



Instrumental and mathematical analysis of Kraft sulfur emissions
by Robert James Robertus

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

An instrument capable of automatic continuous quantitative analysis of sulfur compounds in stack gases has been developed and tested for a one-month period in a Kraft paper mill. The instrument is portable and can easily be moved from stack to stack within a plant.

The equipment is designed to extract a gas sample from the stack, separate the sulfur compounds present, and--using an electrolytic bromine cell as a detector--give a quantitative indication of the amount of each compound present. The device described can separate and analyze mixtures of H_2S , SO_2 , and CH_3SH in the following ranges: H_2S 1 to 1500 parts/million volume/volume SO_2 10 to 2000 ppm CH_3SH 5 to 1500 ppm. The lower end of these concentrations is limited by the separation technique used. If no separation is made, a gaseous effluent with 0.2 ppm total sulfur compounds can be easily analyzed. Techniques to extend either the lower or upper limit are described.

An accessory allowing two or three stacks to be sampled in succession was also built and tested at a Kraft mill.

A purely statistical technique (multiple linear regression) has been used to relate sulfur emissions from a Kraft paper mill to plant operating variables in the recovery area.

Sulfur emissions were recorded continuously either before the black liquor venturi or after the black liquor cyclone. Values of process variables were copied from log sheets maintained at the mill.

Of the two locations sampled, gases out of the black liquor cyclone are most indicative of what will be going out the stack. Temperature of air entering the furnace, liquor flow, primary air flow, venturi header pressure, and salt cake flow were all shown to have a direct effect on H_2S levels out the cyclone. On the other hand, concentrations were shown to vary inversely with secondary air flow, I. D. fan draft, and liquor solids content.

Some unreasonable correlations did occur, but could generally be attributed to questionable data. One or two unlikely, but possible, correlations were explained assuming unusual furnace conditions existed for part of the test period. All things considered, the conclusions were felt to be as reliable as the data that was used.

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OF KRAFT SULFUR EMISSIONS

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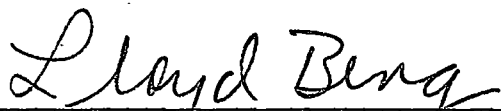
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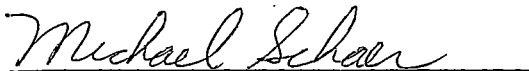
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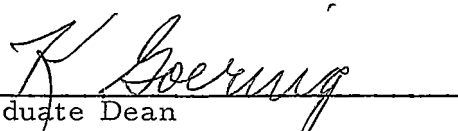
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Approved:


Head, Major Department


Chairman, Examining Committee


Graduate Dean

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PART I

Development of Continuous
Chromatographic Sulfur
Analyzer

ABSTRACT

PART I

An instrument capable of automatic continuous quantitative analysis of sulfur compounds in stack gases has been developed and tested for a one-month period in a Kraft paper mill. The instrument is portable and can easily be moved from stack to stack within a plant.

The equipment is designed to extract a gas sample from the stack, separate the sulfur compounds present, and--using an electrolytic bromine cell as a detector--give a quantitative indication of the amount of each compound present. The device described can separate and analyze mixtures of H_2S , SO_2 , and CH_3SH in the following ranges:

H_2S 1 to 1500 parts/million volume/volume

SO_2 10 to 2000 ppm

CH_3SH 5 to 1500 ppm

The lower end of these concentrations is limited by the separation technique used. If no separation is made, a gaseous effluent with 0.2 ppm total sulfur compounds can be easily analyzed. Techniques to extend either the lower or upper limit are described.

An accessory allowing two or three stacks to be sampled in succession was also built and tested at a Kraft mill.

INTRODUCTION

Today more than half of all the wood pulp manufactured in the United States is made by the Kraft (sulfate) process. When the first Kraft mill was built in 1891, the operators were well aware of the air pollution problem involved (10). The first papers concerning Kraft mill odors appeared in the literature around 1900. Today, despite progress in recent years, most Kraft pulp mills are still living with this problem. Recent legislation, however, makes it mandatory that efforts be directed toward reducing pollution.

In the Kraft process a solution of sodium sulfide and sodium hydroxide in water is used to dissolve lignin from wood by steam cooking. When cooking is complete, chemicals in the spent cooking liquor (black liquor) must be recovered to make the overall process economical. This recovery operation--which involves first concentrating, then burning the black liquor--is a major source of sulfur emissions in Kraft pulp mills. Sulfur dioxide is the major pollutant out of the actual recovery furnace where the black liquor is burned, whereas H_2S is the primary sulfur compound released during the black liquor concentration steps. Some H_2S , CH_3SH , and CH_3SCH_3 can also be found in the recovery furnace effluent.

Several articles have been published (7, 18) proposing means of reducing sulfur emissions from the recovery operation. These range from black liquor oxidation (converts Na_2S to the more stable Na_2SO_4) prior to direct contact evaporation to the use of nitrobenzene-alkali systems (19) in the cooking process.

Regardless of the method used to reduce pollutant levels, the stack gases must be analyzed to determine the effectiveness of the measures taken. There are many different ways of analyzing stack gases (5, 11). Until the last decade or so, methods used to determine concentrations of sulfur compounds in pulp mill effluents were almost exclusively those that required passing the raw sample through general or specific scrubbers or traps followed by manual colorimetric or microvolumetric analysis of the contents of the various scrubbers and traps. Today the methods used seem to fall into four categories: 1) colorimetry, 2) coulometry, 3) direct spectrophotometry, and 4) gas chromatography. Use of colorimetric analyzers for analyzing is comparatively expensive, cumbersome, time-consuming, and demanding of maintenance. Direct spectrophotometry is a new field just being explored (22), but appears to have some sensitivity limitations.

Gas chromatography has suffered from two main drawbacks--
1) analysis of sulfur compounds in the sub parts-per-million range

has not been too successful because of losses on the packing material in the separation column (4). 2) Existing thermal conductivity and flame ionization detectors are not specific to sulfur compounds so peaks for CO_2 , H_2O , and other inert gases are also recorded. Another criticism is that chromatographs become "batch" analyzers--allowing only one sample every 10 to 15 minutes and could not be used in a control network. Nevertheless, process gas chromatographs have been shown to be useful in stack gas monitoring (24).

Presently the trend in sulfur analyzers is toward coulometric titration cells. This technique uses electrolytically generated bromine to react with and give a measure of the sulfur compounds in gaseous effluents. The coulometric detectors offer specificity, sensitivity, and capability for long-term continuous read out.

In order to get meaningful information from the gas analyses, it is imperative that the analyses be carried out on a continuous basis. Several continuous SO_2 analyzers have been developed and tested for ambient air analyses (15, 17, 20). Many of these instruments are, however, not sensitive to H_2S or mercaptans and thus would not be useful in a Kraft mill.

Instruments employing bromine titration cells have been in use for several years. One of the first commercially available ones was

known as the Titrilog analyzer (14). By varying the gas flow rate through this detector, sensitivities as low as 0.05 ppm H_2S were obtained. A majority of the present day sulfur analyzers still use the same basic principle (2, 9, 16) but a slightly different cell design. The commercially available Barton cell reports sensitivities of 0.08 ppm for H_2S and mercaptans, while Adams and Jensen reported sensitivities in the ppb range (2). The cell is in reality a "total" sulfur analyzer. Thus, if more than one component is to be analyzed in a given gas stream, the gas sample must be passed through selective scrubbers or prefilters (1). This means that for any given gas the system has become "batch" in nature because the concentration of a particular gas is not recorded continuously. Also, no prefilters have yet been found that will quantitatively absorb 100% of one sulfur compound and 0% of the rest. Scrubbing solutions are inherently cumbersome.

Perhaps the only serious objection to the analyzers now available is their high cost. The goal of this project is development of a cheaper yet equally reliable system.

RESEARCH OBJECTIVES

The primary objective of the research project was to develop and construct at a reasonable cost a continuous sulfur analyzer for use in Kraft paper mills.

The instrument should have the following characteristics:

- 1) Be sensitive to sulfur compounds and insensitive to the other gases in stack effluents.
- 2) Be able to "survive" at least a one-month continuous test in a Kraft mill.
- 3) Require little or no maintenance during the plant test.
- 4) Be simple to operate.
- 5) Be easily portable so it can be moved about by one person within the plant.
- 6) If possible, allow for sequentially sampling more than one stack.
- 7) Show no degradation in performance with time.
- 8) Be easily and reproducibly calibrated.

EQUIPMENT

The basic items necessary to continuously analyze stack gases are listed below.

- 1) A probe suitable for withdrawing a gas sample from the stack (usually requires a vacuum pump).
- 2) A means of separating the various sulfur compounds in the gas sample.
- 3) A detector for quantitative determination of the sulfur gases.
- 4) Electronics compatible with the detector used.
- 5) A suitable recorder or other data acquisition device.
- 6) An accurate and reliable method of calibrating the instrument.
- 7) An accessory such that more than one location can be sampled sequentially. (Not really necessary, but desirable at times.)

Design of Instrument

The two major decisions which must be made in the design of a sulfur analyzer are: 1) the separation technique to be used, and 2) the type of detector to be employed. Various possibilities for each of these items have been discussed in the Introduction.

Because chromatography columns are simple in design and relatively maintenance free, a packed column was chosen as the separation device. Here there is work to be done to find a single packing which will separate the sulfur compounds in the concentrations found

in pulp mills and show minimum absorption of SO_2 , especially at low concentrations. The column should also perform the separation in a 10 to 15 minute interval so the stack can be sampled at least once every 10 to 15 minutes without fear of peaks overlapping from sample to sample. Still, no two sample peaks should be so close together that the recorder pen does not return to the baseline between them. Satisfying all of these requirements simultaneously is quite a stringent requirement. It should be pointed out that any instrument using chromatographic separations would not be entirely satisfactory in an automatic control loop because of the time lag. However, it is felt that the system's other advantages outweigh this disadvantage because very few mills are considering any type of closed loop control based on sulfur analyses.

Nearly all recent literature articles indicate that the bromine titration cell is the best known detector for sulfur compounds. Data presented in articles by Applebury (6) and Adams (2) give the following sensitivities for H_2S and CH_3SH . (See Table I.)

Because of its superior sensitivity, the bromine cell was chosen as the detector to be used. The cell described by Adams was made of glass and was felt to be too fragile for a portable instrument. The Barton cell (16) also had a drawback--its high cost. The goal here

was to develop an inexpensive, durable, reliable titration cell.

Once the separation technique and detector have been chosen, an overall operation procedure must be specified.

TABLE I. DETECTOR SENSITIVITIES

	H ₂ S	CH ₃ SH
	(ppm, vol)	(ppm, vol)
Flame Ionization	-----	1
Electron Capture	80	2
Thermal Conductivity	500	500
Thermionic Emission	25	10
Bromine Cell	5 ppb	----

Operation

The sequence of events taking place during the analytical process is controlled by a continuous multicam timer set for a cycle time of 10 minutes.

First the vacuum pump is switched on and draws a gas sample from the stack into a sample loop attached to a six-way linear sampling valve (Figure 1). Simultaneously carrier gas is passing through a chromatograph column into the detector. Both the sample loop and the column are in a constant temperature oven.

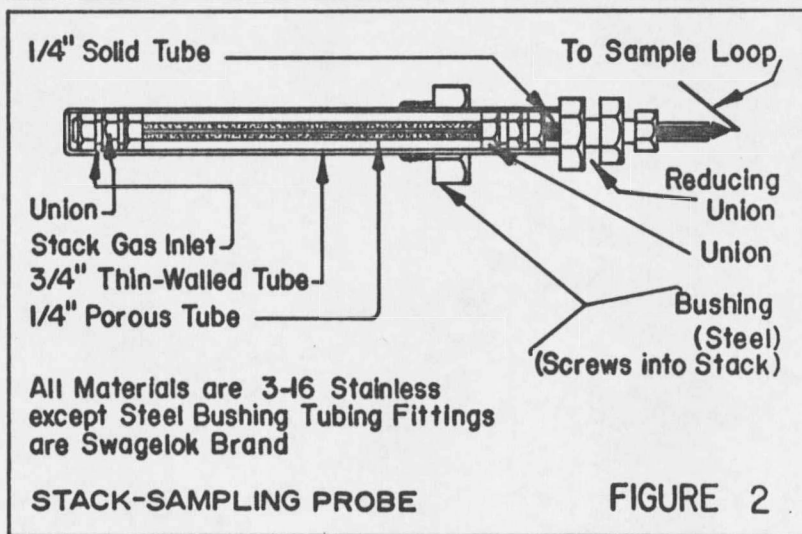
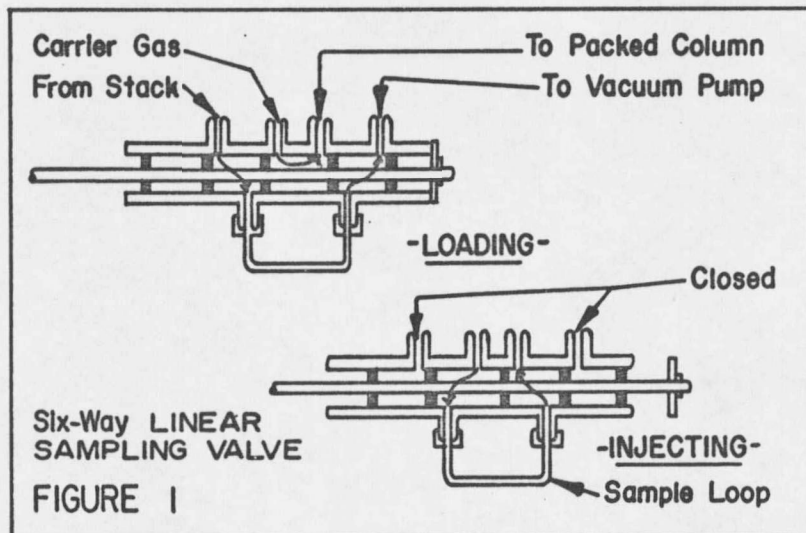
Six minutes later the vacuum pump is switched off, the six-way valve closes, and the carrier gas sweeps the gas sample into the packed column. The column separates the various sulfur compounds and admits them one by one into the detector. The detector (plus associated electronics) will give a peak on a strip-chart recorder for each sulfur compound passing through it. The area underneath a given peak is directly related to the concentration of that compound.

While a sample is being analyzed, two ports on the six-way valve are closed to any gas flow. This permits a blow back phase where compressed air is forced through the probe to 1) clean off solid particles clinging to it, and 2) blow out any water that may have condensed in the tubing between the probe and instrument. This blow back lasts about four minutes during each cycle.

In addition, at the beginning of each cycle a solenoid valve opens and allows a small amount of electrolyte to flow into the detector. This insures that a fresh electrolyte is always present.

Probe Design (Figure 2)

Many of the gas streams to be analyzed in a Kraft mill have a high solid content. This is particularly true of gases just out of the recovery furnace before they are scrubbed. Any solid material entering either the chromatograph column or the detector would cause un-



predictable, but always undesirable results. Thus, the probe must allow no solids to enter the tubing to the instrument. (A separate glass fiber filter is incorporated in the instrument itself as a safety feature.)

A design which has worked quite well is a 1/4-inch porous (100 micron) stainless (3-16) steel tube as the filter media. Lengths will vary depending on the nature of the sampling port. This porous rod is encased in a thin-walled 3/4-inch outside diameter stainless steel tube with a 1/2-inch hole drilled near the end. The hole is pointed to the downstream side of the stack so that solid particles are not forced against the porous tube merely by gas flowing in the stack. Connections to the instrument are made with 1/8-inch polypropylene or teflon tubing and nylon Swagelok tubing fittings. Samples are drawn from the stack at a rate of about 250 cc/minute.

For stack gases which were nearly saturated with water, the blowback procedure described earlier was not always sufficient to keep water from collecting in the lines to the instrument. In these instances a water trap was placed in the line near the probe. The trap was basically a plexiglas U-tube with a long leg (2-3 feet) at the bottom of the U. A check valve was attached to the bottom of the leg so that no air would leak into the lines when a sample was being drawn.

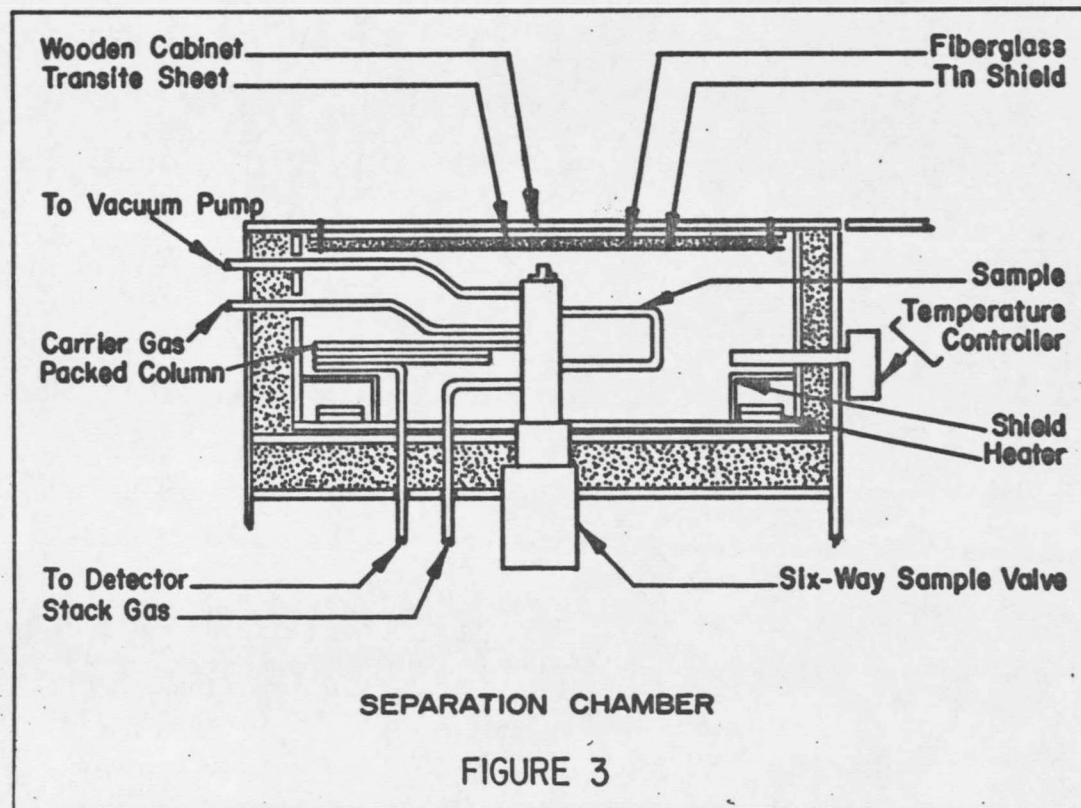
Then during the blowback cycle the check valve opened and compressed air forced any liquid collected in the tube onto the ground.

The reason water must not be allowed to collect in the lines is that it will absorb part of the sulfur gases in any sample being drawn.

The probe itself also meets other more basic requirements of any probe used. 1) It does not readily corrode in the steam-sulfur atmosphere found in many Kraft mill stacks. 2) Stainless steel does not adsorb or react with SO_2 (25) or other sulfur gases. Adsorption of SO_2 in particular is a problem common to many tubing materials, particularly some plastics and most rubbers.

Separation Chamber (Figure 3)

The separation chamber was really a gas chromatograph oven. Very briefly, gas chromatography can be explained as follows (23): It is a process for separation and analysis of the components of a mixture. Separation of a mixture into its components depends on the solubility differences of the sample vapor in a liquid (stationary phase). The stationary phase is coated in a thin layer on solid particles (solid support) of large surface area and then packed uniformly into a column. A constant flow of inert carrier gas passes through the column and transports solute molecules in the gas phase. The



column is enclosed in an insulated oven for precise control.

A sample of the mixture to be analyzed is (at pre-set intervals) carried into the column by the carrier gas. As the carrier gas pushes the sample into the column, the sample gases partition themselves between the gas and liquid phases according to their solubilities in the liquid at the column operating temperature. This equilibrium continues as the sample is moved through the column by the carrier gas. The rate at which the sample travels through the column is determined by the sample solubility in the stationary phase and carrier-gas flow rate. Each component travels at a characteristic rate, and if the column rate has sufficient length, the sample will be completely separated by the time it reaches the end.

Each component is identified by the length of time it remains in the column ("retention time"). The retention time of a gas depends on temperature, column length, type of stationary phase, and carrier gas velocity. If these variables are kept constant, the retention time of a component will remain constant.

Retention time is usually measured with an electrical strip-chart recorder, where the sample components are represented as peaks on a paper chart. The detector (in this case a bromine titration cell) produces an electrical output which is proportional to the

sample component concentration and this output deflects the pen of the recorder. The area under a peak represents the quantity of the component present. This provides the basis for quantitative analysis of the components identified in the separation.

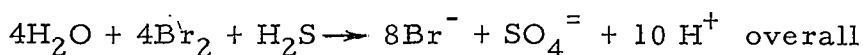
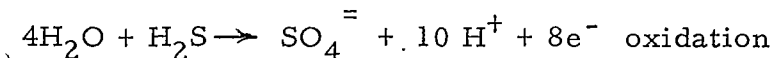
The column used for plant tests of this instrument was a 1/4-inch teflon tube packed with Porapak Q-S 100-120 mesh. The sample loop--a 1/4-inch teflon tube of about 10 cc volume--and packed column are both enclosed in an insulated chamber which is maintained at a constant temperature ($\pm 2^{\circ}\text{C}$) of 90°C . The chamber is heated by two 150-watt strip heaters wired in series. The desired temperature is maintained by an on-off controller. Keeping the sample loop in the insulated chamber ensures that a reproducible amount of gas is always being analyzed.

Detection Cell

Because of its high sensitivity and selectivity for sulfur compounds, the bromine titration cell was chosen as the detector for the instrument being developed.

Theory of Operation

Sulfur gases separated by the packed column enter the detection cell through a porous (glass or polyvinyl chloride) tube. The primary electrochemical reactions which take place for H_2S are (25):



Similar reactions occur for SO_2 and CH_3SH . Thus the change in bromine concentration gives a quantitative measure of the amount of sulfur compound entering the cell. As soon as the bromine ion concentration changes, the change is sensed by the sensor/reference pair of electrodes. The change is really a potential difference which becomes an input to an amplifier of the microcoulometer. The amplifier instantaneously supplies a voltage to the generator/counter electrode pair. 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 a recorder chart. The area beneath this peak is directly related to the concentration of sulfur compound which entered the cell.

The great advantage of using the bromine cell over other types of gas chromatograph detectors is its selectivity for sulfur compounds. Other gases such as C_2H_2 , CO_2 , and H_2O do not react with the bromine; therefore, no extraneous peaks on the chart paper.

Cell Development

Mark 0 (Figure 4)

The first detection cell was built by Applebury (6) and improved by Wan (25). It was a 3-compartment configuration made of Pyrex glass. The three compartments were separated by glass frits so as to partially "isolate" the counter and reference electrodes. Further construction details for this cell as well as others discussed later are shown in Table II.

General information gained from this cell is as follows.

When the volume of titrant exceeded 40 ml, the sensitivity* of the cell tended to decrease. The optimum rate of titrant regeneration was about 3 ml/cycle where the cycle time was set at 10 minutes on a continuous multi-cam timer. Faster rates gave overshoot on peaks, while a slower rate gave lengthy tails. A carrier gas flow rate of 200 cc/minute into the cell gave the best response; a higher rate gave long tails and lots of noise[#], whereas a lower rate produced over-

*Unless otherwise stated, gas samples used were 10 cc volume and injected with a hypodermic gas-tight syringe. The term "sensitivity" then should be taken in a more qualitative than quantitative sense to mean giving a tall sharp peak for a sample concentration of 50 ppm.

[#]Noise is meant to be an unsteady (constantly oscillating) baseline on the recorder chart.

