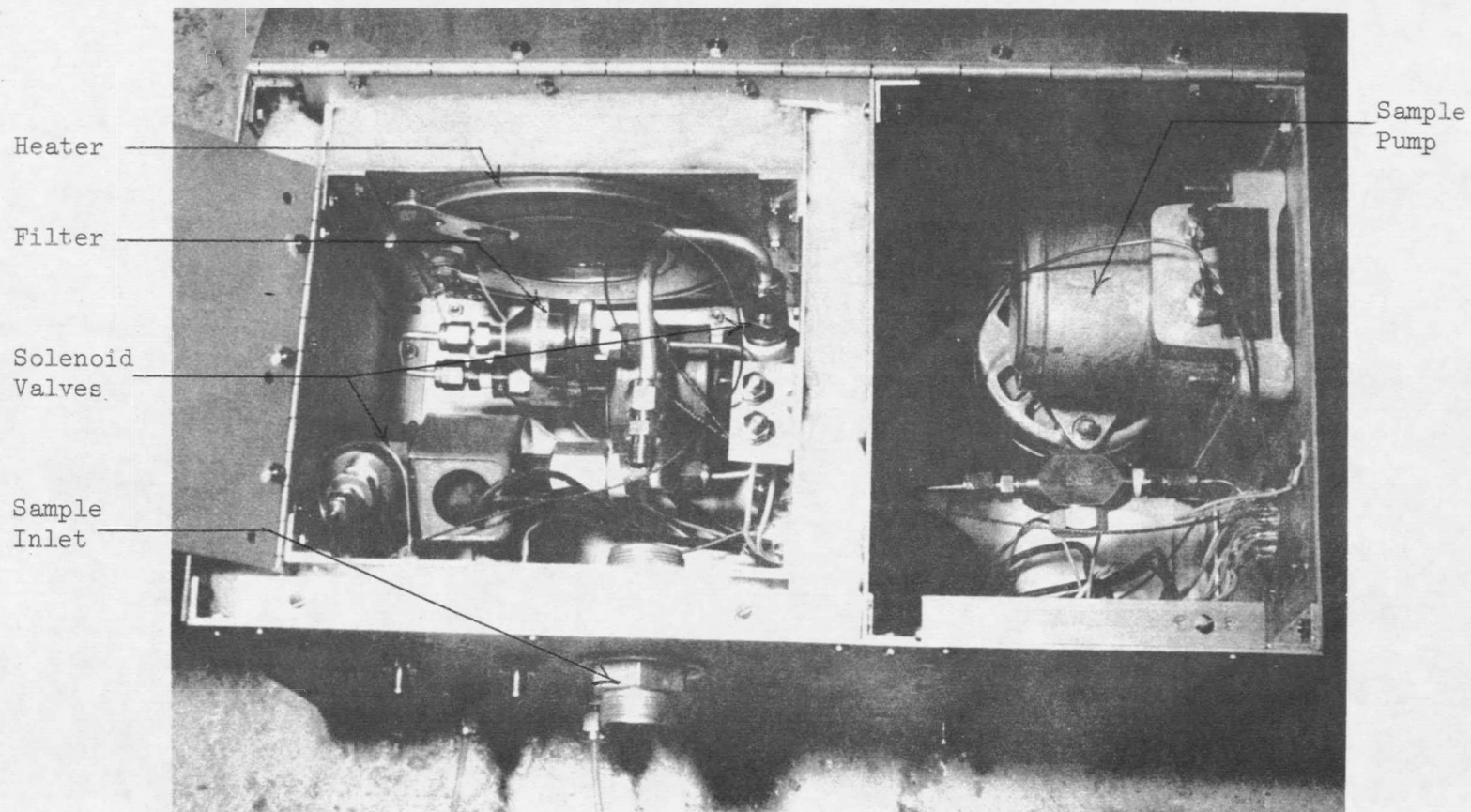


Solution
Pump

Cell

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Figure 9. Column Oven (front)



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Figure 10. Sampling Box

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