TABLE II
DESIGN SPECIFICATIONS FOR THE VARIOUS DETECTORS

	MARK O	MARK I	MARK II	MARK III	MARK IV	MARK V	MARK VI
<u>ELECTRODES</u>							
REFERENCE:	Calomel (G)*	Calomel (G)	Calomel (G)	Calomel (G)	Calomel (G)	Calomel (P)	Calomel (P,G)
GENERATOR:	1cm ² plate Pt	.010 x 2 1/2 Pt wire	.025 x 1" Pt wire	.025 x 1 Pt wire	.010 x 5/8 Pt wire	.020 x 1/2 Pt wire	0.10 x 1/2 Pt wire
SENSOR:	1cm ² plate Pt	.010 x 2 Pt wire	.025 x 1/4 Pt wire	.025 x 1/4 Pt wire	.010 x 1/4 Pt wire	.020 x 1/4 Pt wire	0.10 x 3/16 Pt wire
COUNTER:	.015" diam x 1 1/2" Pt wire	.010 x 2 1/2 Pt wire	.025 x 1/4 Pt wire	.025 x 1/4 Pt wire	.010 x 1/8 Pt wire	.020 x 1/8 Pt wire	0.10 x 1/8 Pt wire
<u>ELECTROLYTE</u>							
Vol in Cell:	40 mls	15 mls	20 mls	20 mls	15 mls	10 mls or less	
KB ₂ Conc:	8.64 g/l H ₂ O	.76 g/l	7.2 g/l	0.72 g/l	0.216 g/l	0.216 g/l	0.216 g/l
H ₂ SO ₄ Conc:	7.2 ml/l H ₂ O	6 mls/l	6 ml/l	.6 ml/l	1.8 ml/l	1.8 ml/letr	1.8 ml/l
Regeneration Rate:	3 cc/cycle cycle = 10 min	None	None	None or ~ 3 cc ^o periodically	None	2 - 3 cc/cycle	<1cc/cycle
<u>PHYSICAL STRUCTURE:</u>							
Mat'l of Constr'n:	Glass(Pyrex)	Plexiglas	Polypropylene	Plexiglas	Plexiglas	Plexiglas	Plexiglas
#Compartments	3	1 ^o	1	1	1	1	1
Diam Electrode Cham:	1"	1/2"	1 1/2"	1 1/4"	3/4"	1/2-5/8" ^o	11/16"
Ht. Electrode Chamber:	6"	4	3/4"	1"	4"	2 1/2"	1"
Approx Over- all Size:	6"x1"x8"	4x2 1/2x5	4"diam by 1/1/2 4x2 1/2x3		2x4x6	3x2 1/4x6	1 1/2x1 1/2x6

*(G) Refers to Commercial Glass Electrode

(P) Plexiglas type

^o See Discussion Section

shoot. It was noticed several times during these laboratory experiments that even stainless steel would react enough with the electrolyte to produce undesirable results. Therefore, no metal fittings could be used to connect the cell to the electrolyte reservoir.

Another frequent source of contamination was from the copper leads connected to the platinum electrodes. Although the platinum electrode was sealed in a soft glass tube (Pyrex would not seal) to keep solution from contacting the copper, small cracks developed quite easily and would allow the electrolyte to leak inside the tube. This problem was one objection to Mark 0.

Another major objection was the glass frits separating the three major compartments. They are quite difficult to clean; thus, once the cell becomes contaminated, it is a major chore to remove all of the impurities.

Furthermore, the noise level in this cell seemed unduly high. The thought here was that a better mixing pattern would give less noise because there would be fewer concentration gradients to cause a change in the Br_2/Br^- equilibrium. It is this change in equilibrium when no sample is passing through the cell that causes noise.

The first modifications on Mark 0 were a new gas inlet tube and new electrode configurations. The gas inlet was made from a

1/4-inch porous ceramic rod, and the sensor/generator electrodes were changed from the plate configuration to Pt wires wrapped around the ceramic rod. This gave noticeably less noise than the original Mark 0, but there were still voids in the bottom of the chamber where mixing was not complete. Some noise still persisted.

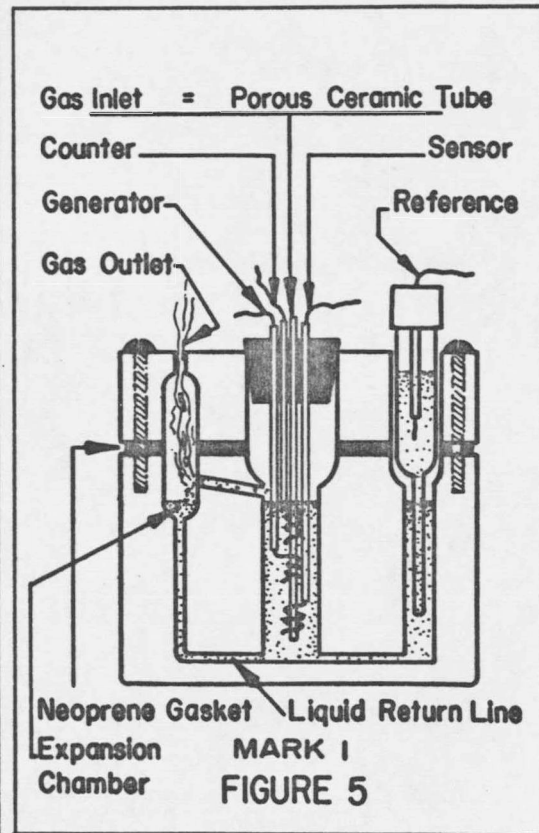
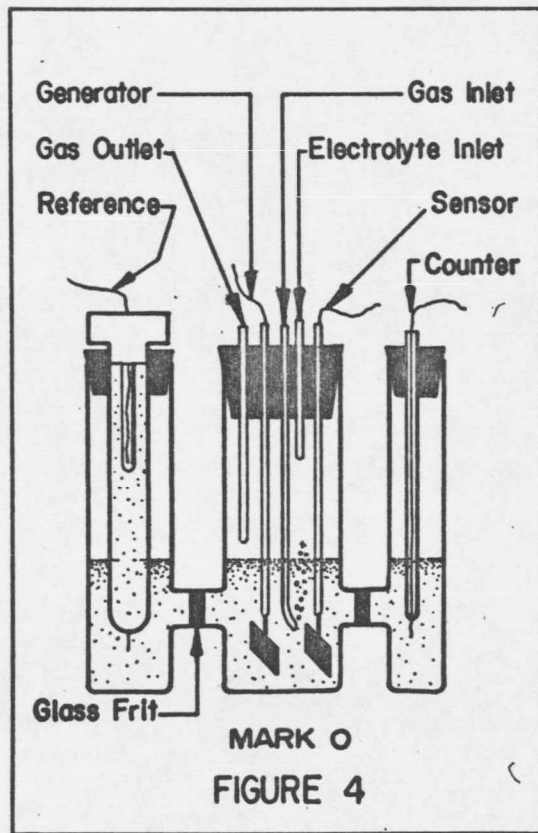
Before a new cell was constructed, tests were made with the counter electrode in the same compartment as the generator/sensor pair. The cell's performance was affected very little by this change. This indicated that at least one cell and one glass frit could be eliminated.

Any new cells would be designed to alleviate two other minor drawbacks of Mark 0. These were its rather large size physically speaking, and its fragility because of its construction from glass.

Mark I (Figure 5)

The thoughts which led to this design were that a smaller volume reaction chamber would give higher sensitivity and the thorough mixing occurring because of the small volume would reduce noise levels.

It might be well to add at this point that better mixing could be achieved using a mechanical stirrer with a magnetic spin bar.



This, however, would increase the cost of the instrument. Because high costs were inconsistent with one of the research objectives, efforts were directed toward making a cell which developed its own good mixing pattern merely by the action of the carrier gas passing through it. Besides adding to the cost of the instrument, an external stirrer also adds to its bulk--another undesirable feature.

In Mark I, electrodes were sealed in soft glass--again Pyrex was unsatisfactory. No glass or porous materials were used between chambers.

Problems with this cell were numerous. The most serious one involved the liquid return line from the expansion chamber. The solution entering the bottom of the electrode chamber was not the same composition as that in the chamber itself. Since the liquid volume in the electrode chamber was so small, even a little liquid from the return would appreciably change concentrations. Thus, in spite of good mixing in the electrode chamber itself, overall mixing was poor and a high noise level resulted.

Still it was felt that a small volume of electrolyte would give greater sensitivity and less noise. Thought was also given to changing electrode lengths; in particular, shortening the counter electrode so that "large" amounts of bromine would not cling to it. If bromine

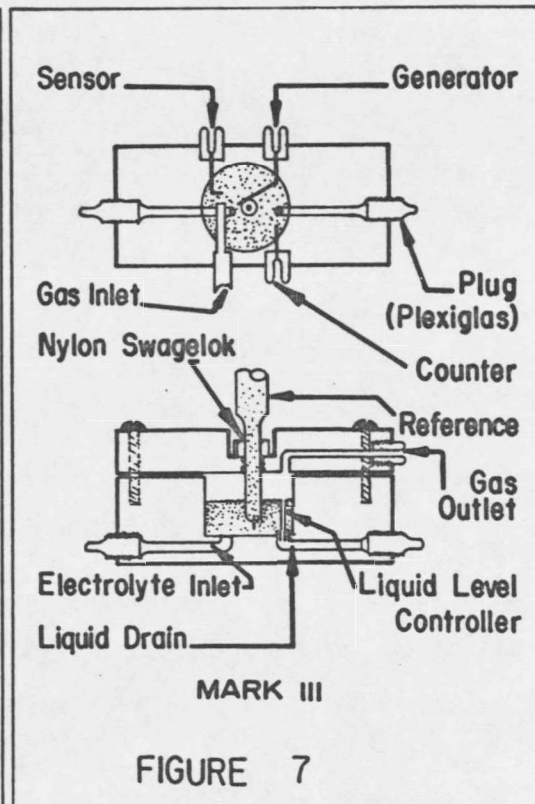
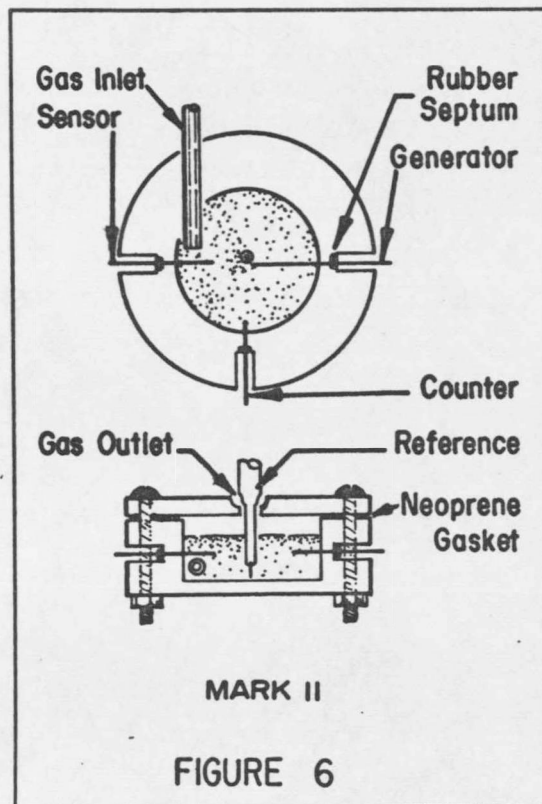
did cling to the electrode, it would eventually be broken loose by the bubbling of gas through the cell. This would give a slight excess of bromine to the solution, thereby changing the equilibrium conditions and producing undesirable noise "peaks".

Mark II (Figure 6)

This cell was also small volume, but, unlike Mark I, it had a shallow electrode chamber. Furthermore, all electrodes were in the same chamber and three were made of short lengths of platinum wire. (See Table II.) The gas inlet tube was a short piece of glass capillary tubing. The cell was made rather hastily and in a crude manner. There was no real outlet for the gas--it just leaked out around the reference electrode. Neither was there any provision for adding new electrolyte. The electrodes were merely "sealed" into the walls of the cell with soft rubber septums. Still, the design showed remarkable stability and good sensitivity.

Mark III (Figure 7)

This model was simply a more sophisticated version of Mark II. It was made of plexiglas with individual gas outlet and titrant inlet ports. Although the design was very similar to that of Mark II, performance was quite inferior. Noise levels were unusually high even when no new titrant was added over a one-hour period. (Recall



that some noise is to be expected when fresh titrant is added because the titrant does not have the same Br_2/Br^- concentration as the solution in the cell.) Adding fresh electrolyte only made things worse. One cure for the high noise was physically shaking the cell. Conclusion: Mixing was incomplete. Changing the gas inlet from a capillary tube to a "multi-hole" plastic tube coiled around the bottom of the cell reduced the noise somewhat but not sufficiently.

Another factor which affected the noise level was the sealing of the reference electrode in the lid of the cell. When the reference was properly sealed, noise levels were tolerable. But when a leak developed, noise levels immediately increased.

Some work was done with this cell studying the effects of electrode lengths and placement. In general, a shorter counter electrode (1/4-inch to 1/8-inch) reduced noise; a longer generator (1-1/2-inch to 2-inch) gave faster response; and letting the gas stream sweep the sensor gave a more stable response, i. e., smooth rather than jagged peaks.

Mark IV (Figure 8)

To achieve better mixing, designs again returned to the tall thin electrode chamber. As before, all electrodes were in the same chamber. No provision was made in this model for the periodic

addition of electrolyte. It was built primarily to either verify or refute the proposed "small volume - low noise" theory. This time a porous polyvinyl chloride (PVC) rod was used for the gas inlet tube and was sealed in the bottom of the cell. It was felt that using a porous material for the gas inlet would create more dispersion of gases in the electrolyte and hence result in better mixing.

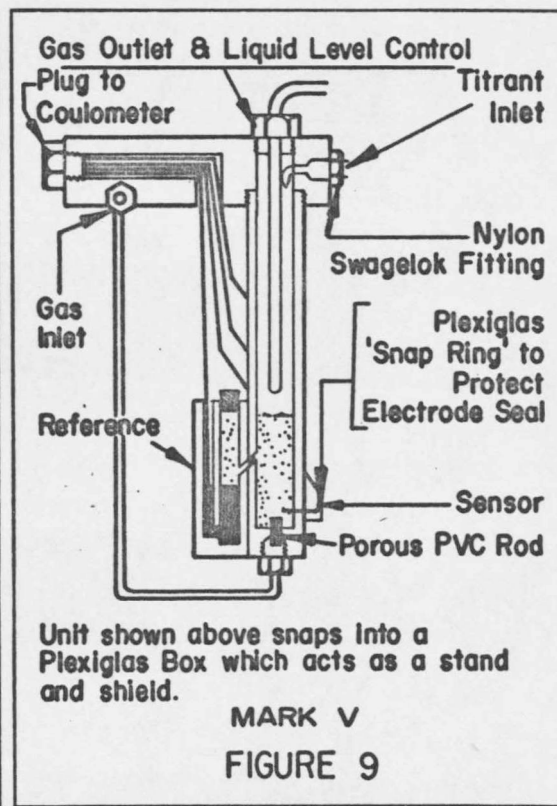
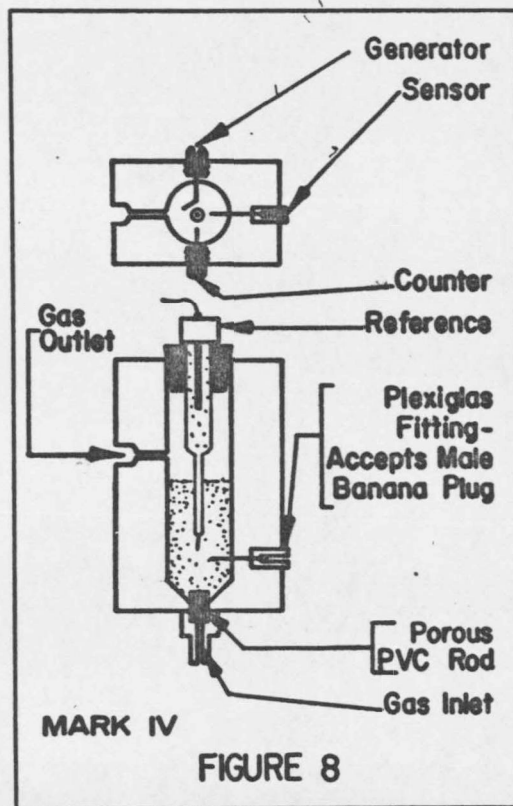
As predicted, noise levels were unbelievably low. However, to get a good response using this cell, gas flow rates had to be raised to 400 cc/minute compared with the 200 to 250 cc/minute rate used in other cells. In all previous cells the carrier gas had been nitrogen so at first it was also used in Mark IV. This high flow rate of nitrogen prompted thoughts of using compressed air--properly dried and filtered--as the carrier gas. Switching from nitrogen to compressed air showed absolutely no deterioration in the cell's performance either from a noise or a sensitivity standpoint. Avoiding the use of nitrogen as a carrier was indeed a plus for the completed analyzer because now no bottled gas would have to be moved around with the instrument.

Using this particular cell design, some work was done to determine the best diameter for the electrode chamber. For the 400 cc/minute gas flow rate the best chamber diameter appeared to be 3/4-inch. (Lengths remained constant at 4 inches.) Larger diameters

increased noise because of incomplete mixing and smaller diameters caused liquid droplets to hang up between the cell wall and reference electrode. When these droplets fell back into solution, a tall but very narrow peak appeared on the recorder because of the concentration difference between droplet and solution.

Mark IV was the first of the plastic cells to be used with a gas chromatograph. This gave another design criteria for the overall instrument. The carrier gas flow rate had to be fast enough to give good chromatographic separations, yet it also had to be slow enough to give good detector response. Recall that it had been decided that a sample should be extracted from the stack and analyzed once every 10 minutes. This meant that retention times for a gas sample in the column should be less than 10 minutes to avoid possible overlapping of peaks between samples. In reality, this becomes more of a column design problem than a cell design limitation although there is some interaction.

Early lab work was done using a commercial Aerograph Model 200 chromatograph. Results obtained using different column packing materials are discussed in a later section. Using a six foot long, 1/4-inch teflon column packed with Porapak Q-S and a compromise flow



rate of 300 cc/minute with Mark IV gave acceptable separations and a pretty good cell response.

Mark V (Figure 9)

Mark V was an attempt to overcome the two faults of Mark IV. The commercial reference was replaced by one made from plexiglas. The new reference was still the calomel electrode (recipes for making them can be found in any text on electro-analytical chemistry) and was attached permanently to the side of the electrode compartment. Since the reference was now contacting the solution through the side of the chamber, it was occupying almost no volume within the reaction portion of the cell. Therefore, it was felt that a smaller diameter--less than 3/4-inch--chamber could be used. Then a lower gas flow rate would still give good mixing and possibly better chromatographic separations. Most bromine cells either on the market or described in the literature show the best cell response when the flow rate through them is 200 to 250 cc/minute. Even though cell configurations for the Mark series are quite different from the commercial ones, designs were made to give optimum performance at this flow rate.

As a starting point, a chamber diameter of 5/8-inch was used. Initial results looked very promising, but after five to six hours' use,

noise increased markedly and sensitivity declined rapidly. The seemingly obvious answer was the "homemade" reference electrode had ceased to function properly. The ingredients for it were prepared several times but the same phenomenon occurred each time--good initial performance but serious degradation with time. Eventually modifications were made on the cell so the commercial reference could be used (in a chamber physically separated but tube-connected to Mark V). Quite surprisingly the same thing happened again. After many frustrating hours of studying the cell, an explanation was found.

When the cell is started up, the inside walls are clean. After it has been operating for a time, water droplets begin to collect on the walls above the electrolyte. When sufficient time has passed the bubbles become large enough to break away from the walls and fall back into solution. This upsets the equilibrium and causes noise. The effect could be magnified by passing a concentrated sulfur sample --say 800 ppm H_2S --through the cell. Not all the sample gets absorbed in the liquid. Some passes up the cell and is absorbed by liquid droplets on the wall. When these droplets fall back into solution there is a huge increase in noise for almost 30 minutes after the sample was injected.

This deterioration with time was but one serious fault of Mark V. Another was the reference electrode. Once the electrolyte had been drained out of the cell, it was difficult to keep air bubbles from forming in the arm connecting the reference to the electrode chamber; these air bubbles prevented electrical contact with the reference when the cell was started up again. Consistency in making up the cells was another problem. The reason why was never determined, but some were very sensitive to sudden vibrations, while others were not noticeably affected at all.

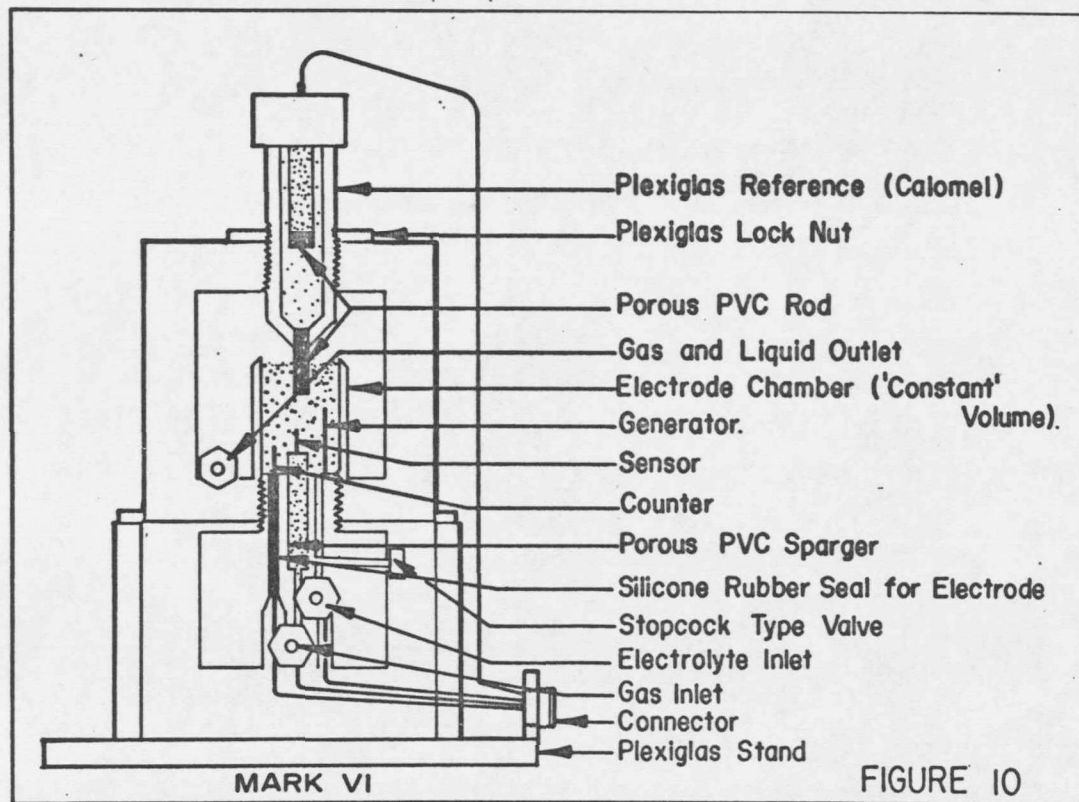
Just a point of interest--when electrolyte was added to the cell (at 10-minute intervals) a peak much like that of an H_2S peak would appear on the recorder. The pen returned to its normal baseline about 30 seconds after the electrolyte addition was stopped.

In spite of its above mentioned faults, Mark V was used for about six hours worth of actual plant data in a Kraft mill. This was done to determine what problems might develop at a plant site that would not occur in any laboratory test. In such a short time interval no unexpected problems did arise, so the cell was brought back to the lab for further studies and modifications.

Mark VI (Figure 10)

Mark VI introduced several new changes over previous models.

- 1) The electrolyte chamber was concentric with a larger compartment used as the gas outlet portion of the cell. This essentially made the electrolyte chamber with no walls for liquid droplets to cling to. It also gave a constant volume electrolyte chamber since any excess would merely overflow.
- 2) The calomel electrode was again made of plexiglas but in a style very much like the commercial glass one used earlier. Threading the body of the electrode provided an easy method of sealing it into the cell block.
- 3) The three platinum electrodes were sealed in a removable block in the bottom of the cell. This electrode arrangement greatly simplified cleaning and/or removal of the electrodes if they became contaminated. Too, these electrodes were much easier to keep sealed than those entering the side of the wall.



The entire bottom of this cell was also removable so electrode chambers of different heights and inside diameters could easily be inserted in the cell. By trial and error it was found that an electrode chamber 11/16-inch in diameter by one inch high was best to accommodate the desired gas flow rate of 200 to 250 cc/minute. Larger volumes tended to give slightly more noise and long tails on peaks. Smaller volumes resulted in enough of the electrolyte being blown out that electrical contact with the reference was lost.

The performance of this cell was quite superior to any previous models. A continuous laboratory test of 48 hours showed no degradation in its performance. Because it was purposely designed so that parts could be easily interchanged, the cell was considered too bulky for a portable instrument. After the "best" electrode design and spacing as well as the "best" electrode chamber size had been determined, a smaller model called the "Mini-Mark VI" was built to be the compact unit used in plant tests. The only major design change was the discarding of the plexiglas reference. Though many different things were tried, leakage of fluid out of the salt bridge compartment of the reference could not be stopped. After a 48 to 60 hour period the compartment had to be filled in order to

make it operable. Replacement of the porous PVC rod in the bottom of the reference with either an asbestos thread or a nylon thread did not significantly decrease the leakage rate.

The commercial reference was again used in "Mini-Mark VI" but was covered by a specially built plexiglas housing to make it less susceptible to breakage. The reference was sealed in the housing and the housing in turn sealed in the cell block. Performance of the "Mini-Mark VI" was in every way comparable to that of the original Mark VI. Consequently, it was chosen to be the detector for the portable sulfur analyzer being developed.

Electronics

Microcoulometer

Early work in this project was done by using the commercially available Dohrmann Model C-200-A Microcoulometer. The function of this electronics is described in Dohrmann's Manual (8) and summarized below.

Any change in the titrant ion concentration within the cell is detected by the reference/sensor electrodes as a potential difference. The difference between the voltage output of the reference/sensor electrode pair and the opposing voltage from the BIAS SET (a control knob on the front of the instrument) is the input to the

coulometer amplifier. Changing either titrant ion concentration or BIAS SET voltage will cause a potential to be seen by the amplifier. When these two voltages are equal, the amplifier receives a zero signal. Any shift in the reference/sensor voltage is sensed by the amplifier which produces a current flow between the generator anode and cathode (counter) in the titration cell. This current generates or removes titrant ions through an oxidation/reduction at the anode.

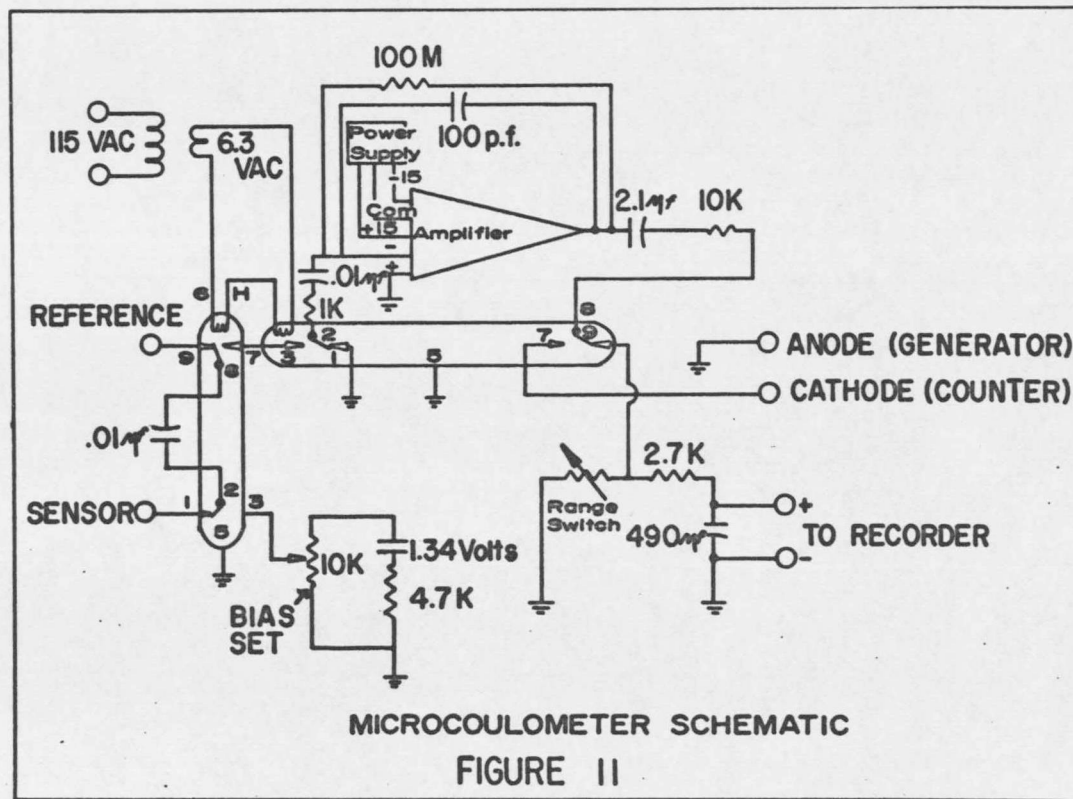
When sufficient titrant has been produced by the generator pair to re-establish the original titrant concentration, the voltage to the amplifier will be zero and the system will again be at equilibrium. During the course of the regeneration, the current passes through a series of resistors and capacitors. A strip chart recorder measures the voltage drop across one of the capacitors. This recorded voltage (shown as an almost triangular peak) can be related to the original concentration of sulfur compound which caused the change in titrant ion concentration.

For all the titration cells just described except Mark VI and "Mini-Mark VI" this Dohrmann coulometer was used. Because the Model C-200-A is rather large and would be impractical in a portable instrument, a circuit was assembled in the lab to perform

the same function. The circuit diagram for it is shown in Figure 11. When this unit was assembled it occupied less than one tenth of the space of the commercial model and it fit quite nicely into the case for the portable analyzer.

The only external adjustment (thinking now in terms of the final instrument) on the circuit is the RANGE switch. This is an 11-position single pole switch which changes the resistance in the path to ground. As the resistance is increased, more of the current is forced through the capacitor across which the recorder is connected. Now, consider several samples of identical concentration passing into the cell at preset intervals. These will each give the same voltage input to the amplifier and also the same voltage output. But if the RANGE setting is changed between samples, different voltages will appear on the recorder. Thus, the RANGE switch is merely a means of changing the sensitivity of the instrument.

During the development of the circuit a compromise had to be made between sensitivity and stability. The rather arbitrary criteria for a good circuit was chosen to be one which gave a full scale deflection for a 1 ppm H_2S sample (70 ml but not passing through a packed column) at an intermediate sensitivity range set-

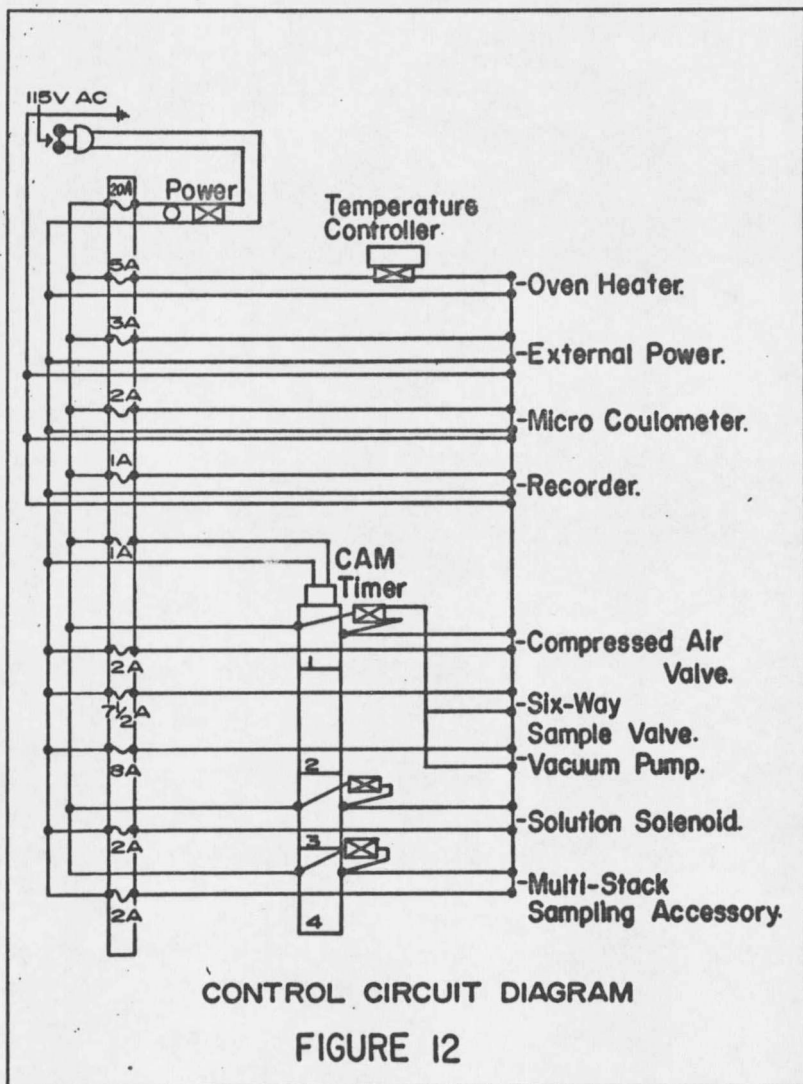


ting of 100. At the same time, noise levels should be very low. Using the resistor and capacitor values shown in Figure 11, this goal was achieved.

The most critical component from a stability standpoint was the capacitor in the feedback path on the amplifier. Lowering the value to 10 picofarads increased stability greatly and simultaneously reduced sensitivity but to a lesser degree. Better sensitivities could be achieved by decreasing either the resistance or the value of capacitance in the path to ground where the recorder was connected. Here the noise levels did increase in direct proportion to the gain in sensitivity.

Control Circuit (Figure 12)

The function of the control circuit is to determine the sequence of events taking place when the instrument is operating continuously. The events have already been described in the Operation portion of this section and will not be repeated here. Note from the circuit diagram that whenever the main power switch is on, power is delivered to the coulometer, timer, and external power plug. Current flows through the oven heaters until the temperature controller breaks the circuit.



The heart of the control circuit is the continuous multi-cam timer. Cycle time can be altered by a simple gear change between the drive motor and cam shaft. The cams are adjustable and can be set to any desired "percentage of cycle time" (between 1% and 99%) that a given microswitch is to be open or closed. The microswitches are the single-pole-double-throw type which means that they can close one circuit and simultaneously open another one. In the instrument, timing of three items is quite important. When the vacuum pump is on, the sample valve must open so that a sample can be drawn into the sample loop. More important is the fact that the solenoid valve controlling the compressed air used for blowback be closed then and not opened until the six-way valve closes. The easiest way to ensure that this happened is illustrated in Figure 12. All three items are controlled by a single switch. The vacuum pump and six-way valve are essentially wired in series so that both are on and off together. The compressed air valve is wired to the other pole of the switch so that it is off when the pump is on and vice versa.

One microswitch is used to control a solution solenoid valve which admits electrolyte to the cell for about 30 seconds of each cycle. Exactly when the addition occurs is not critical.

The remaining microswitch activates a solenoid operated stepping switch in the multi-stack sampling accessory. This unit is described later. Here the stepping switch should be activated as close as possible to the same time that the vacuum pump is turned on. The switch, however, is not energized when the pump shuts off but gets activated again only at the beginning of the next cycle.

Recorder

Inexpensive, non-continuous, low impedance recorders were tried but proved unsatisfactory because they overloaded the micro-coulometer circuit. Also, the non-continuous trace made data interpretation quite difficult. A better unit is the Varian G-11A potentiometric recorder with five-inch chart paper.

Calibration Device

Several devices exist for preparing accurate gas samples. These include Mylar bags, spinning syringes, screw-driven syringes, and permeation tubes.

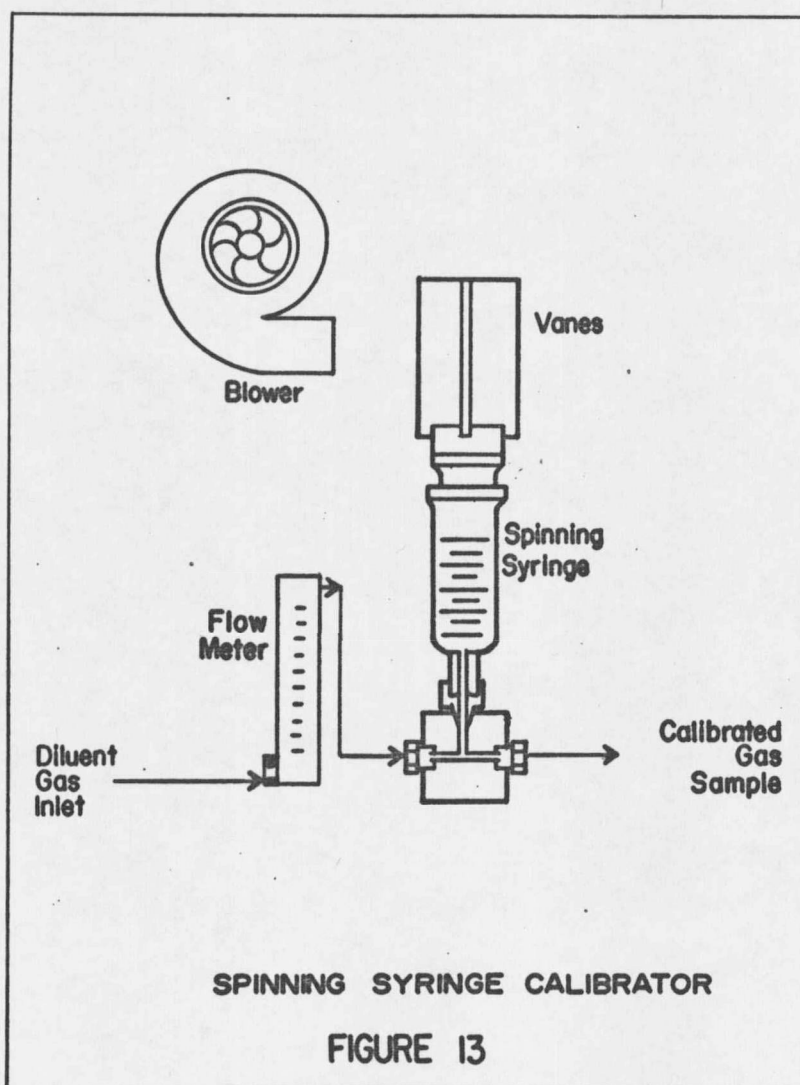
Samples in Mylar bags are prepared by injecting--usually with a gas-tight syringe--a known volume of the pure gas into the bag. Then a measured amount of diluent gas is pumped in. Further dilutions are made by adding more diluent gas. Reproduc-

bility using this method was given a range of $\pm 12 - 16\%$ by Adams (5).

Permeation tubes are a very accurate way of preparing gas samples provided that a constant temperature can be maintained. This limitation alone dictates that they be used only in a laboratory where ambient temperatures do not vary much and a constant temperature bath will indeed stay at a constant temperature. Another serious limitation is the relatively slow rates of permeation generally encountered. Producing sample concentrations in the 100 ppm range on a continuous basis would be nearly impossible with any reasonable lengths of permeation tubes.

Screw-driven syringes have been used for quite some time (12) but some commercial units do not give a truly constant delivery rate of gas because the syringe plunger is not securely fastened to the screw-driven shaft. This permits the plunger to stick in the barrel and results in non-uniform delivery rates. When a modification is made and the plunger securely fastened to the shaft, this method is considered a fairly reliable method of preparing gas samples. It is about as accurate as the method used to measure the flow rate of diluent gas past the delivery tip of the syringe.

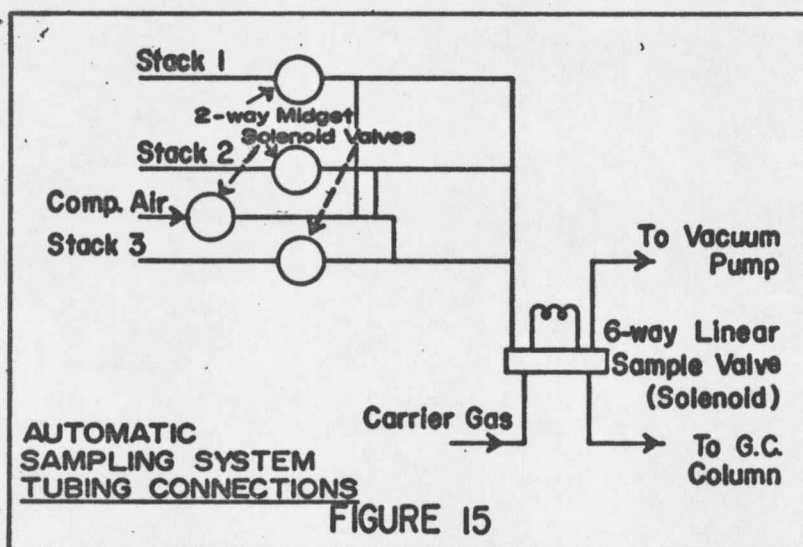
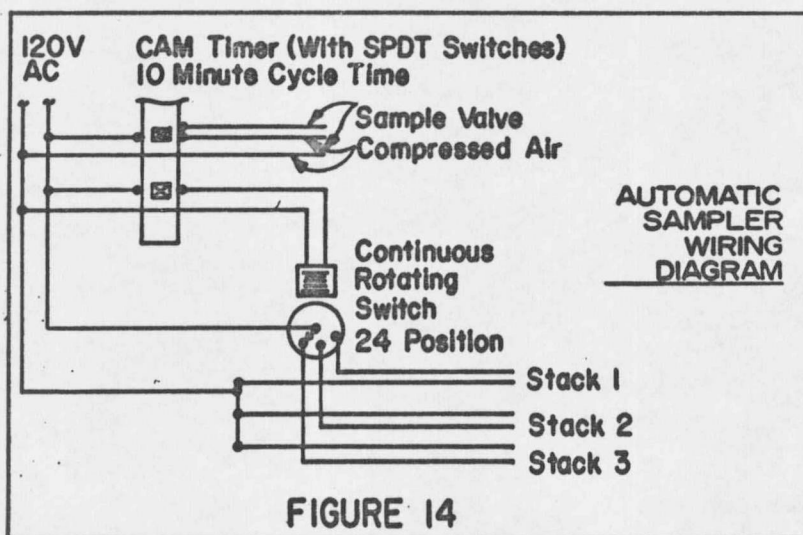
A more recent development in preparation of gas samples is the spinning syringe (Figure 13). The system is based on the frictionless bearing formed by carefully polished surfaces of a glass barrel and a rotating plunger. The air bearing allows a constant load to be placed on the air column. Regardless of leakage past the bearing--generally insignificant--the delivery rate of the gas mixture is said to be constant as long as the piston is spinning. Conversation with several different individuals in the air pollution field revealed varying degrees of satisfaction with this device. In reality, the falling rate of the syringe is dependent to a certain degree on how fast it spins. Thus, to ensure truly reproducible delivery rates, the spinning rate of the syringe should be the same each time the unit is used. Among users of spinning syringes it is generally agreed that the setups using a small fan as the air source to spin the syringe are reliable enough to be used as calibration standards. Again, the accuracy of the sample concentration is about that of the method used to measure the diluent gas flow. This was the calibration method used during construction and testing of the continuous analyzer.



Multi-Stack Sampling Accessory

A unit which electrically plugs into the main analyzing instrument has been built to allow sampling of three different locations in succession. A slight modification, taking less than five minutes to complete, must be made to the master unit. It involves disconnecting a tube at a tee, attaching the tube to a bulkhead union, and plugging the open branch of the tee. If all sample lines have been strung and end in the vicinity of the analyzer, the total time required to change from single stack to three stack sampling or back again is less than 10 minutes.

A wiring diagram for the sampler is shown in Figure 14. The figure does not represent the actual wiring layout in the accessory, but rather shows the circuit after the unit is plugged into the main analyzer. The cam timer in the main unit activates the rotating switch once during each cycle. This switch then opens one and only one (of the three) midget solenoid valves in the accessory. It remains open for one complete cycle; i. e., for both the sample drawing and the blowback phases. At the beginning of the next cycle the switch advances and a different solenoid valve opens--the previous one closes.



The tubing diagram (Figure 15) again does not show physical layout but was done to illustrate more clearly the relationships to items in the main analyzer. Neither the compressed air valve nor the six-way sample valve are in the accessory unit. The operation of these two valves is identical to single stack operation. Note: when sampling from three different locations, a sample will be extracted from a given stack only once every 30 minutes, assuming the timer is still set for a 10-minute cycle time.

Miscellaneous

Besides the major items discussed above, smaller items which either improved performance or simplified its operation are mentioned now.

When the instrument was first built there was no control device to regulate the carrier gas flow. It was controlled only by the pressure regulator at the source of the air supply. Later, a stainless steel micrometering valve and check valve were installed in the gas line leading to the detection cell. The check valve was inserted to ensure that no electrolyte from the cell would be drawn into the metering valve when the instrument was shut down.

An indicating dial thermometer was stuck into the oven so that actual oven temperature could be seen and appropriate action

taken if the set point on the temperature controller is accidentally moved.

Thought was given to installing a rotameter, but bearing in mind that one of the objectives of the project was to keep costs down, it was decided to use the detection cell itself as the rotameter. In other words, by observing the bubbling action in the cell one could readily judge whether the gas flow rate was too high or too low. This was actually a much more sensitive "meter" than the reader might think. Changes of as little as 20 cc/minute in the flow rate cause noticeably different bubbling patterns in the cell. The cell could easily be seen when a plexiglas window was installed in the front face of the instrument.

Control of the carrier gas flow rate became important when it was decided to use peak heights as an indication of concentrations. When gas flow rates change (+ 20%) the peak areas remain constant but peak heights will change. To get meaningful results using peak heights, flow rates must remain constant.

RESULTS

All of the research objectives as stated have been satisfied. A continuous sulfur analyzer has been built which is sensitive to only sulfur compounds. It will easily separate and analyze for H_2S and SO_2 in concentrations found in the Kraft mill. CH_3SH , however, is only detected at very irregular intervals because of its relatively low (compared to H_2S and SO_2) concentrations at the mill.

At the time of this writing it had been operating continuously in a Kraft mill for five weeks with almost no attendance. The only malfunction to date was a faulty recorder component. The only "maintenance" required has been periodic removal of the chart paper and filling the recorder pen with ink. Every four to five days the probe (if in a high solids content area) has been scraped off even though it is felt that it could be left unattended for as long as ten days.

After the first three weeks of use, the electrolyte reservoir was refilled. Consumption is about 1.5 liter/week of continuous operation. Although the unit weighs only 50 pounds and can be readily moved from place to place, this has not been necessary because sample lines to all the stacks of interest are very close to the location of the analyzer.

The multi-stack sampler was operated successfully for about 18 hours. Despite the shortness of this test it did demonstrate that the idea was sound and operable.

The instrument was calibrated twice at the plant site. This was done to check for any degradation in performance with time. None was noticeable after three weeks of continuous operation.

DISCUSSION OF RESULTS

Albeit the overall performance of the chromatographic sulfur analyzer was quite successful, there were problems which cropped up. Some were easily solved; others still have no satisfactory solutions.

Column Packing

Since most of the cell design problems and solutions have been discussed in the EQUIPMENT section, this discussion will concern other portions of the final chromatographic analyzer unit.

Perhaps the major fault with this instrument lies in the packed column used for separating the gas mixtures. From the calibration curves* in Figure 16 it will be noted that samples of H_2S below 5 ppm even on the more sensitive ranges were difficult to detect. Also, at the lower concentrations there was no linear relationship between peak areas and concentrations; e. g., a sample of 20 ppm might give an area of 100 arbitrary units but a same sized sample of 10 ppm would give an area of 10 of these arbitrary units. This phenomenon was believed to be caused by adsorption of some of the sulfur gases on the packing material. If the gases

*Made using a 10-ml sample and a six foot long by 1/4-inch column packed with Porapak Q-S in laboratory tests.

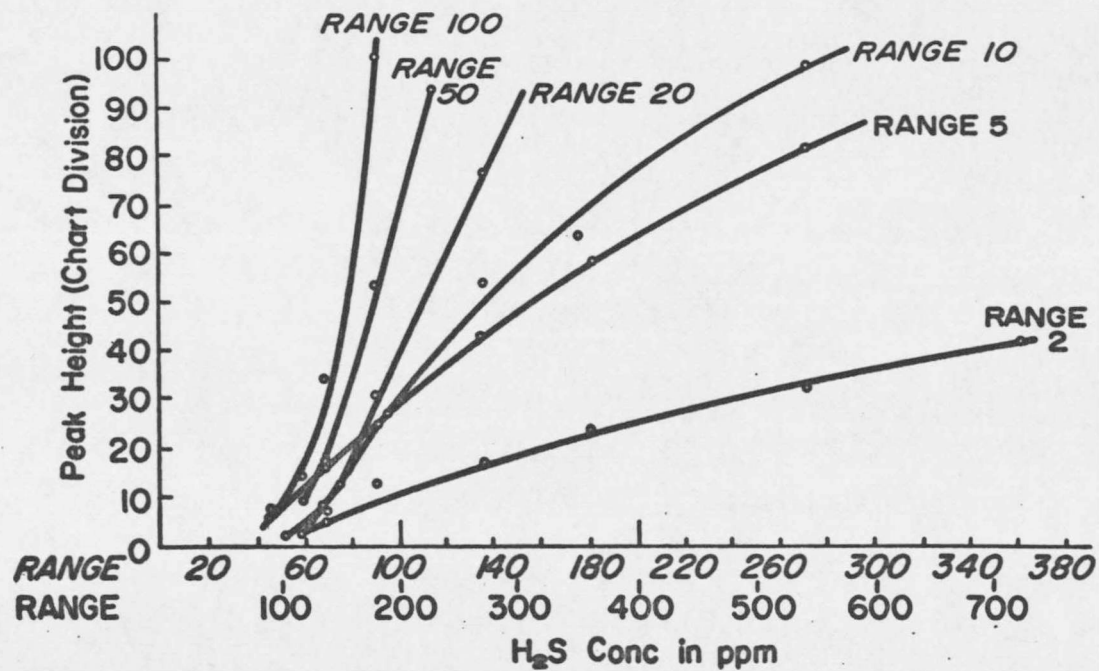


FIGURE 16: H₂S CALIBRATION DATA-
WITH PACKED COLUMN

did desorb at all it was at such a slow rate that no peaks appeared. At higher concentrations (above 50 ppm H_2S) this adsorption is only a small percentage of the total sulfur compound and is not readily noticeable. Therefore, at intermediate concentrations (between 50 and 300 ppm H_2S), there is a very nearly linear relationship between peak area and concentration of H_2S ; i. e., if a 100 ppm sample gave a peak area of 20 arbitrary units, the same size sample of 200 ppm H_2S would give a peak area of 40 of these units.

At concentrations much above 300 ppm, not all of the H_2S will get absorbed in the titration cell and again non-linearities were observed but in the opposite direction. That is, if a 300 ppm sample gave an area of 50 units, a 600 ppm sample might give an area of only 75 units. This phenomenon made results quite difficult to interpret, at least by eye, at the very high concentrations.

In order to detect sulfur concentrations below 5 ppm H_2S , the separation column had to be removed and replaced with a short length of clean teflon tubing. Sample size was increased to 70 ml. Then concentrations of H_2S below 0.2 ppm could be detected on the more sensitive RANGE settings. (See Figure 17.) Again, at concentrations below 1 ppm non-linearities began to appear. This was

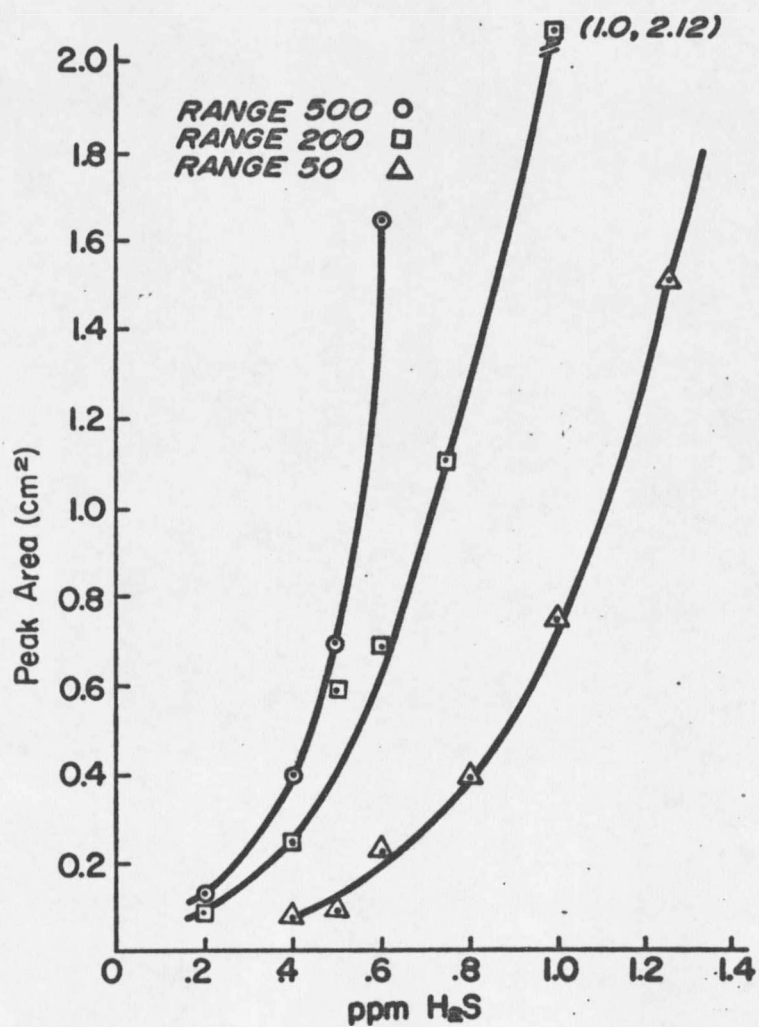


FIGURE 17: CALIBRATION DATA FOR H₂S ^w6% PACKED COLUMN.

blamed on adsorption on the tubing in the instrument. This conclusion was reached after three things were tried. First, the tubing was changed from polypropylene to nylon. Nylon was expected to adsorb more of the H_2S and SO_2 , and did exactly that. Second, the possibility of a leak causing the non-linearities was ruled out when a small hole was punched in the tubing to allow a leak. Results here were much different from previously observed data. Primarily there was no reproducibility even though the leak should have been fairly constant. Thirdly was the possibility that the detector should have the reference and counter electrodes in separate compartments. Such a cell was built and tested in the lab but the same non-linearities existed at the low concentrations.

Similar calibration results were observed for SO_2 . The difference was the concentrations at which they occurred. Condensing the discussion given above for H_2S and talking now about SO_2 , the following things were observed. With the packed column installed, concentrations below 40 ppm were difficult to detect. Intermediate linear range was 150 - 450 ppm. High non-linear end started about 500 ppm. Without the packed column, concentrations of SO_2 below 2 ppm were difficult to detect. Non-linearities were significant from 10 ppm downward.

Since SO_2 , generally speaking, adsorbs more readily than H_2S , these results were not too alarming but certainly did show avenues for improvement. This observed adsorption of SO_2 contradicts an earlier finding by Wohlers (26) that SO_2 did not adsorb on polypropylene tubing. No attempt was made here to get quantitative measures of the amount, but it was found to be significant when SO_2 concentrations in the tube dropped below 10 ppm.

Changing the instrument tubing to teflon tubing was one possible solution to the problem. This was not done because teflon tubing is quite "soft" by comparison and it was feared that leaks might develop at the fittings in the instrument.

Using stainless steel tubing is another answer, but it is rather difficult to bend and will corrode after extended periods of use in a sulfurous - H_2O atmosphere.

The adsorption problem with the packed column itself can only be solved when a new packing material is found. Several things were tried in the lab but Porapak Q-S still seemed to be the best material available. A six foot length of teflon packed with Triton X-305 on Chromosorb T gave poorer separation and very broad SO_2 peaks at the desired and necessary flow rate of 200 - 250 cc/minute.

Increasing the length of the tube would give better separation but the SO_2 peak would still not be sharp enough.

A literature article found recently (20) reports a column packing good for separation of SO_2 , H_2S , and CH_3SH in the sub part/million range. It is prepared using a 5% solution of polym-phenyl ether (5-ring) and 0.05% H_3PO_4 on a powdered perfluoroethylene support. Only one attempt was made here to make the column but met with little success. Even with a 16 foot by 1/4-inch column, separations were not adequate. The article recommends a 36 foot by 1/8-inch column but this is exceedingly difficult to pack properly.

A frequently encountered problem at the plant resulted from this adsorption problem. Because of SO_2 's being more strongly adsorbed than H_2S , the instrument gave much larger peaks for H_2S than for SO_2 when concentrations of the two gases were the same. Consequently, in areas of high H_2S concentration, the RANGE on the instrument had to be set low enough to keep the H_2S peaks on scale. Then no SO_2 would be detected.

In stacks with high SO_2 concentration the RANGE was set so that most of the peaks fell about midscale or slightly higher. Then an H_2S peak of only about 1/5 the concentration of SO_2 would be off

scale. This was the only real complaint about the instrument's performance during the plant tests. Repeating--this problem should be solved when a packing material is found which does not adsorb SO_2 and still gives good separation.

A final note on column packings--performance of different Porapak Q-S columns prepared in the lab was significantly different from column to column in terms of retention times and amount of gases adsorbed. This indicated inconsistent column packing procedures. The above discussion and Figure 16 applied to the column used in the plant tests. The sample size was 10 ml. Increasing the sample size will give larger peaks for the same concentration of sulfur compound. This, in essence, is a method of increasing the sensitivity of the instrument.

Interpretation of Data

It has already been stated that concentrations of sulfur compounds is proportional to the area of the peak on the recorder. With the Porapak Q-S column, peaks for both H_2S and SO_2 are nearly triangular in shape except for very short peaks. Therefore, accurate calibrations can be made in terms of peak heights. This becomes a real time-saving feature when large amounts of data are to be analyzed.

After some experience is acquired with the instrument, concentrations can usually be guessed within $\pm$ 10-15% by visual inspection of the peak sizes. Comparison of the peak heights with a calibration curve will, of course, give the exact concentrations.

A sample of some typical plant data for a 24-hour period is shown in Figure 18. Because of a secrecy agreement with the mill, actual concentrations are not shown but the extreme variation is illustrated. This variation was bothersome until it was discovered that an upset had occurred in the recovery area shortly before the sulfur emissions began to climb.

Multi-Stack Sampling Accessory

When this unit was first put on line, leaks through the solenoid valves were detected almost immediately. Replacing the existing hard rubber seats with a soft silicone rubber solved this problem.

Although the unit was running for four days, only about 18 hours worth of meaningful data were obtained because of recorder problems. Still, this was sufficient time to demonstrate the operability of the system. Using such a device with the chromatographic analyzer (a semi-continuous instrument) presents no problems. With continuous analyzers like the Barton, problems could be encountered when switching from stack to stack.

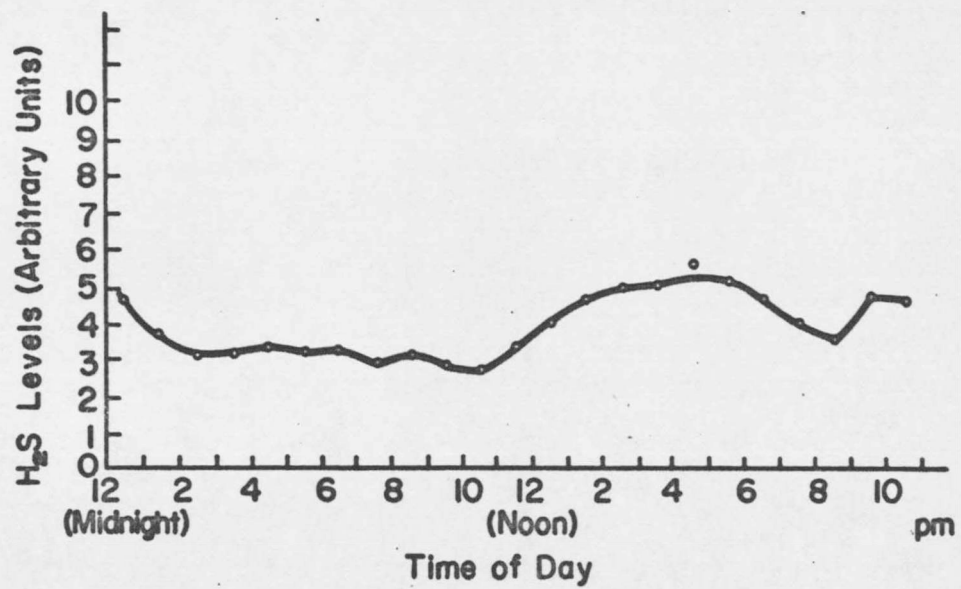


FIGURE 18: SAMPLE OF PLANT DATA TAKEN

Merits of Blowback Feature

For about four minutes of each 10-minute cycle, compressed air is forced through the sample lines and probe. This procedure not only helps to clean solid particles clinging to the probe, but it also cleans the line of any water that may have condensed in the lines to the stack.

When samples are drawn continuously (as in the Barton) water begins to collect in the lines. Water will absorb significant amounts of both H_2S and SO_2 . Then, as the ambient temperature changes, the partial pressure of these gases in H_2O will change and sulfur gases can be released into the lines. When concentrations are low this can cause serious errors in the analysis of stack gases.

SUMMARY

The continuous chromatographic sulfur analyzer developed has survived a five-week plant site test and has given some quite meaningful data. It easily detects and separates the H_2S and SO_2 concentrations found in the stack. Periodically some CH_3SH peaks have also appeared on the recorder. The only maintenance required is replenishing the recorder chart paper and ink from time to time. Also, the probe is cleaned once every four to five days if in a stack with high solids content. If a two-gallon electrolyte reservoir is used, it will have to be filled every three to four weeks.

The main improvement needed is a different separation column which does not adsorb SO_2 . Then H_2S and SO_2 samples of the same concentration will give more nearly equal peak areas.

A digital integrator would be helpful if a large amount of emission data was to be used for correlation purposes.

RECOMMENDATIONS FOR FUTURE STUDY

Of immediate importance is the development of a column which will not adsorb SO_2 or H_2S . Hopefully, one can be made which will allow separations of concentrations well below 1 ppm.

Further studies should be made to determine why detection limits even with the chromatograph column out of the unit were so much higher than those reported by Adams and Applebury. Evidence points toward adsorption on the tubing in the instrument but there exists a possibility that the fault lies in the detector itself. Other cell designs should be tried in order to improve detection limits.

If the emission data is to be used later for correlation purposes, data acquisition devices other than the strip-chart recorder should be employed at least on a trial basis. Even a digital integrator would be helpful. No doubt cost will be the deciding factor in the selection of an alternate to the recorder.

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APPENDIX

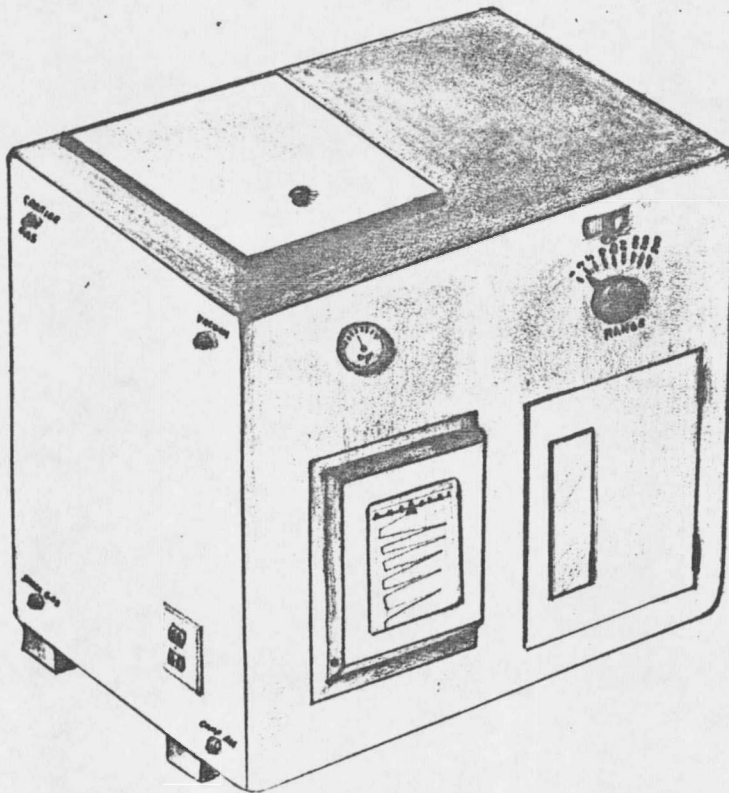
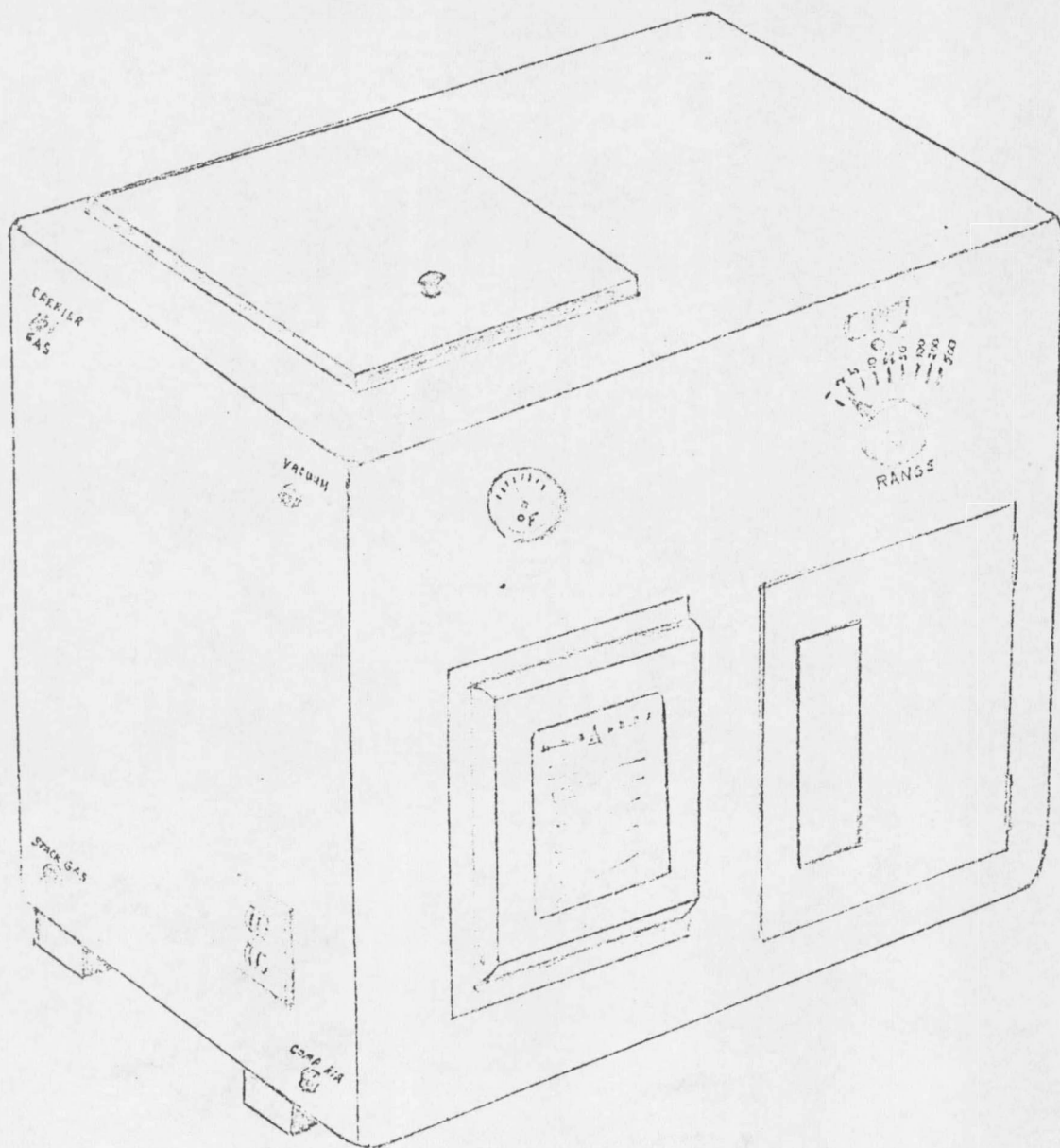


FIGURE 19: FINAL INSTRUMENT.

Related Information

The following supplement is an operations manual for the instrument whose development was described in the body of this report. It is presented here primarily as an aid to anyone using the instrument who is not already familiar with its operation.

CONTINUOUS CHROMATOGRAPHIC
SULFUR ANALYZER



OPERATIONS MANUAL

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Section 1.

General Information

1.1 Product Description

The Continuous Chromatographic Sulfur Analyzer is an inexpensive easy-to-operate sulfur analyzer developed for use in Kraft paper mills. The instrument is designed to extract a gas sample from the stack, separate the sulfur compounds present, and--using an electrolytic bromine titration cell as a detector--give a quantitative indication of the amount of each compound present. The instrument described can separate and analyze mixtures of H_2S , SO_2 , and CH_3SH in the following ranges:

H_2S - 1-1500

SO_2 - 10-2000

CH_3 - 5-1500

The lower end is limited by the separation technique used. If no separation is made, a gaseous effluent with 0.2 ppm total sulfur compounds can be easily analyzed. Techniques will soon be available that allow separations in the sub-parts per million range.

1.2 Operation Description

The sequence of events taking place during the analytical process is controlled by a continuous multicam timer set for a cycle time of ten minutes. Cycle times can be varied by making a simple gear change between the motor and cam shaft.

First the vacuum pump is switched on and draws a gas sample from the stack into a sample loop attached to a six-way linear sampling valve. Simultaneously carrier gas is passing through a chromatograph column into the detector. Both the sample loop and column are in a constant temperature oven.

Six minutes later the vacuum pump is switched off, the valve closes, and the carrier gas sweeps the gas sample into the packed column. The column separates the various sulfur compounds and admits them one by one into the detector. The detector (plus associated electronics) will give a peak on a strip-chart recorder for each sulfur compound passing through it. The area underneath a given peak is directly related to the concentration of that compound. Because the

peaks are so nearly triangular in shape, concentrations can be more conveniently related to peak heights.

While a sample is being analyzed, two ports on the six-way valve are closed to any gas flow. This permits a blow-back phase where compressed air is forced through the sample line, out the probe, and into the stack. This procedure not only helps to clean solid particles off the probe, but also blows any water--that may have condensed while the sample was being drawn--out of the sample line.

In addition, at the beginning of each cycle a solenoid valve opens and allows a small amount of electrolyte to flow by gravity into the detector. This ensures that a "fresh" electrolyte solution is always present.

1.3 Separation Chamber

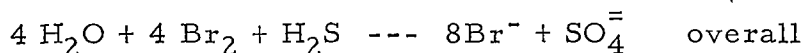
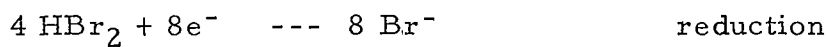
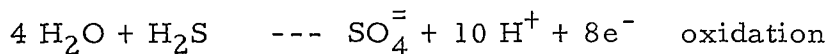
The technique used to separate the sulfur compounds is simply passing them through a packed chromatograph column. The column presently in use is a 1/4-inch teflon tube six feet long and packed with Porapak Q-S 100-120 mesh.

The packed column and a 10-ml sample loop are both enclosed in an insulated chamber which is maintained at a constant temperature. Keeping the sample loop at constant temperature assures a constant sample volume is always passed through the column.

1.4 Detection Cell

The detection cell is a small compact unit built of durable plexiglas. The plexiglas is transparent so liquid levels and bubbling action can be observed, and any malfunctions quickly spotted.

Sulfur gases separated by the packed column enter the detection cell through a porous glass plate or polyvinyl chloride rod. The primary electrochemical reactions which occur for H_2S are:



Similar reactions occur for SO_2 and CH_3SH . Thus the change in bromine concentration gives a quantitative measure of the

amount of sulfur compound entering the cell. As soon as the bromine ion concentration changes, the change is sensed by the sensor/reference pair of electrodes. This change is in reality a potential difference which is then an input to the amplifier of a microcoulometer. The amplifier almost instantaneously supplies a voltage to the generator counter/electrode pair. 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 a recorder chart. The area beneath the peak is directly related to the concentration of the sulfur compound which entered the cell.

The cell is selective to sulfur compounds only. It gives no recorder response to other gases, such as CO_2 and H_2O , that are always present in Kraft effluents.

Electrodes--except the reference--are sealed in a removable block in the bottom of the cell. When the block is removed, the electrodes are easily accessible for cleaning in case of contamination.

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Waste gas is vented out the side of the cell and carries with it any spent electrolyte that may overflow from the electrode chamber.

Section 2

Specifications

2.1 General:

Electrolyte	0.216 g KBr/liter + 1.8 ml Conc. H ₂ SO ₄ /liter consumption rate (approx. 200 cc/24 hr continuous operation)
Range	1, 2, 5, 10, 20, 50, 100, 500 Numbers are arbitrary but give indication of proportional increase in sensitivity. Higher numbers give larger peaks for same sample concentration. Selection made using rotary switch on front panel.
Carrier gas —	filtered compressed air-25 psi source needed
Flow rate regulator	200-250 cc/min 216 stainless micrometering valve
Tubing connections	1/8" zytel Swagelok brand
Internal tubing	1/8" polypropylene except for 1/4" teflon chromatograph column and sample loop
Power	115 volts AC, 60 cycle, 1800 watts max, <1000 average
Power Connection 1 AC outlet - 3 amp -	3 conductor cable, 3 prong plug can be used as external power source
Samples analyzed/hour	standard is 6 — any more is not recommended. Changes can be made to analyze fewer.
Size	
Height	24 in
Width	30 in
Depth	18 in
Weight	50 lbs (approx.)

2.2 Recorder:

continuous recording potentiometric;
10 mv range
floating input
5" chart paper
4 chart speeds — choose from many

2.3 Chromatograph Oven:

Temperature range	ambient to 200°C						
Column	1/4 in x 6 ft teflon tube packed with Parapak Q-S						
Sample loop	1/4" teflon tube — 10 ml volume						
Separation: lower limit — retention time (other packings will be available soon for separation in sub parts per million range)	<table><tbody><tr><td>H₂S</td><td>1 ppm — 1 1/2 min</td></tr><tr><td>SO₂</td><td>10 ppm — 3 min</td></tr><tr><td>CH₃SH</td><td>5 ppm — 4-5 min</td></tr></tbody></table>	H ₂ S	1 ppm — 1 1/2 min	SO ₂	10 ppm — 3 min	CH ₃ SH	5 ppm — 4-5 min
H ₂ S	1 ppm — 1 1/2 min						
SO ₂	10 ppm — 3 min						
CH ₃ SH	5 ppm — 4-5 min						
Temperature monitoring	Dial thermometer 0-200°C						

2.4 Detection Cell:

Lower limit (using 70 ml) sample	H ₂ S	0.08 ppm
	SO ₂	0.25 ppm
	CH ₃ SH	0.1 ppm

2.5 Options and Accessories:

- | | |
|------------------------|---|
| 1) Air manifold | 1 inlet 2 outlet ports
1 outlet filtered and dried
Both outlets regulatable |
| 2) Multistack sampler | for 2 or 3 stack sampling |
| 3) Gear sets | to change cycle time |
| 4) Larger sample loops | for increased sensitivity — should be used only when concentrations are below 100 ppm |

- 5) Stainless steel probe especially effective in stack gases with high solids content
- 6) Water trap sometimes needed for stacks with very high water content

Section 3 Installation and Operating Instructions

3.1 Installation

3.1a Installation of cell

- 1) Remove small panel door in front of instrument.
- 2) Place cell in recessed portion of styrofoam block in bottom of analyzer.
- 3) Connect tube from check valve to gas inlet port.
- 4) Connect tube coming through side of instrument to gas outlet port.
- 5) Connect tube from solenoid valve to electrolyte inlet port.
- 6) Open stopcock type valve on side of electrode block.
- 7) Connect electrical male connector to female outlet on cell.

3.1b Location

- 1) Instrument will work best and last longer if in an area where there are no large temperature changes. In winter it should not be used in areas exposed to temperatures below 30°F because electrolyte will freeze.
- 2) Sheltering it from dust and debris will increase its life expectancy.

3.1c Connections just prior to start-up (all lines should be inert plastics or stainless steel, e.g. polypropylene)

- 1) Connect a filtered and dried compressed air line to carrier gas port.
IMPORTANT: The carrier gas absolutely must be dried and filtered to ensure proper operation.
- 2) Connect unfiltered air line to compressed air port.
- 3) Connect sample line from stack probe to stack gas port.
- 4) Connect a line from vacuum pump (a rotating vane type is recommended; rubber diaphragm types are not adequate especially if the sample line is long) to vacuum port.
- 5) Connect electrolyte reservoir to electrolyte port. (Since the electrolyte feed is by gravity, an 8-liter Nalgene

carboy with its own spigot is recommended. NOTE: Under NO circumstances should any kind of metal valve be used to regulate the electrolyte flow.)

- 6) Manually depress plunger on solution solenoid inside instrument and allow electrolyte chamber of cell to fill. When chamber is almost full adjust electrolyte flow (using external plastic valve) so the level is moving so slowly it is just noticeable. Later adjustment might be necessary if it is obvious the electrolyte addition is too slow or too fast.
 - 7) Replace small panel door on front of instrument.
 - 8) Plug power cord into grounded 3 prong 115 volt AC outlet.
- Instrument is ready for operation.

3.2 Operation

3.2a Start-up

- 1) Turn RANGE switch to 2.
- 2) Turn MAIN POWER switch of instrument on.
- 3) Turn recorder power switch on and select desired chart speed.
- 4) Plug vacuum pump into proper electrical outlet on side of instrument. (It is important that the pump be plugged in here because the outlet is connected to the timer inside, and the pump is automatically shut off at periodic intervals.)
- 5) Open air valve on main air supply. Outlet pressure should not exceed 30 psig.
- 6) Observe bubbling action in the cell.
- 7) Adjust gas flow rate using micrometering valve on side of instrument while observing the bubbling action inside the cell.

Flow rate should be set so gas is bubbling quite vigorously. At the beginning of a cycle the liquid level should be $\frac{1}{8}$ " above bottom of reference electrode tip.

Subsequent adjustments can be made by observing retention times and shapes of peaks out of recorder. Refer to

"Specifications" for appropriate retention times*. If these do not apply a special supplement will be given with the instrument giving expected retention times. Retention times too long mean flow rate too slow. Retention times too short mean flow rate too high.

- 8) Allow instrument to operate 45-60 minutes before making further adjustments. This allows column oven to reach proper temperature — should be 90°C for Parapak Q-S column.

3.2b Adjustments after start up.

- 1) Check to see that oven temperature is $90^{\circ}\text{C} \pm 2^{\circ}\text{C}$. If not change set point on temperature controller. Refer to Maintenance section 4.2 g.
- 2) Observe peaks on recorder. If they are less than 50% of full scale deflection increase RANGE setting until peaks reach this value.
- 3) If a small peak appears when the solution solenoid is open electrolyte addition is too fast. Adjust valve on electrolyte reservoir.

* Retention time is defined as time interval between start of sample injection — a small spike appears on recorder when valve closes — and beginning of sample peak.

Section 4

Maintenance

4.1 Routine Maintenance

4.1a Every two or three days

- 1) Remove chart paper so take-up roll does not start binding.
- 2) Check amount of chart paper remaining.
- 3) Check ink level in recorder pen and replenish as necessary.

4.1b Weekly

- 1) Remove probe from stack and clean.
Times between cleanings will vary depending on type of probe and solids content of stack gas.
- 2) Check electrolyte level.
Replenish as necessary with solution containing 0.216 g KBr and 1.8 ml conc. H_2SO_4 /liter H_2O .
If consumption rate is over 300 cc/day, rate of addition is too fast. Close valve slightly on electrolyte reservoir.

4.2 Instrument Repair and Adjustment

4.2a Recorder

- 1) For malfunction of any kind consult Recorder manual.
- 2) If not operating at start up be sure it is plugged into receptacle inside instrument. Then check to see that its power switch is on.

4.2b Detection cell

A. Cleaning

1. Turn off both MAIN POWER switch and main air supply valve.
2. Remove small front panel of instrument.
3. Shut stopcock valve (on electrode block) off.
4. Disconnect all tubing and electrical connections from cell. Then remove cell.
5. To avoid breakage remove reference electrode from top of cell.

6. Disconnect electrical wires from cell stand to electrode block.
7. Remove electrode block from cell.
8. If no black coating is visible on the platinum wires, cleaning with an eyedropper and concentrated HNO_3 is generally sufficient. Rinsing immediately with distilled H_2O is imperative.
CAUTION: Avoid prolonged or repeated contact of the HNO_3 with the plexiglas block or the block will be deformed by the acid.
9. If any of the electrodes have a black coating they must be heated with a torch to burn the impurity off. The torch used burns natural gas and oxygen and has an ultrafine tip — flame is invisible unless room is dark.
EXTREME CARE must be used to keep from melting the electrode block or igniting the sealant around the platinum wires.
10. If the body of the cell is to be cleaned a mild detergent used with a soft brush and followed by a distilled water rinse is usually sufficient. Neither strong acids nor organic solvents should be used.
11. Reassemble cell and replace in the instrument.

B. Sealing leaks around electrodes

1. This is a tricky procedure and the ordering of a new electrode block is recommended.

C. Sealing leaks around threaded fittings

1. Wrap threads with teflon tape.

4.2c Changing chromatograph columns

- 1) Shut both MAIN POWER switch and main air supply valve off.
- 2) Open lid on top of instrument.
- 3) Remove column from reducing union (NOT at six-way sample valve) and bulkhead union connection.
- 4) Replace with new or false column and close lid.

4.2d Changing sample loops

- 1) Shut off MAIN POWER and main air supply valve.
- 2) Open lid on top of instrument.

- 3) Remove both ends of sample loop at the reducing union — not at six-way valve ports.
 - 4) Replace with new loop and close lid.
- 4.2e Replacing O-rings in 6-way sample valve.
- 1) Remove back cover of instrument (after shutting instrument off).
 - 2) Disconnect the three wires to the solenoid valve at lower terminal strip — position of the wires is important so take note (they should be color coded).
 - 3) Open lid on top of instrument.
 - 4) Remove all tubing from valve. Mark positions as you do so the connections will be made properly when the valve is installed.
 - 5) While holding the valve with one hand, unscrew the solenoid from the valve body. The stem containing the O-rings should remain attached to the solenoid.
 - 6) Pull valve body free of stem and remove all old O-rings.
 - 7) Clean valve body and stem if necessary.
 - 8) A special tool is required to put new O-rings on. One supplier is Varian Aerograph of Walnut Creek, California. Avoid getting perspiration or oil on the sealing edges of the O-rings when placing them on the shaft.
 - 9) Once the O-rings have been replaced, reassemble the valve by reversing the above procedures.
Warning: Each of three wires must be attached to the same place it was removed. Otherwise the valve will either not open, or the solenoid will burn out depending on which wires are improperly connected.
- 4.2f Repairing or cleaning compressed air solenoid valve.
- 1) Shut instrument off (very important here to keep solenoid from burning up).
 - 2) Remove back panel of instrument.
 - 3) Remove red cap from solenoid valve.
 - 4) Lift off solenoid coil.
 - 5) Remove plunger cover from valve body using a spanner wrench.

- 6) Clean valve body (steel wool usually works fine) or replace O-ring or replace rubber seat in plunger — whichever is necessary.
 - 7) Reassemble valve.
- 4.2g Changing set point on temperature controller.
- 1) Can be done with instrument running if care is exercised.
 - 2) Remove back panel on instrument.
 - 3) Loosen lock nut on set screw for adjustment.
 - 4) Turn set screw only a small fraction of a turn in the desired direction — direction for increase indicated on controller.
 - 5) Tighten lock nut but be careful not to move set screw.
 - 6) Wait about 20-30 minutes to see if desired temperature is attained — if not repeat steps 3-5 above.
- 4.2h Adjustment of BIAS on microcoulometer.
- The BIAS has been pre-set at 0.73 volts and should never be changed from this value. Before attempting to adjust it, make certain the mercury cell (section 4.2i) is delivering its rated voltage.
- If the BIAS must be adjusted proceed as follows (instrument on or off).
- 1) Remove back cover.
 - 2) Locate middle lead on BIAS potentiometer. Connect positive lead of a volt meter to this lead.
 - 3) Connect negative lead of voltmeter to any good ground inside the instrument — preferably on the coulometer circuit.
 - 4) Adjust BIAS pot until voltmeter reading is +0.73 volts.
- 4.2i Replacement of battery in BIAS circuit.
- 1) Turn instrument off.
 - 2) Remove back cover.
 - 3) Remove circuit board nearest the front of the instrument.
 - 4) Replace old mercury cell with new 1.34 volt cell.
 - 5) Replace circuit board.

- 4.2j Changing of cycle time.
(Times less than 10 minutes are NOT recommended if a chromatograph column is being used.)
- 1) Remove back cover.
 - 2) Locate timer motor.
 - 3) Loosen screw above motor which secures a plate holding two gears.
 - 4) Replace plate with another to give desired cycle time.
- 4.2k Fuse replacement.
- 1) Shut MAIN POWER switch off.
 - 2) Remove back panel.
 - 3) Locate fuse of faulty component (check chart inside instrument).
 - 4) Replace with fuse of identical rating.
- 4.2l Microcoulometer removal and repair.
- 1) Shut instrument off.
 - 2) Remove back cover.
 - 3) Remove all leads to terminal strip on coulometer and make notes of positions.
 - 4) Locate and remove the two bolts securing the coulometer to the cross brace just underneath the terminal strip.
 - 5) Coulometer unit should slide out freely.
 - 6) Refer to circuit diagram — isolate weak component — and replace or check for loose connections.
- 4.3m Replacement of internal sample-gas filter.
- 1) Remove back cover — instrument can still be operating.
 - 2) Locate 1 inch diameter plastic filter holder close to recorder.
 - 3) Note which end is attached to which line.
 - 4) Remove both lines.
 - 5) Disassemble filter by unscrewing it.
 - 6) Replace old filter with new glass fiber filter.

- 8) If a small wad of angel hair is available insert it in filter end without the screen support — this gives the filter paper support if a slight flow of air goes backwards through the filter at the beginning of a cycle.
- 9) Reassemble filter using teflon tape to seal threaded body.

Section 5

Calibration

5.1 Instrument Connections

Assuming the instrument is set up for stack sampling

—Refer to installation instructions.

- 1) Remove stack gas line from instrument.
- 2) Remove compressed air line from instrument and turn this air off if separate valve is present.
—NOT carrier gas line — just compressed air.
- 3) Attach outlet line of calibration device to stack gas port —leave compressed air port open with the line attached.
- 4) Begin calibration. Note: Only one calibration sample will be analyzed every 10 minutes — assuming the instrument operates on a ten minute cycle time.

5.2 Recommended Calibration Devices

- 1) Commercial spinning syringe with small fan as air source for spinning the syringe and rotameter for measurement of diluent air flow. For best results this calibration device should be operated in a sheltered area so dust will not plug delivery tip or prevent free rotation of syringe plunger in barrel.
- 2) Screw driven syringe.
Modified so screw driven shaft is rigidly attached to syringe plunger.
Again a rotameter to measure diluent air flow is needed.

Section 6

Trouble Shooting

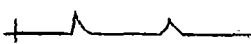
This section is shown in tabular form and lists many problems that might be encountered in operating the instrument. Listed with each problem is at least one possible cause and a subsequent remedy.

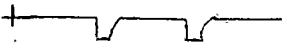
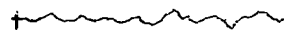
Under normal operating conditions small spikes will appear on the recorder at the beginning of each cycle because of the power drain on the system when the vacuum pump and sample valve are switched on. At higher range settings, a smaller spike will also appear when the pump is shut off and the valve closed.

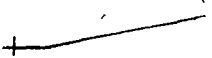
At high range settings (100 and above) some noise in the base-line is to be expected. The level will increase as the range setting increases. Excessive noise — more than 3% of full scale deflection at any setting — indicates problems. Read on —

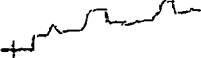
Symptom	Possible Cause	Checks and/or Remedy
1. No peaks injection ↓ + time →	1a. Leads from coulometer not plugged into recorder b. No carrier gas flow c. Microcoulometer not operating	1a. Replace banana plug leads in rear of recorder b. Check for bubbling action in cell 1) be sure gas inlet valve is connected to cell 2) open micrometering valve on side of instrument 3) open main air supply valve 4) check chromatograph oven for leaks or melted tubing* c. 1) check fuses (1 in instrument fuse panel and 1 on power supply) 2) be certain all circuit boards and choppers fit tightly in their connectors

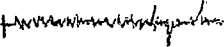
Symptom	Possible Cause	Checks and/or Remedy
		3) check all leads to terminal strip on coulometer board; be sure all are connected and tight
		4) remove microcoulometer (Paragraph 4.21)
	d. Timer has stopped	d. Observe small window on timer motor --if no moving disc, check timer fuse --if fuse or timer are faulty, replace
	e. Recorder defective	e. Check recorder manual
	f. Connections loose on 6-way sample valve	f. Tighten connections
	g. Detector cell not connected to coulometer	g. Plug male electrical connection into cell
	h. Stack probe is plugged	h. Clean as per manufacturer's instructions
	6-3	

Symptom	Possible Cause	Checks and/or Remedy
2. Poor sensitivity with normal retention time 	i. Vacuum pump not operating 2a. RANGE setting too low b. BIAS setting wrong c. Recorder not set at 10 mv range d. Carrier gas leak e. Stack probe is plugging f. Filter inside instrument is dirty 6-4	i. Check to see if it is plugged into side of instrument. Check fuse inside instrument and replace if necessary. Plug in some other outlet to see if it has frozen up. If so, repair as per manufacturer's instructions. 2a. Increase RANGE setting b. Reset BIAS to .73 volts (Paragraph 4.2h) c. Consult recorder instruction manual to reset d. Check connections--in chromatograph oven--at check valve --at entrance to cell e. Clean as per manufacturer's instructions f. Remove filter and replace with new filter paper (Paragraph 4.3m)

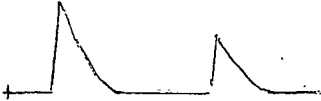
Symptom	Possible Cause	Checks and/or Remedy
3. Poor sensitivity with increased retention time 	3a. Carrier gas-flow rate too low b. Leaks downstream of sample valve	3a. Increase carrier gas flow using micrometering valve. If lines have become plugged, locate and remove obstruction or replace tubing. b. Locate and correct
4. Reversed peaks 	4a. Leads to recorder are backwards	4a. Reverse leads
5. Irregular baseline 	5a. Instrument not properly grounded b. Carrier gas leak c. Coulometer choppers not functioning properly d. Recorder defective	5a. Make sure instrument and recorder are connected to good earth ground b. Locate leak and correct* c. If they are seated well in sockets and still don't work, should be replaced. d. Check recorder manual

Symptom	Possible Cause	Checks and/or Remedy
6. Baseline drift upward 	e. Oven temperature too low 6a. Detector has become contaminated b. Battery in BIAS circuit is weak c. Column contaminated d. Sample loop or instrument lines are dirty 6-6	e. If not set at 90°C for Q-S column change controller set point (Paragraph 4.2g). For other columns temperature setting will change; consult data sheet for column. 6a. Remove cell and clean (Paragraph 4.2b) b. Check battery in coulometer and replace if necessary (Paragraph 4.2i) c. Replace column--sometimes only the glass wool in end of column need be replaced d. Locate contamination and clean or replace tubing If lines are dirty beyond filter, filter inside instrument has failed--replace immediately. Replace or clean dirty lines

Symptom	Possible Cause	Checks and/or Remedy
7. Baseline stepping --does not return to zero, and peaks are flat-topped 	7a. Recorder gain and/or damping control im- properly set, b. Instrument improperly grounded	7a. Refer to recorder instruction manual b. Make sure instrument is con- nected to good earth ground
8. Baseline cannot be zeroed	8a. Detector has become contaminated b. Recorder defective c. Battery weak in coulometer d. Recorder zero not properly set e. No or low level electrolyte in cell	8a. Remove cell and clean (Paragraph 4.2b) Check instrument lines for contamination before re- inserting cell b. Refer to recorder instruction manual c. Check and replace if needed (Paragraph 4.2i) d. Refer to recorder instruction manual e. Fill cell with electrolyte and adjust electrolyte flow rate (Paragraph 3.2a, b)

Symptom	Probable Cause	Checks and/or Remedy
9. High background noise on <u>low</u> RANGE settings 	9a. Cell is becoming contaminated b. Electrolyte has impurities in it c. Carrier-gas flow rate too high--solution is not contacting reference electrode (particularly noticeable at end of cycle) d. Carrier-gas flow leak e. Bad ground connection	9a. Remove and rinse with distilled water. Contamination has not become serious enough to merit cleaning electrodes. Check tubing for obvious contamination. b. Drain electrolyte reservoir, clean, and fill with fresh electrolyte. Also drain electrolyte tubing. c. Reduce gas flow rate d. Locate leak and correct* e. Ensure all ground connections are tight and connected to good earth ground

6-8

Symptom	Probable Cause	Checks and/or Remedy
10. Fading peaks 	f. Connections are loose on terminal strip by coulometer	f. Check and tighten if necessary
	g. Defective recorder	g. Short input terminals--if noise persists, check recorder manual
	h. Electrolyte addition too slow or stopped--stopped if noise throughout cycle--too slow if just at end of cycle	h. Fill electrolyte reservoir or open valve slightly on electrolyte reservoir. Be sure solution solenoid is opening--check fuse first--if still inoperable check connections. Replace if valve still inoperable.
	10a. Gas flow rate too low	10a. Increase gas flow with micro-metering valve
11. Unresolved peaks	b. Column oven temperature too low	b. Change temperature control set point (Paragraph 4.2g)
	11a. Column oven temperature too high	11a. Lower column oven temperature (Paragraph 4.2g)

Symptom	Probable Cause	Checks and/or Remedy
	b. Column too short c. Gas flow rate too high d. Liquid phase has baked off column support material	b. Use longer column c. Lower gas flow rate using micrometering valve d. Replace column
12. Round topped peaks (usually happens only on low range settings) 	12a. Column and/or micro-microcoulometer saturated--sample size too large b. Recorder gain too low	12a. Reduce sample size b. Adjust recorder gain to proper setting; see recorder manual
13. Jagged peaks 	13a. Recorder pen sticking b. Microcoulometer choppers are defective--will also give irregular spikes on baseline	13a. Clean slide wire or bar as per manufacturer's instructions b. Replace choppers

Symptom	Probable Cause	Checks and/or Remedy
14. Water has collected in sample line--chromatogram not predictable	14a. Compressed air valve is sticking and preventing blowback b. Samples are being withdrawn too fast from stack c. Water content of gases is so high a condenser must be used by the probe	14a. Disassemble solenoid valve (Paragraph 4.2f) and clean or repair as necessary. Check fuse for solenoid valve. b. Adjust vacuum pump suction so sample drawing rate is slower c. Install some type of water trap and condensing coils if necessary

* Final Notes:

When checking the instrument for gas leaks, if all tubing connections were tight leaks may be occurring in either the six-way sample valve or compressed air valve.

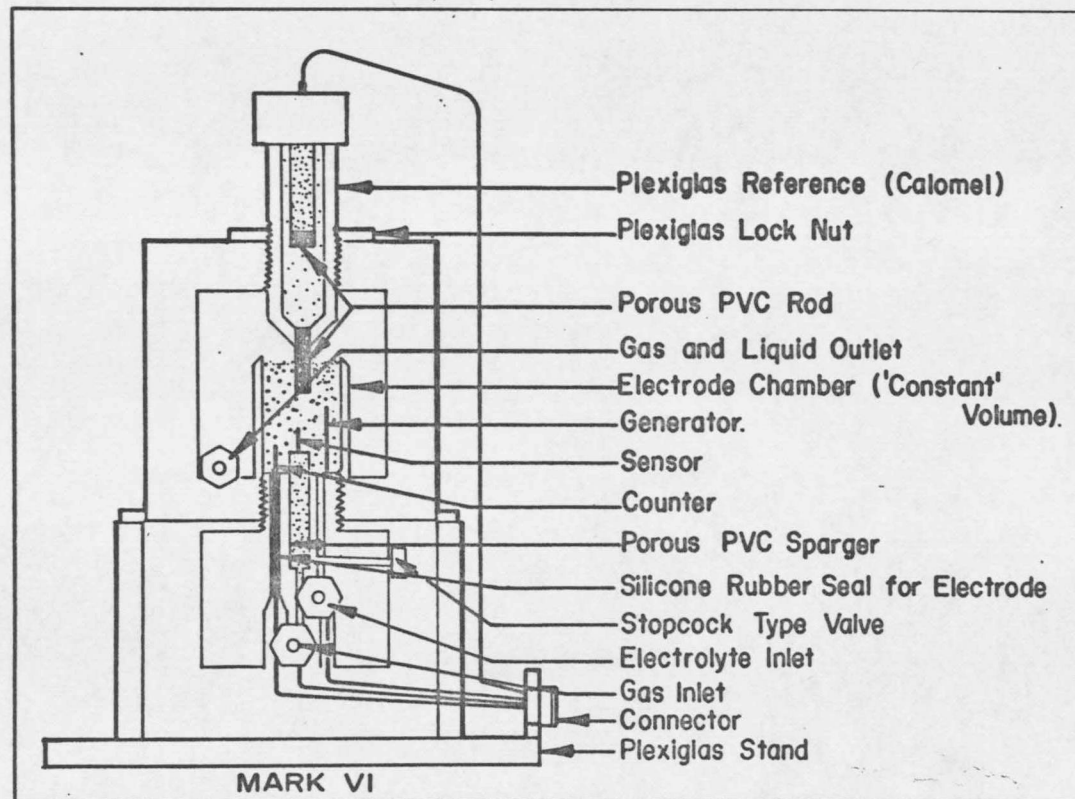
6.1 Checking 6-way Valve for Leaks

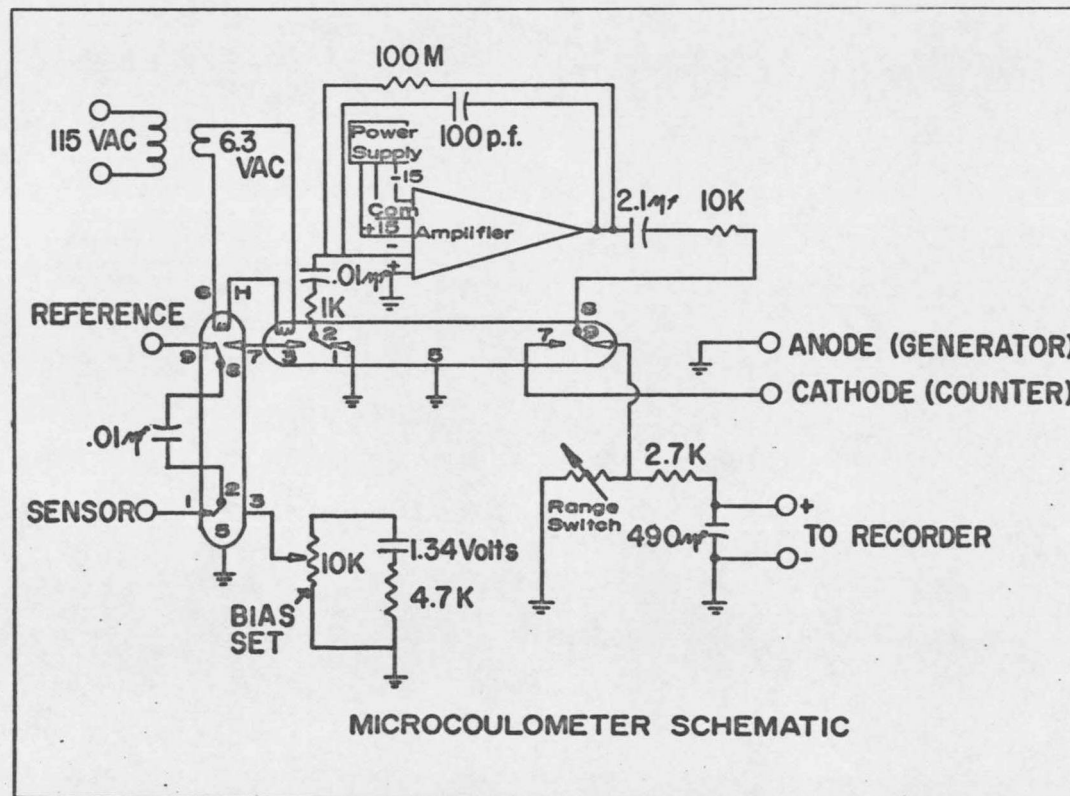
- 1) Leave instrument running, but shut recorder power off.
- 2) Unplug vacuum pump.
- 3) Disconnect sample loop from ports on 6-way valve.
- 4) If the valve stem is sticking above valve body, air should be flowing out of one of the ports.
- 5) Wait until valve opens and stem is about flush with valve body.
- 6) If any gas is coming out of the ports, then the O-rings inside are leaking.
- 7) Replace O-rings (Paragraph 4.2e).
- 8) If no leak is noticed here, connect sample loop to six-way valve.
- 9) Plug vacuum pump in.
- 10) Disconnect tubing on carrier gas port of 6-way valve.
- 11) Disconnect tubing on packed column port of 6-way valve.
- 12) Allow vacuum pump to switch on.
- 13) If any suction is noticed at either port, replace O-rings.
- 14) If no leaks were detected in either steps 6 or 13, assume valve is not leaking and connect tubing to all ports.

6.2 Checking Compressed Air Valve for Leaks

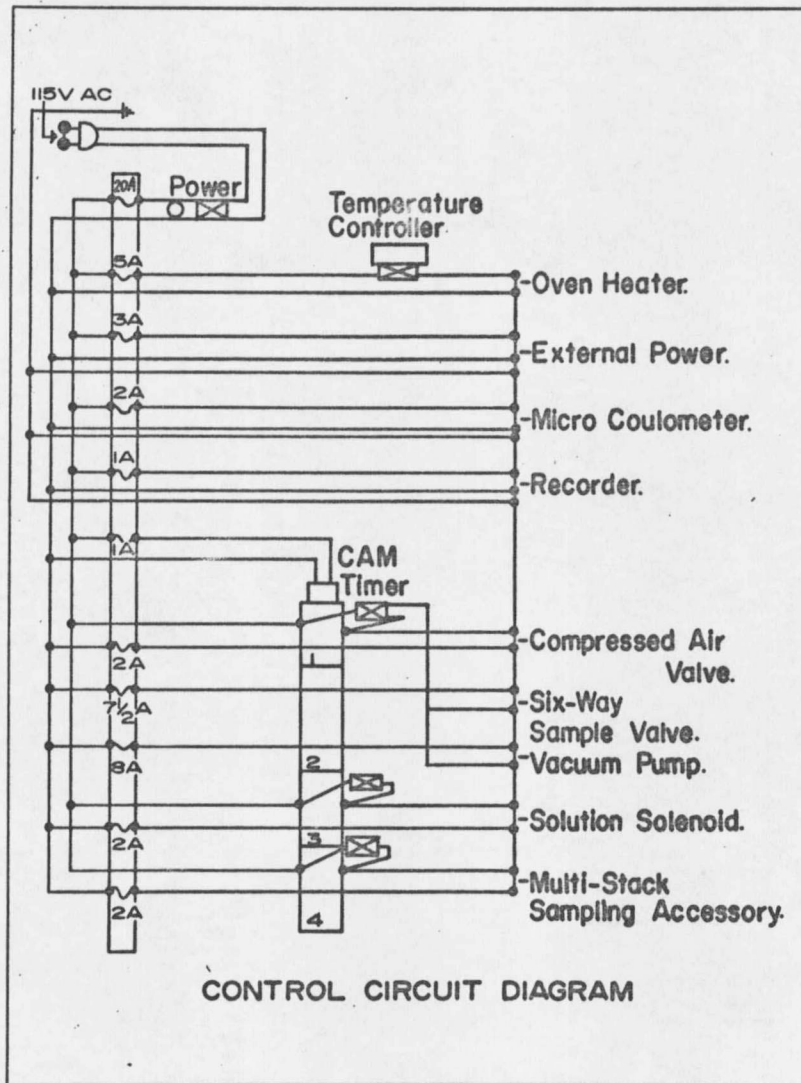
- 1) Leave instrument running.
- 2) Disconnect tubing from compressed air port on side of instrument.

- 3) When the vacuum pump is operating, check the compressed air port for any suction.
- 4) If any suction is felt, repair valve (Paragraph 4.2f).
- 5) If no suction is felt, connect compressed air line to its appropriate port.
- 6) Select a time when the vacuum pump has just begun to operate.
- 7) Disconnect tubing from vacuum port on side of instrument.
- 8) Check port for any air flow.
- 9) If there is air flow, the compressed air valve is leaking.
- 10) The leak may be caused by two things:
 - a) Pressure at compressed air port exceeds 25 psi.
If so, reduce pressure and check for leaks again.
 - b) It is dirty and sticking or rubber seat is worn out.
If so, repair it (Paragraph 4.2f).





MICROCOULOMETER SCHEMATIC



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PART II

Correlation of Sulfur Emissions with Kraft Mill Operating Conditions

ABSTRACT

PART II

A purely statistical technique (multiple linear regression) has been used to relate sulfur emissions from a Kraft paper mill to plant operating variables in the recovery area.

Sulfur emissions were recorded continuously either before the black liquor venturi or after the black liquor cyclone. Values of process variables were copied from log sheets maintained at the mill.

Of the two locations sampled, gases out of the black liquor cyclone are most indicative of what will be going out the stack. Temperature of air entering the furnace, liquor flow, primary air flow, venturi header pressure, and salt cake flow were all shown to have a direct effect on H_2S levels out the cyclone. On the other hand, concentrations were shown to vary inversely with secondary air flow, I. D. fan draft, and liquor solids content.

Some unreasonable correlations did occur, but could generally be attributed to questionable data. One or two unlikely, but possible, correlations were explained assuming unusual furnace conditions existed for part of the test period. All things considered, the conclusions were felt to be as reliable as the data that was used.

INTRODUCTION

Before any plant operating data can be meaningfully analyzed, a familiarity with the plant's process must be attained.

Kraft pulp is made by cooking wood chips in digesters with a cooking liquor ("white liquor") which contains the active chemicals, sodium hydroxide (NaOH) and sodium sulfide (Na_2S) (4). (A flow sheet for the process being described is shown in Figure 20.) This action separates lignins from the cellulose of wood. Lignins are the binder material which holds cellulose fibers of wood together. The cellulose, upon separation from the lignins, provides the pulp for manufacture of paper. The residual liquor (black liquor) containing spent chemicals and dissolved binder is drawn off primarily to permit reclamation of chemicals to make new cooking liquor, and also to provide fuel for the recovery unit. During the digesting process, chemicals in the "white liquor" undergo change. Sodium hydroxide becomes primarily sodium carbonate (NaCO_3), and the Na_2S forms sodium sulfate (Na_2SO_4) and organic compounds. For each ton of paper produced, black liquor remaining contains about 3000 pounds of solids of which 1300 pounds are reclaimable chemicals.

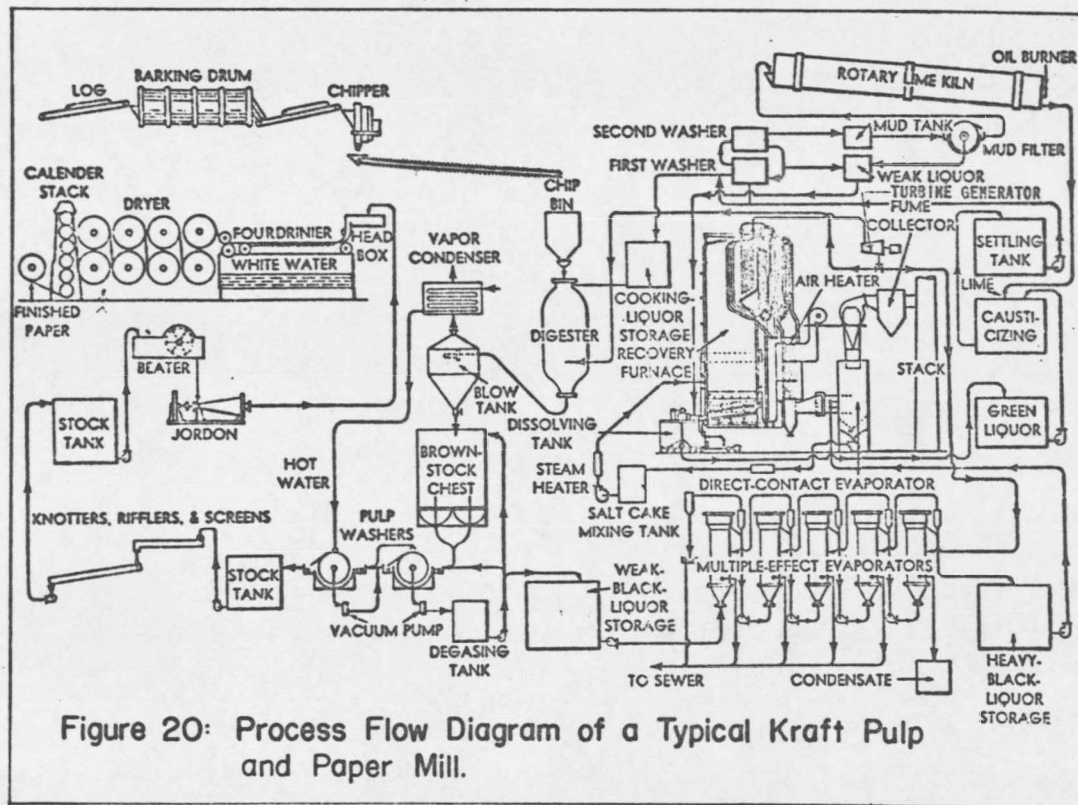


Figure 20: Process Flow Diagram of a Typical Kraft Pulp and Paper Mill.

Diluted black liquor or "weak liquor" (about 15% solids) leaving digesters or pulp washers must be concentrated to 65-70 percent solids before being fired in the furnace so it will sustain combustion. Concentration is accomplished by passing liquor through multiple-effect evaporators. In most plants, further concentration is obtained in a direct contact evaporator or venturi scrubber using sensible heat of the recovery unit flue gas to evaporate some of the water in the black liquor. Since there are unavoidable losses of chemicals in the pulp making process, chemical supply is replenished by addition of sodium sulfate (salt cake) to the liquor in the mixing tank. Black liquor is pumped through the line heater (where temperature is increased to that desired for burning) and then black liquor is sprayed into the furnace.

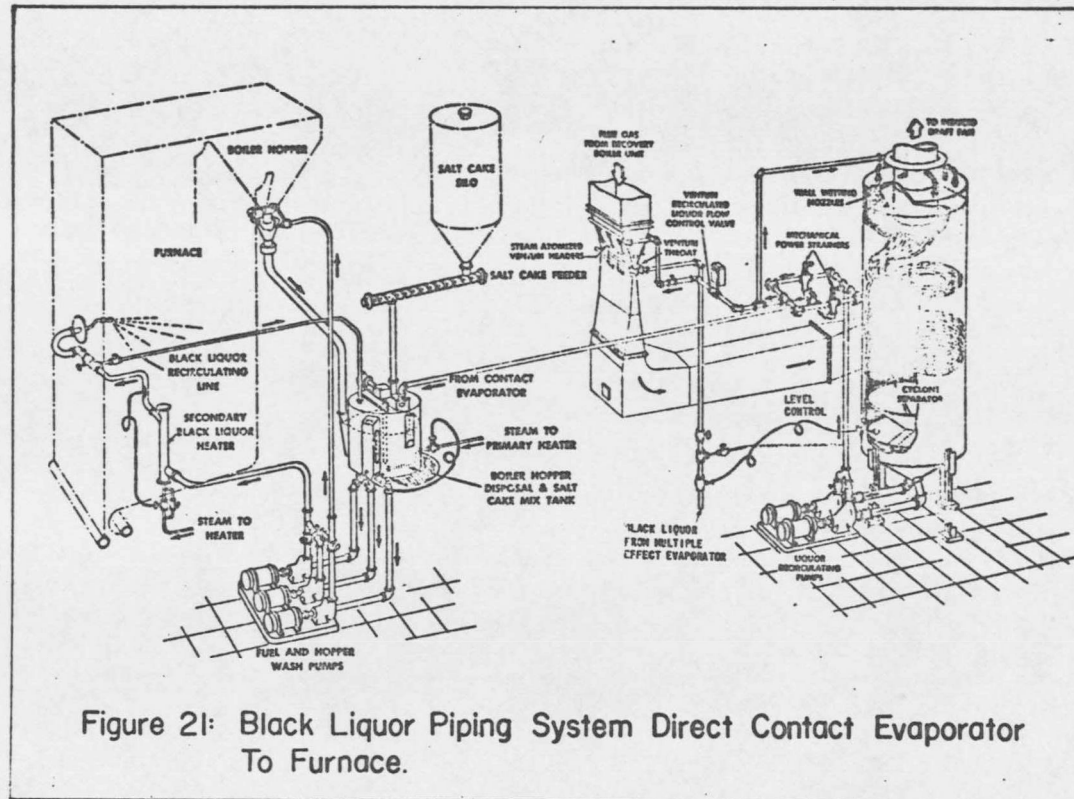
In the recovery furnace, solids are dehydrated, heat is obtained from combustion of liquor constituents dissolved from wood, and chemicals are smelted out. In the smelting process, sodium carbonate is unchanged, but sodium sulfate is reduced by hot carbon in the fuel bed to sodium sulfide.

Smelted chemicals flow into a smelt dissolving tank where they are treated with lime (calcium hydroxide-- Ca(OH)_2) to convert sodium carbonate to sodium hydroxide. This "white liquor", con-

taining both Na_2S and NaOH is now ready for re-use as cooking liquor in the digester. Calcium carbonate sludge reclaimed from the causticizing operation is reburned in a lime kiln to yield calcium oxide which can then be re-used to convert green liquor to white liquor.

In the past, the recovery furnace and its auxiliary equipment have been considered the major source of malodorous emissions (7). About 88% to 90% of the total reduced sulfur emissions in a typical pulp plant are generally attributed to the recovery furnace. Several methods have been suggested for reducing pollution from the recovery area (6). Most of these involve major equipment changes. Little work has been done to rigorously determine quantitatively the effects of operating variables on sulfur emissions, although some investigations have been reported (2, 7). Until recently, such investigations were nearly impossible because reliable instruments for continuous monitoring of sulfur emissions have been widely available for only about a decade.

An overall picture of where the recovery furnace fits into the pulping operation has just been given. In order to make worthwhile studies in the recovery area, a more detailed knowledge of its operation is needed. (Refer to Figure 21.)



Consider first the black liquor venturi evaporator-scrubber. Black liquor from the multiple-effect evaporators is not of sufficiently high solids content for stable combustion. Further concentration of liquor, or reduction of moisture content, is accomplished in the black liquor venturi evaporator-scrubber.

In addition to recovering a large percentage of chemicals in the flue gas, the venturi scrubber reduces exit gas temperature by evaporation of water from partially concentrated black liquor which is thereby concentrated (1). This evaporator-scrubber is based on the principle of impaction of the fume particles with finely atomized liquid droplets in a high velocity gas stream. Fine particles of chemicals entrained in the flue gas are wetted by finely atomized liquor, and these droplets are then separated from the gas stream by centrifugal force in the cyclone separator which follows the venturi. The venturi itself has a throat damper which provides a means of maintaining venturi throat differential at low loads by varying the effective flow area of the venturi throat.

In some plants the gases out the cyclone are further scrubbed with a brine scrubber to recover still more of the particulate matter in the stack gases.

After leaving the cyclone, the black liquor is pumped to the salt cake mixing tank to ensure that the solids content is high enough to sustain combustion. From here it is pumped through a secondary liquor line heater to an oscillating spray nozzle where it is sprayed onto the furnace walls for dehydration.

Liquor on furnace walls, which has been partially dehydrated in flight, is dried on the walls and falls onto a bed of smelt on the furnace floor.

Only about 60% of the total air requirement is supplied to the lower furnace (3). This is done because a reducing atmosphere is required to reduce sodium sulfate and other sodium sulfur compounds to sodium sulfide. Oxygen released in the reduction process provides part of the total oxygen required for burning combustible constituents of the char. Smelted char drains down the sloping furnace floor to a smelt spout through which it discharges into a dissolving tank. Hot gaseous products from partially completed combustion of char pass upward in the furnace, where they are mixed with additional air from secondary and tertiary air ports to complete combustion and to dry liquor on furnace walls. Gases then pass through convection sections of the unit where their sensible heat is used to form steam.

In the furnace itself, it has been reported (6) that odorous sulfur compounds at the furnace outlet can be reduced to negligible amounts if the furnace is operated within design capacity with enough excess air to provide about 3% O₂ in the flue gas, and if sufficient turbulence is obtained in the oxidation zone of the furnace. In order to maintain sufficient excess oxygen at the furnace outlet, the black liquor firing rate must be controlled at an optimum air/solids ratio. If the furnace becomes overloaded, high level sulfur emissions will result.

The primary source of sulfur emissions in the recovery operation is the black liquor venturi evaporator-scrubber. With unoxidized black liquor, carbon dioxide in the flue gas displaces hydrogen sulfide and methyl mercaptan from the black liquor, increasing odorous gas concentration at the evaporator outlet. Emissions of these gases from black liquor is reported (6) to be favored by high sulfide content in the liquor, low pH level, and low reduced sulfur content in the flue gas. Absorption of H₂S from the flue gas can take place if the liquor has been previously oxidized to low sulfide content, and is at high pH. Fully oxidized black liquor will absorb H₂S at all operating levels of pH.

EXPERIMENTAL PROCEDURE

Data Collection

The continuous chromatographic sulfur analyzer, whose development was described in Part I of this report, was used to record sulfur emissions from two different locations in the recovery area of Mill X*. The two sampling points were (see Figure 21): Point 1-- just before the black liquor venturi, and Point 2-- out the top of the cyclone separator. A third location Point 3-- beyond an additional brine scrubber (not shown in Figure 21) was available for sampling, but at the time of this writing no useful data had been obtained there. Samples were taken from the other two stacks at a rate of six samples per hour on a continuous basis.

Other plant data taken included operating conditions in the recovery area. This data was copied from the log sheets maintained at the mill and recorded on an hourly basis.

*Mill X is a Kraft mill whose location will not be disclosed because of a verbal secrecy agreement with the plant personnel. Likewise, no actual plant data will be shown for fear of misinterpretation by uninformed persons who may read this report. The "data" presented will be only the statistical parameters calculated from actual plant data.

Data Analysis

All of the data taken at the plant--emissions and log sheet for a five-week period--was transferred to punched cards and analyzed on a digital computer using multiple linear regression techniques (5). A brief description of the program as well as a complete listing are shown in the Appendix of this section.

RESEARCH OBJECTIVES

The purpose of this investigation was to apply statistical methods of data interpretation to relate operating conditions of a Kraft recovery unit to sulfur emissions. Not all of the process variables were expected to affect the emissions. Thus, the real goal was to determine which operating variables do have an effect and rank them as to the amount they will influence odorous emissions. It was felt that such a determination would prescribe a set of operating conditions which ought to minimize the amount of pollutants emitted from the recovery area.

A secondary objective was to keep all the conclusions directly in terms of the actual plant operating variables. Then no tedious calculations would be necessary to relate the conclusions to actual operating conditions.

RESULTS

The following operating variables have[#], solely by statistical methods, been found to affect sulfur emissions in the recovery area of a Kraft paper mill. (Only H_2S and SO_2 were studied because emissions of CH_3SH were recorded less than 5% of the total time period studied. Other organic sulfides were never detected.)

Before the black liquor venturi for SO_2

Total air flow	(-.60)*	(-.60)*
Salt cake flow	(+.67)	(+.67)
Liquor temp. at nozzle	(-.62)	
Green liquor alkalinity	(+.54)	
Nozzle pressure	(+.42)	
Water flow	(-.50)	
Tertiary air flow	(-.38)	
Liquor flow	(+.42)	
Liquor solids content	(+.34)	

Before the black liquor venturi for H_2S

Total air flow	(-.88)
Venturi header pressure	(-.82)
Tertiary air flow	(-.68)
Secondary air flow	(-1.07)
Nozzle pressure	(+.63)
I. D. fan draft	(-.68)
Primary air flow	(-.52)
Temp. of air into furnace	(+.33)
Cyclone exit gas temp.	(-.34)

[#]For an explanation of where the variables are measured, refer to the Discussion of Results section.

*The numbers in parentheses are from a normalized scale (range -1 to +1) based on the T-statistic. The numbers show the relative quantitative effect of any variable compared with other

After the black liquor cyclone for H_2S

Temp of air entering furnace	(+.90)
Liquor flow	(+.64)
Primary air flow	(+.58)
Secondary air flow	(-.56)
I. D. fan draft	(-.54)
Economizer exit gas temp.	(-.38)
Venturi header pressure	(+.50)
Liquor solids content	(-.48)
Salt cake flow	(+.35)
Steam temperature	(+.84)

variables in the list. Variables with values nearest ± 1 have the most effect on sulfur emissions. Negative numbers mean that as the value of the operating variable increases, sulfur emissions will decrease, and vice versa.

DISCUSSION OF RESULTS

Mathematical Technique Used

The mathematical technique used in this investigation is that of multiple linear regression (5). For this study it basically involves finding multipliers for an equation of the type

$$S = M_0 + M_1V_1 + M_2V_2 + \text{----} + M_nV_n$$

where

S = concentration of the sulfur gas

V_i = plant operating variable

M_i = multiplier for variable V_i *

One reason for using multiple linear regression is that it will give quantitative information about the variables being analyzed. Another is that the choice of variables analyzed can be quickly and easily changed.

Generally speaking, those variables with well defined multipliers are the ones which will have the greatest effect on the amount of sulfur emitted. When the value of the multiplier is given as, say 10, and the range* (+ or -) is less than 1.5, it is considered well

*In statistical terminology the multiplier is the estimated regression coefficient and the range is the estimated standard deviation of the estimated regression coefficient. The multipliers measure the expected change in S when the associated V changes by one unit, all other V 's remaining unchanged.

defined. On the other hand, if the value of the multiplier is 10 and the range (+ or -) is 8, this multiplier is not well defined, and chances are that the variable associated with that multiplier will not significantly affect emissions. In all cases, the value of a statistical parameter--called the t-statistic--should be checked to see if the particular variable in question really does have an effect on the sulfur emissions. The output from the computer program will show 1) the multiplier, 2) its range--given as a + or - value, and 3) the value of the t-statistic. For those not familiar with statistics, it is safe to say for results in this report, that any multiplier with an associated t-value whose magnitude is greater than 1.7 designates that the corresponding variable will have an effect on sulfur emissions at least 95% of the time. A negative value for the t-statistic means that an inverse relationship exists between the variable and the sulfur being emitted. The larger the t-value, the greater the effect of that variable.*

*This crude explanation of multiple linear regression has been a deliberate oversimplification to avoid undue confusion to those readers who have no background in statistics but are familiar with Kraft recovery units. Those interested in a more detailed mathematical discussion are referred to almost any textbook on statistics (5).

Cautions

Analysis of data using any statistical procedure must be done with some care. It requires a knowledge of both the nature of the data being taken and the statistical procedure being used. For example, it is quite possible that the amount of rain falling in Vietnam could statistically show a strong dependence on the amount of ice cream sold in the United States. However, no one would conclude that stopping the sale of ice cream here would decrease the rainfall in Vietnam. In a pulp mill the amount of SO_2 before the black liquor venturi might show a mathematical dependence on the brine flowing to the secondary scrubber beyond the venturi. But it would be most difficult to convince a recovery foreman that lowering the brine flow rate would reduce emissions before the black liquor venturi. A causal relationship simply does not exist in either of the above examples.

The point of the above discussion is that the variables to be used in a statistical analysis must be chosen carefully. Some simple quantitative examples will help show other problems which could arise from an unwise choice of variables.

Example 1

Consider the following set of data using Y as the dependent variable and X's as the independent ones.

<u>Y</u>	<u>X₁</u>	<u>X₂</u>
102	1	2
304	3	4
506	5	6
708	7	8

If both X_1 and X_2 are considered, the Y values fit the equation

$$Y = 100X_1 + 2X_2 + 0$$

If only X_1 is considered

$$Y = 101X_1 + 1$$

In this example, omitting X_2 from the equation does not greatly change the coefficient on X_1 because Y depends much more on X_1 than it does on X_2 .

Example 2

Again consider Y as the dependent and X's as the independent variables.

<u>Y</u>	<u>X₁</u>	<u>X₂</u>
8	1	2
18	3	4
28	5	6
38	7	8

$$\begin{array}{lll} \text{Using both } X_1 \text{ and } X_2: & Y = 2X_1 + 3X_2 + 0 \\ \text{Using only } X_1 & : Y = 5X_1 + 3 \\ \text{Using only } X_2 & : Y = 5X_2 - 2 \end{array}$$

This example shows that omission of a variable which actually does have a significant effect on Y will cause considerable change in the multiplier on the other variable.

In reality, when 10 or more variables are being analyzed, omission of one significant variable will not change multipliers of the other variables as seriously as indicated in Example 2. The primary point of the examples is to show that the multiplier on a given variable will change when the total number of variables being analyzed varies. This will happen even if all the variables omitted had little or no effect on the dependent variable.

A final caution is to avoid extrapolation of the conclusions from a regression analysis. For example, if H₂S emissions are shown to decrease when the tertiary air flow rate is increased from 10 to 15 arbitrary units, there is no guarantee that they would continue to decrease if the tertiary flow were increased to 20 arbitrary units.

Variables Considered

For simplicity in interpretation of results, only the variables shown on log sheets at Mill X were used for the regression analysis. A complete list is shown in Table III.

Comments About Data

All of the data used in this investigation were copied from either log sheets maintained at the mill or the sulfur analyzer recorder charts. No attempt was made to get emission data by operating the recovery unit at a set of pre-determined conditions. It was decided that there was enough variation occurring during 'normal' operation of the unit to give meaningful results. During the test period (4 weeks total) some upsets (such as furnace 'blackout' or other malfunction of the recovery train) occurred and were noted on the log sheets. Because no number can be assigned to such phenomenon, emission data taken during these upsets was excluded from the regression analysis.

An important assumption in development of regression equations is that the values of the independent variables are known 'exactly'. For nearly all temperature or static pressure measurements, this assumption is valid. However, for several of the flow measurements, the data recorded was an 'eyeball averaging' of a rapidly and continuously fluctuating meter reading. The least reliable readings were the primary, secondary, and tertiary air draft readings. Discussion with personnel at the mill revealed that the probes used to get the above draft readings were subject to frequent

Table III. Process Variables

Variable	Location	Units
1. Steam drum pressure	Convection section of furnace	psi
2. Steam temperature	Same	°F
3. Steam flow	Same	1000#/hr
4. Water pressure	Same	psi
5. Water flow	Same	1000#/hr
6. Primary air flow	Bottom of char bed in lower furnace area	1000#/hr
7. Secondary air flow	Top of char bed	1000#/hr
8. Tertiary air flow	Upper furnace section	1000#/hr
9. Total air flow	To entire furnace	1000#/hr
10. Air temperature	Before entering furn.	°F
11. Liquor solids content	Before the nozzle	wt %
12. Liquor temp at nozzle	Same	°F
13. Liquor flow	Through the nozzle	1000#/hr
14. Nozzle size	At nozzle	no units
15. Nozzle pressure	Same	psi
16. Salt cake flow	To salt cake mix tank	#/min
17. Green liquor alkalinity	Dissolving tank exit	#Na ₂ O/ft ³
18. Boiler exit gas temp	Out furn convec sec	°F
19. Cyclone exit gas temp	Out black liquor cyc	°F
20. Econ. exit gas temp	Just before black liquor venturi	°F
21. Primary air draft	Primary air duct	in. H ₂ O
22. Secondary air draft	Secondary air duct	in. H ₂ O
23. Tertiary air draft	Tertiary air duct	in. H ₂ O
24. Furnace draft	Across entire furnace	in. H ₂ O
25. Screen and super-heater draft	Boiler section of furnace	in. H ₂ O
26. Fan speed	Shaft of I. D. fan	RPM
27. Econ. diff. draft	Across Econ. in furn convection section	in. H ₂ O
28. Venturi diff. draft	Across black liq venturi	in. H ₂ O
29. Cyclone diff. draft	Across black liq cyclone	in. H ₂ O
30. I. D. fan draft	Between inlet and outlet	in. H ₂ O

Table III. Process Variables (continued)

<u>Variable</u>	<u>Location</u>	<u>Units</u>
31. Brine Cyclone draft	Across brine cyclone	in. H ₂ O
32. Brine pH	At brine scrubber	pH units
33. Brine density	Same	g/cc
34. Vibr. of fan shaft	At I. D. fan bearing	I. R. D.
35. Brine venturi press.	At brine scrubber	psi
36. Venturi header press.	At black liq venturi	psi
37. Cyc. header press.	Top black liq cyclone	psi
38. TDS in boiler water	Water in boiler	ppm

plugging so little faith could be put in these values. For these reasons, the draft readings were generally omitted from the regression analyses.

Another data item with only limited accuracy is the H₂S concentration before the black liquor venturi. Here, close to 20% of the recorder peaks had gone off scale and heights could only be approximated. However, over 95% of the H₂S readings after the black liquor cyclone were on scale and should be quite accurate.

Log sheet values for green liquor alkalinity, black liquor solids content, brine pH, brine density, and TDS boiler water were not recorded on an hourly basis but usually there were at least 4-6 values each day. Missing values for these variables were recorded as intermediate values between the two closest recorded points.

Computer Output

When the user specifies that all check codes are 'on', a series of data check messages will be printed out to indicate inconsistencies in the input data. When a new set of data is being analyzed, it is advisable to have all these codes 'on'. In rare instances some valid data will generate an error message. After all the 'bad' data is corrected, the check codes can be set to 'off' to suppress printing of the extraneous error messages.

Formal output generated by the regression program consists of the following items:

- 1) The date and time plus sulfur emission at designated stack.
- 2) A list of all the variables considered in a given regression analysis, their mean value, standard deviation, sum of squares, maximum and minimum.
- 3) A table of correlation coefficients for each variable with every other variable.
- 4) A table giving multipliers to fit an equation,

$$S = M_0 + M_1V_1 + M_2V_2 + \text{-----} + M_nV_n \text{ (page 125)}$$

the range (+ or -) of each multiplier, and a t-statistic to judge the significance of the multiplier.

- 5) Other statistical parameters R , R^2 , and F to check the overall correlation significance.

Items 1) and 2) are not shown in this report because they are actual plant operating conditions and presenting them would violate a prior secrecy agreement. Item 3) is omitted from this discussion because values for the correlation coefficients do not vary when the number of variables being analyzed is changed. They change only with the number of observations. After examining several sets and many subsets of data, it was decided that conclusions based on the t-statistic were much more reasonable.

Explanation of Results

The purpose of this statistical study has been twofold. The first objective was to discover which operating variables really do affect sulfur emissions. The second and more important goal was to rate the variables in order of their importance.

In an 'ideal' regression problem all independent variables (V) would individually affect the dependent one (S) the same, regardless of the values of the other variables (V's). Typically, however, when a large number of variables are considered, there is a correlation between the V's as well as between the V's and S. Then the effect of each V on S is underestimated. By reducing the number of independent variables analyzed a more indicative measure of their relative contributions can be obtained. The statistical methods

for choosing which variables to eliminate are quite time consuming, even with digital computers. In this study, variables were eliminated by examining the recovery operation and deciding which ones could not logically affect sulfur emissions. Highly questionable data was also eliminated from further consideration. All results and conclusions were based on the 17 or 22 variables believed most likely to be independent of one another and to affect production of odorous gases. Thus, no conclusions have been based on the results shown in Tables Va, VIa, and VIIa, since all 38 variables were examined in these tables.

The real value of the results of this study lies not so much in the fact that it has shown which variables affect sulfur emissions but that it also shows quantitatively the effect of each variable relative to the others.

The rest of this section will attempt to explain in terms of the actual recovery process the conclusions that have been reached by mathematical methods. Each variable shown to have an effect on sulfur emissions is listed and an explanation of why it should (or how it could) affect odorous emissions from the furnace is given.

Total Air Flow

More air to the furnace means more complete combustion and therefore less emissions.

I. D. Fan Draft

This is an indication of total air being supplied to the furnace, so the reason given above applies.

Primary Air Flow

As the primary air flow is increased, more combustion and less reduction takes place in the lower furnace. Therefore, less H_2S is seen before the black liquor venturi. Other studies (6) have shown that H_2S emissions from the venturi evaporator are favored by low concentration of reduced sulfur in the flue gas. This, then, explains the direct dependence of H_2S out the black liquor cyclone on primary air flow.

Secondary Air Flow

Ordinarily an increase in secondary air flow would mean better combustion and less sulfur emissions. This was found to be the case after the black liquor cyclone.

Yet, during another time period* H_2S levels before the black liquor venturi were found to increase as the secondary air flow increased. This apparent contradiction can only be explained if we assume some unusual conditions existed in the furnace during part of the time period involved. The H_2S levels could increase with secondary air if a very thick blanket of char had built up temporarily on the furnace walls. With an excess of char present, a reducing atmosphere could exist in more of the furnace than is normal. Then the increase in secondary air would produce more H_2S instead of decreasing its level. If this excess char existed for as much as 10% of the total test period, it could explain the indicated correlation.

Tertiary Air Flow

As the amount of tertiary air is increased, combustion efficiency in the upper portion of the furnace is increased and sulfur emissions should decrease.

*Data taken before the black liquor venturi was taken during one two-week period, while data after the black liquor cyclone was obtained at a different time, so furnace operating conditions had changed somewhat.

Salt Cake Flow

Increasing the salt cake added to the black liquor effectively raises the sulfidity of the liquor. When black liquor sulfidity is increased, both H_2S and SO_2 levels are expected to increase.

Liquor Temperature

When the liquor temperature at the nozzle is increased, the spray is finer and some carry-over of black liquor droplets into the upper or poor combustion zone of the furnace will occur. These tiny droplets are capable of absorbing SO_2 from the flue gas, so its concentration will decrease.

Nozzle Pressure and Liquor Flow

As the nozzle pressure is increased, more liquor is forced into the furnace. The more liquor that is burned, the more emissions that will result, especially if the furnace is operating close to or already above design capacity.

Steam Drum Pressure and Steam Temperature

An increase in either of these quantities is an indication that the furnace is being overloaded. This means a poor air/solids ratio, and an increase in malodorous emissions is to be expected.

Water Flow

Water flow to the boiler is not as sensitive an indicator to furnace overloading as either steam temperature or pressure, but in an extreme case it could be. This seems to be the only logical reason why SO₂ emissions would correlate with water flow.

Air Temperature

This temperature is measured just before the air enters the recovery furnace. As the air temperature is increased, it will strip more of the H₂S out of the black liquor drying on the walls and sulfur emissions should increase.

Liquor Solids Content

The liquor solids content is a direct measure of the sulfidity of the black liquor. This means that an increase in emissions before the venturi scrubber is to be anticipated. A word of caution here--if the furnace is operating slightly below design capacity, an increase in solids content would not necessarily raise emission levels. The emission increase occurs only if the furnace is operated at or above capacity.

Explaining how an increase in solids content would relate to a decrease in H₂S emissions out the black liquor cyclone is more complicated. First, recall that the solids content is measured just

before the nozzle. Then assume that the increase in solids content is due to the addition of more than the normal amount of salt cake. Next, assume that the excess salt cake had to be added because black liquor out the venturi evaporator-scrubber was of lower than usual solids content. Other things being normal, this would mean that the solids content of the liquor entering the venturi was lower than normal; consequently the low H_2S levels. Admittedly, this explanation depends on several assumptions, but they are not entirely unreasonable.

Venturi Header Pressure

This variable gives a direct indication of the flow rate of dilute black liquor to the venturi evaporator-scrubber. As the flow increases, there is more contact between flue gas and liquor. Consequently, more H_2S would be expected.

There is no obvious reason why H_2S levels before the black liquor venturi should show an inverse relationship to this header pressure. The erroneous correlation here can only be attributed to the fact that some 20% of the H_2S levels at this location were estimated values. The values had to be estimated because peaks on the sulfur analyzer had gone off scale.

Cyclone Exit Gas Temperature

This variable showed a strong effect only on H_2S before the black liquor venturi. Again no practical explanation can be offered, and this correlation is also considered a consequence of the questionable H_2S data.

Green Liquor Alkalinity

This is a measure of the sulfide and carbonate content of the liquor leaving the smelt tank after the recovery furnace. This green liquor is then used in the pulp digesting step before being returned as black liquor to the recovery furnace. It seems unlikely that the sulfidity here would bear any strong relationship to sulfur emissions. Recall, however, that values for this variable were recorded only 4 to 6 times daily. Other values were taken as intermediate between any two given points. Once again 'bad' data is considered to be the cause of the correlation.

Economizer Exit Gas Temperature

Hydrogen sulfide emissions after the black liquor cyclone were shown statistically to vary inversely with this variable. The temperature is measured out at the furnace but before the venturi scrubber. Recall that this gas then contacts the black liquor at the venturi and will strip out H_2S . Previous investigations (6) have shown

that the vapor pressure of H_2S in black liquor increases with increasing temperature. This means that if any correlation does exist, it should be direct. However, the experiments just mentioned also showed that this temperature effect was dwarfed by the effect of pH on this stripping action. Although the inverse correlation is meaningless, it might have arisen because of the temperature-pH interaction. Unfortunately, the pH of this liquor stream was not measured, so its effect here remains unknown. This argument is presented only as a possible explanation. Otherwise the conclusion would have to be taken as erroneous for inexplicable reasons.

Final Comments

During this investigation it became apparent that the mathematical conclusions are only as reliable as the data used to calculate them. The only 'questionable' correlations obtained could be attributed to either insufficient or unreliable data. Inadequate reliability was already mentioned as the justification for omitting part of the original 38 variables from most of the regression analyses.

It should be noted here that separate conclusions have been reached for each gas at each location. Some variables (salt cake flow, liquor temperature at nozzle) might decrease SO_2 emissions

but simultaneously increase the H_2S levels (or vice versa). Still others, (temperature of air into the furnace, primary air flow, secondary air flow, salt cake flow, venturi header pressure) might increase H_2S levels before the black liquor venturi, but decrease them out the black liquor cyclone (or vice versa). Thus, decisions will have to be made about which emissions are least desirable at which location. Then furnace variables can be adjusted--using the regression results as guidelines--to reduce emissions of the specified sulfur compound. The numerical values associated with each variable shown in the Results section indicate which operating parameters will have the most significant effect on reducing emissions. For example, reducing secondary air flow (+1.07)* would be a more effective way of reducing H_2S emissions before the black liquor venturi than would decreasing temperature of air into the furnace (+.38)*.

*Values taken from Results section, page 123.

CONCLUSIONS

This investigation has shown that multiple linear regression does indeed lead to reasonable conclusions about which plant variables do affect sulfur emissions. With few exceptions, the conclusions can logically be explained in terms of what is actually happening in the furnace. No special furnace operating conditions are needed to arrive at the conclusions. The conclusions are directly in terms of variables recorded on log sheets at the mill. Using conclusions from the regression program as guidelines, it should be possible to appreciably reduce emissions from the furnace area. It should be pointed out here that just the regression results shown in this report are not sufficient to specify a set of operating conditions. Other information calculated by the program, but considered confidential, is also needed to put a numerical value on the operating variable.

Using statistical methods to analyze plant data still requires a fair knowledge of what the operating variables actually measure, where they are measured, and how reliable the measurements are. This knowledge is necessary in order to make a reasonable choice of the variables to be studied. Unless a good choice is made, some extraneous and erroneous conclusions can arise.

RECOMMENDATIONS FOR FUTURE STUDY

Although the mathematical techniques have given seemingly logical conclusions about how to reduce sulfur emissions, their real value can be judged only by a plant site implementation of the recommendations. This mathematical approach has made no attempt to predict what will happen to steam production or chemical recovery if the furnace is operated so as to reduce sulfur emissions. Repeating, only an in-plant study can show the real worth of the results.

If further regression studies are made, some attempt should be made to look at a few variables not listed directly on the log sheets. These would include 1) pH of the black liquor at the furnace and/or at the venturi scrubber, 2) sulfidity of the black liquor entering the furnace, and 3) percent excess O_2 in the flue gas in the convection section of the furnace. Then conclusions could be more easily compared with experimental findings of other investigators (6, 7). Frequent checking of instrumentation (particularly the sulfur analyzer) during a second study would result in more of the data being reliable enough for analysis. In some cases, a slight change of instrumentation or at least instrumentation location (e. g., the draft probes) might improve the accuracy of the variables being measured.

APPENDIX

Program Description

A detailed explanation of the program will not be given here because much of the program is simply 'bookkeeping' to get the data arranged properly for multiple linear regression and/or for well labelled output. The program will handle emission data from either the Barton titrator (which gives a continuous line) or from a chromatographic analyzer (which gives discrete peaks for each sample). It is set up to handle a maximum of 38 plant operating variables, but will accept any number between 2 and 38.

The following data is read in by the computer:

- 1) Labels--alphabetic titles for the plant operating variables, sampling locations, and gases
- 2) Check codes--to suppress printing of certain error messages
- 3) Tolerances--logical bounds for the operating parameters--used to check for errors in punched data
- 4) Calibration data--peak heights and concentrations for various ranges of each sulfur gas
- 5) Log sheet data--values for all plant operating variables recorded on log sheets at the mill
- 6) Emission data--peak heights for each sulfur sample
- 7) Variables to be analyzed--only 1 dependent (always the concentration of sulfur compound) and up to 38 independent variables. Only the variables specified will be run through the regression part of the program.

The program performs the following functions:

- 1) Checks to see if the log sheet data is reasonable--error messages can be printed out, but bad data does not halt the operation.
- 2) Calculates equations for various calibration curves from the calibration data.
- 3) Calculates emission concentrations from peak heights using above calibration data
- 4) Matches up emissions with log sheet data--deficiencies ignored
- 5) Performs multiple linear regression only with variables specified
- 6) Looks for another set of variables--if none, stops.

A listing of the entire program is shown beginning on the next page.

Program Listing

The entire program--mainline and subroutines--is listed on the following pages.

Table IV. Program Listing

Table IV. Program Listing.

```

1:      REAL MAXI,MINI
2:      DIMENSION IND(38),INTX(38)
3:      DIMENSION R(50,50)
4:      DIMENSION PKHT(9),CONC(9),CURV(30,5) ,ITEM(5),C(3)
5:      COMMON A(24),DATU(550,50),LINE
6:      COMMON MAXI(39),MINI(39)
7:      COMMON /WORDS/ LABEL (42,5), NSTA(3,5), NGAS(6,5)
8:      COMMON /HILOW/ DMIN(38), DMAX(38)
9:      COMMON/REGV/ NR,NC,R,NV,NGBS
10:     NAME LIST DMIN,DMAX
11:     INTEGER CK1,CK2, CK3, DA, HR, GAS, RANGE
12:     INTEGER PKS
13:     MAX = 50
14:     NVT= 39
15:     LAST = 38
16:     NDUM = 46
17:     NLNE = 550
18: C READ LABELS FOR VARIABLES, STACKS, GASES
19:     DO 361 I=1,LAST
20:       361 READ(105,362) (LABEL(I,J),J=1,5 )
21:       DO 333 I=1,3
22:         333 READ (105,362) ( NSTA(I,J), J=1,5)
23:         DO 3333 I= 1,6
24:           3333 READ(105,362) (NGAS(I,J), J=1,5)
25:         362 FORMAT(5A4)
26: C FIND CHECK CODES 1= YES 0=NO
27:     READ (125,1000,ERR=991) CK1,CK3,CK4

```

```

28: 1000 FORMAT(4I3)
29: C READ TOLERANCES ON DATA ITEMS --- NAMELIST INPUT
30:     INPUT
31:     N=0
32: 218 READ(105,1004,END=152,ERR=881)GAS,RANGE,NPNTS,(PKHT(I),C0NC(I),
33:     1I=1,NPNTS)
34:     N=N+1
35: 1004 FORMAT(I1,I3,I2,18F4.0)
36: C GET EQNS FOR CALIBRATION DATA JUST READ IN
37:     CALL CURVE0 (PKHT,C0NC,C,NPNTS)
38:     CURV(N,1)=GAS
39:     CURV(N,2) = RANGE
40:     D0 247 K=3,5
41: 247 CURV(N,K)=C(K-2)
42:     G0 T0 218
43: 152 NT= N
44:     D0 243 I=1,NLNE
45:     D0 243 J=1,MAX
46: 243 DATU(I,J)=0.
47:     LINE = 0
48:     NCARD= 0
49:     D0 2000 I=1, LAST +1
50:     MAXI(I) = 0
51: 2000 MINI(I) = 10000
52:     G0 T0 6
53: 5 D0 55 I5 = 1, LAST
54:     IF(DATU(LINE,I5+3).GT.MAXI(I5)) MAXI(I5)=DATU(LINE,I5+3)
55:     IF(DATU(LINE,I5+3).LT.MINI(I5)) MINI(I5)=DATU(LINE,I5+3)
56: 55 CONTINUE
57: C READ LOG SHEET DATA AND CHECK TO SEE IF IT IS REASONABLE
58: 6 READ(105,1001,END=98,ERR=999) (A(I),I=1,24)
59: 1001 FORMAT(F1.0,3F2.0,F4.0,3F3.0,3(F3.0,F4.0),2(F4.0,F3.0),F4.0,
60: 1F2.0,F3.0,F4.0)2F3.0)

```

```

61:      NCARD=NCARD+1
62:      CK2 = A(1)
63:      IF(CK2.EQ.1.OR. CK2 .EQ. 2 ) GOTO 8
64:      WRITE(108,1002)NCARD
65:      GOTO 5
66: 1002 FORMAT(1H0,'ILLEGAL CARD NO. ON CARD',I5 )
67:      8 IF(CK1.NE.1) GO TO 9
68:      MO = A(2)
69:      DA = A(3)
70:      HR = A(4)
71:      CALL TIMECK( MO, DA, HR, CK2, NCARD)
72:      CALL DLOGCK (CK2)
73:      9 GO TO(10,20), CK2
74:      10 LINE = LINE +1
75:      DO 19 ID = 1,23
76:      19 DATU (LINE,ID)= A(ID+1)
77:      GO TO 5
78:      20 DO 13 M=1,LINE
79:      13 IF (A(2).EQ.DATU(M,1).AND.A(3).EQ.DATU(M,2).AND. A(4).EQ.DATU(M,3)
80:      1) GO TO 30
81:      IF(CK1.NE. 1) GO TO 27
82:      WRITE(108, 1003) ( A(I), I=1,24)
83: 1003 FORMAT ('NO DATE MATCH FOR CARD',24 F5.0 )
84:      27 LINE =LINE-1
85:      GO TO 5
86: C READ RECORDER DATA, CALCULATE CENCS, MATCH UP WITH LOG DATA
87:      30 LINE2 =M
88:      DO 29 ID = 1,18
89:      29 DATU(LINE2,ID+23) = A(ID+4)
90:      GO TO 5

```

```

91:      98 NC=0
92:      99 READ (105,1007, END= 599, ERR=998 ) (A(I), I= 1,20 )
93:      NC=NC+1
94: 1007 FORMAT( 20F4.0 )
95:      IF( A(1)) 400,401,401
96: 400 LOC= A(2)
97:      PKS =0
98:      GAS= A(3)
99:      XGAS= A(3)
100:      RANGE =A(4)
101:      XRAN = A(4)
102:      XM0 =A(5)
103:      DAY =A(6)
104:      XHR =A(7)
105:      N0STA=A(8)
106:      GO TO 99
107: 401 L=0
108:      DO 302 N=1,NT
109: 302 IF(XGAS.EQ. CURV(N,1).AND.XRAN.EQ. CURV(N,2)) GO TO 399
110:      WRITE(108,1008) GAS,RANGE
111: 1008 FORMAT(1H0,'NO CALIBRATION DATA FOR GAS',I3,3X,
112: 1'RANGE',I4/'PEAK DATA IGNORED')
113: 303 READ(105,1007,END=599,ERR=998)(A(I),I=1,20)
114:      NC= NC+1
115:      IF(A(1).EQ. -1.) GO TO 400
116:      GO TO 303
117: 399 NCUR=N
118: 402 L = L+1
119:      IF (L -20 ) 403,403, 99
120: 403 IF (A(L).EQ. -99 ) GO TO 99
121:      PKS = PKS +1
122:      IF(PKS .GT.6/N0STA)PKS = 1

```

```

123:      CON = 0
124:      DO 404 J= 1,3
125:      K= 4-J
126:      404 CON = CON *A(L) + CURV(NCUR,K+2)
127:      IF(A(L).GT.110.AND.CK4.EQ.1)WRITE(108,2003)XMO, DAY, XHR, (NGAS(GAS,
128:      1 N5),N5=1,5), (NSTA(LBC,N5),N5=1,5) ,CON
129:      2003 FORMAT(1H ,F4.0,'/',F4.0,'/',F4.0,' ' PEAK OFF SCALE FOR ',5A4,2X,
130:      1 5A4,F12.2)
131:      IF (PKS.EQ.1 ) AVCON = 0.
132:      AVCON = AVCON + CON /6/NOSTA
133:      IF(PKS.NE.6/NOSTA) GO TO 402
134:      DO 512 J2 = 1,LINE
135:      512 IF(XMO.EQ.DATU(J2,1).AND. DATU(J2,2) .EQ. DAY .AND. XHR .EQ.
136:      1DATU( J2,3)) GO TO 409
137:      IF(CK1.NE.1) GO TO 4090
138:      WRITE (108,1010) XMO, DAY,XHR
139:      1010 FORMAT( 1H0'NO LOG SHEET FOR EMISSION DATA ON' F4.0,'/',F4.0,'/',
140:      1F4.0 )
141:      GO TO 4090
142:      409 IF(DATU(J2,MAX).NE.LBC.AND.DATU(J2,MAX).NE.0)GO TO 4009
143:      4008 DATU(J2,MAX-GAS) = AVCON
144:      DATU(J2,MAX) = LBC
145:      GO TO 4090
146:      4009 LINE = LINE+1
147:      DO 4007 I3=1, LAST
148:      4007 DATU(LINE, I3) = DATU(J2, I3)
149:      DATU(LINE, MAX-GAS) = AVCON
150:      DATU(LINE,MAX) =LBC
151:      4090 XHR = XHR+1
152:      IF(XHR -24) 402,402,408
153:      408 XHR =XHR-24

```

```

154:      DAY=DAY+1
155:      NDY=DAY
156:      NMN=XMO
157:      CALL DMCK(NDY,NMN)
158:      XMO=NMN
159:      DAY =NDY
160:      IF(XMO-12)402,402,411
161:  411  XMO = XMO-12
162:      GO TO 402
163:  599  ITEM(1) =1

164:      ITEM(2)=2
165:      ITEM(3)=3
166:      ITEM(4)=MAX
167:  C CHECK FR DUPLICATE DATES ON SAME STACK
168:      LINE1 = LINE-1
169:      DO 1005 LL=1,LINE1
170:      LL1 =LL+1
171:      DO 1005 LM=LL1,LINE
172:      DO 2220 IL= 1,4
173:  2220 IF(DATU(LL,ITEM(IL)).NE.DATU(LM,ITEM(IL)))GO TO 1005
174:      DO 2221 J=LAST,MAX
175:  2221 IF(DATU(LM,J).NE.0) DATU(LL,J)=DATU(LM,J)
176:      DO 2222 JJ=1,MAX
177:  2222 DATU(LM,JJ)=0
178:  1005 CONTINUE
179:  C ARRANGE DATA ACCORDING TO STACK
180:      CALL RANK(1,LINE,MAX)
181:      DO 276 I = 1,LINE
182:  276  IF (DATU( I,MAX ).EQ. 0) GO TO 277
183:      I = I-1
184:  277  NLINE =I
185:      IF(NLINE.EQ.LINE) GO TO 208

```

```

186:    206 DO 207 I=NLINE, LINE
187:        DO 207 J=1,MAX
188:    207 DATU(I,J) =0
189:        LINE=NLINE
190:    208 IF(CK3.NE.1) GO TO 726
191:        WRITE(108,1011)
192:    1011 FORMAT( 15X, 'CHECK ON DATA'/
193:        14X2HMO,4X2HDA,3X2HHR,4X5HSTACK,4X3HH2S,8X3HS92 ,15X8HBRINE PH )
194:        DO 1101 I=1,NLINE
195:    1101 WRITE(108,1012)DATU(I,1),DATU(I,2),DATU(I,3), DATU(I,50) ,
196:        1DATU( I,49), DATU(I,48)
197:        2,DATU(I,35)
198:    1012 FORMAT(4F6.0,3F11.2,20X, F9.2 )
199: C
200: C      CODES FOR DEPENDENT VARIABLES
201: C      IY = 49  =H2S              =NGAS 1
202: C      IY = 48  =SO2              =NGAS 2
203: C      IY = 47  =CH3SH            =NGAS 3
204: C      IY = 99  = H2S/SO2        =NGAS 4
205: C      IY = 98  = H2S/CH3SH      =NGAS 5
206: C      IY = 97  = S92/CH3SH     =NGAS 6
207: C
208:        KN=0
209:    726 DO 7755 IA= 1,NLINE
210:    7755 DATU( IA,NDUM) =0.
211:        IF(KN.EQ.0) GO TO 1
212:        DO 2 IA = 1,NLINE
213:        DO 2 J=1,KN
214:        2 DATU(IA, LAST +J+3) =0
215:        KN=0
216:        1 READ(105,727,END =51) IY,IN,(IND(IY), II= 1,IN)
217:    727 FORMAT (40I2)
218:        READ(105,727)   INX,(INTX(II), II =1,INX )

```

```

219:      CALL CHEK1(IND,IN,KN,LAST,MAX,NLINE, 8726)
220:      CALL CHEK1(INTX,INX,KN,LAST,MAX,NLINE,8726)
221: 7717 IF ( IY.LT.100 .AND. IY .GT.96 ) CALL RATIO(IY,NDUM,NLINE,MAX,NG,
222: 18777 )
223: 7727 FORMAT (1H0,' ILLEGAL   DEPENDENT VARIABLE ', I3)
224:      IF(IY.LT. 47.OR.IY.GT.49) GO TO 7737
225:      GO TO 7738
226: 7737 WRITE(108,7727) IY
227:      GO TO 726
228: 7738 NG=MAX-IY.
229:      DO 737  JL =1,NLINE
230:      IF (DATU(JL,IY).GT.MAXI(LAST+1))MAXI(LAST+1) =DATU(JL,IY)
231:      IF (DATU(JL,IY).LT.MINI(LAST+1)) MINI(LAST+1)= DATU(JL,IY)
232: 737 DATU(JL, NDUM) =DATU(JL,IY)
233: 777 L1=1
234: 728 CALL FNDLN(L1,L2,MAX)
235:      IF (L1.EQ.L2 ) GO TO 726
236:      CALL RANK (L1, L2,NDUM)
237:      CALL FND0 (L1,L2,L3,NDUM)
238:      IF (DATU(L3, NDUM)) 828,829,828
239: 828 N955 = L3-L1+1
240:      NS = DATU(L3,MAX)
241:      CALL REG (NDUM,NG,NS,IND,INTX,IN,INX, LAST ,L1,KN)
242:      NDUM = 46
243: 829 L1= L2+1
244:      IF(L1-NLINE) 728, 726, 726
245: C DIAGNOSTICS
246: 988 WRITE(108,1020) NCARD
247: 1020 FORMAT('BAD LOG DATA  BEFORE CARD',I5 )
248:      GO TO 5
249: 998 WRITE(108,1021) NC
250: 1021 FORMAT('BAD EMISSION DATA  ON CARD', I4 )
251:      GO TO 99

```

```

252: 991 WRITE (108,992)
253: 992 FORMAT('BAD CHECK CARD')
254: CK1=1
255: CK3=1
256: GOT0218
257: 881 WRITE( 108,882)
258: 882 FORMAT('BAD CALIBRATION DATA')
259: GO TO 218
260: 51 CALL EXIT
261: END

```

```

1: SUBROUTINE CHEK1(FAKE,FK,KN,LAST, MAX, NLINE,*)
2: INTEGER FAKE(38),FK
3: COMMON A(24),DATA(550,50),LINE
4: COMMON/WORDS/ LABEL(42,5), NSTA(3,5), NGAS(6,5)
5: DIMENSION NEND(5)
6: IF(FK.EQ. 0) RETURN
7: DO 9032 I= 1,FK
8: IF(FAKE(I) .GT. 46 .AND. FAKE(I) .LT. 50) GO TO 9033
9: IF (FAKE(I) .GT. 50) .GO TO 9934
10: GO TO 9032
11: C
12: C SPECIAL CASE---GAS CONC IS INDEPENDENT VARIABLE
13: 9033 KN=KN+1
14: NO1 =FAKE(I)
15: FAKE(I) =LAST +KN
16: DO 9031 J2=1,5
17: 9031 LABEL(FAKE(I),J2) =NGAS(MAX=NO1,J2)
18: NSTK = DATA(1,MAX)
19: IF(NSTK .LE. 1) GO TO 9130
20: L1 = 1

```

```

21:      L2 = NLINE
22:      DO 9036 MM= 1,NSTK
23:      CALL FNOLN( L1,L2,MAX )
24:      L1 = L2+1
25: 9036 NEND(MM+1) =L2
26:      NEND(1) =0
27:      NSTK1= NSTK -1
28:      DO 100 NK = 1,NSTK1
29:      KUO = NEND(NSTK-NK)
30:      KLO = KUO +1
31:      KU1 = NEND(NSTK -NK+1)
32:      KL1 = KU1 +1
33:      KU2 = NEND(NSTK-NK+2)
34:      DO 100 KA =KL1,KU2
35:      DO 100 KB= KLO,KU1
36:      IF( DATA(KA,1) .EQ. DATA(KB,1) .AND. DATA(KA,2).EQ. DATA(KB,2)
37:      1 .AND. DATA(KA,3) .EQ. DATA(KB,3)) DATA(KB,FAKE(I)+3)
38:      2 =DATA(KA,N01)
39:      100 CONTINUE
40: 9032 CONTINUE
41:      RETURN
42: 9130 WRITE(108,1002)
43: 1002 FORMAT( 1H0,'ONLY ONE STACK---NO CORRELATION POSSIBLE!')
44:      RETURN1
45: 9934 WRITE(108,1003)FAKE(I)
46: 1003 FORMAT( 1H0,' ILLEGAL INDEPENDENT VARIABLE', I4)
47:      RETURN1
48:      END

```

```

1:      SUBROUTINE FNDQ (L1,L2,L3,N)
2:      COMMON A(24),DATA(550,50),LINE
3:      DO 10 I = L1,L2
4:      10 IF (DATA(I,N) .EQ. 0 ) GO TO 20
5:      20 L3 = I-1
6:      IF (L3 .EQ. 0) L3=1
7:      RETURN
8:      END

```

```

1:      SUBROUTINE FNDLN(L1,LO,N)
2:      C FINDS LINE WHERE DATA POINT N CHANGES VALUE
3:      COMMON A(24),DATA(550,50),LINE
4:      L3 = LINE-1
5:      DO 20 I = L1,L3
6:      20 IF (DATA(I,N) .NE. DATA(I+1,N)) GO TO 30
7:      30 LO = I
8:      RETURN
9:      END

```

```

1:      SUBROUTINE CURVEQ (XCAL, YCAL, A, NPTS)
2:      C RETURNS COEFF ONLY FOR LEAST SQS FIT OF CALIB POINTS
3:      C SET UP FOR SECOND ORDER CURVE
4:      C MULTIPLE REGRESSION FOR UP TO 50 VARIABLES
5:      DIMENSION XMTX(3,4), A(3), YCAL(9), XCAL(9)
6:      NORDR = 2
7:      NROW = NORDR+1
8:      NCOL = NROW+1
9:      DO 10 I=1,NROW

```

```

10:      DO 10 J=1,NCOL
11:      10 XMTX(I,J)=0.
12:      DO 20 K= 1,NPTS
13:      VAL =1.0
14:      YVAL= YCAL(K)
15:      XVAL= XCAL(K)
16:      DO 30 I= 1,NROW
17:      XMTX(1,I) = XMTX(1,I)+ VAL
18:      XMTX(I,NCOL) = XMTX(I,NCOL) +YVAL
19:      VAL =VAL * XVAL
20:      30 YVAL = YVAL *XVAL
21:      DO 40 I= 2,NROW
22:      XMTX (I, NROW) = XMTX(I,NROW) +VAL
23:      40 VAL= VAL * XVAL
24:      20 CONTINUE
25:      IF(NORDR-1) 41,41, 51
26:      51 DO 50 I= 2, NORDR
27:      DO 50 J= 1,NORDR
28:      50 XMTX(I,J) = XMTX (I-1, J+1)
29:      41 DO 60 I=2,NROW
30:      DO 60 J=I,NCOL
31:      DO 60 K=2,I
32:      60 XMTX(I,J)= XMTX(I,J) - XMTX(K-1,I)*XMTX(K-1,J) /XMTX(K-1,K-1)
33:      A(NROW) = XMTX(NROW, NCOL ) /XMTX (NROW, NROW)
34:      DO 70 I= 2, NROW
35:      K=NCOL -I
36:      VAR = XMTX(K, NCOL)
37:      DO 80 J =2,I
38:      L= NROW +2 -J
39:      80 VAR = VAR - A(L) * XMTX (K,L)
40:      A(K) = VAR/ XMTX(K,K)

```

```

41:    70 CONTINUE
42:    RETURN
43:    END

```

```

1:    SUBROUTINE TIMECK (M,D,H,IC,N)
2:    C CHECKS FOR ILLEGAL TIME SPECIFICATION
3:    INTEGER D, H
4:    IF (M.LT.1 .OR. M.GT. 12) WRITE (108,100) D, H, N
5:    IF (D.LT.1 .OR. D.GT. 31) WRITE (108,200) M, H, N
6:    IF (H.LT.1 .OR. H.GT. 24) WRITE (108,300) M, D, N
7:    100 FORMAT('BAD MONTH FOR', I3, 'DAY', I3, 'HOUR---CARD', I5)
8:    200 FORMAT('BAD DAY FOR', I3, 'MONTH', I3, 'HOUR---CARD', I5)
9:    300 FORMAT('BAD HOUR FOR', I3, 'MONTH', I3, 'DAY---CARD', I5)
10:    RETURN
11:    END

```

```

1:    SUBROUTINE RATIO ( IY,NDUM,NLINE,MAX,NG, * )
2:    COMMON A(24),DATA(550,50),LINE
3:    NUM = IY/2
4:    NDEN = (IY+1) /2 +2
5:    NG = 2* MAX - IY + 3
6:    DO 10 I=1,NLINE
7:    IF (DATA(I,NUM).EQ.0 .OR. DATA(I,NDEN).EQ. 0) GO TO 10
8:    DATA(I,NDUM) = DATA(I,NUM) /DATA(I,NDEN)
9:    10 CONTINUE
10:    RETURN
11:    END

```

```

1:      SUBROUTINE 105050
2:      DIMENSION A(50,50), INT(50)
3:      COMMON /RE6V/N, M, A, LL, LLL
4:      DO 1 I=1,N
5:          1 INT(I)=I
6:          IW=1
7:          2 IF(IW-N) 101,5,101
8:      C      FIND THE LEAST I GREATER THAN OR EQUAL TO IW SUCH THAT A(I,IW)
9:      C      IS GREATER THAN OR EQUAL TO A(J,IW) FOR ALL J GREATER THAN
10:     C      OR EQUAL TO IW.
11:         101 I=IW
12:         K=IW+1
13:         DO 4 J=K,N
14:             IF(ABS (A(J,IW))-ABS (A(I,IW))) 4,4,3
15:             3 I=J
16:             4 CONTINUE
17:             IF(I-IW) 7,5,7
18:     C      INTERCHANGE ROWS
19:         7 DO 8 J=1,M
20:             Z=A(IW,J)
21:             A(IW,J)=A(I,J)
22:             8 A(I,J)=Z
23:             K=INT(IW)
24:             INT(IW)=INT(I)
25:             INT(I)=K
26:         5 IF(A(IW,IW)) 9,6,9
27:         6 PRINT 202
28:     202 FORMAT (18HMATRIX IS SINGULAR)
29:     RETURN
30:         9 Z=1.0/A(IW,IW)
31:         IF(IW-1) 13,13,10
32:     10 K=IW-1
33:     DO 11 I=1,K

```

```

34:      11 A(IW,I)=A(IW,I)*Z
35:      IF(N-IW)12,12,13
36:      12 IF(M-N)15,15,13
37:      13 K=IW+1
38:      DO 14 I=K,M
39:      14 A(IW,I)=A(IW,I)*Z
40:      15 IF(IW-N)16,23,23
41:      16 DO 22 I=K,N
42:      W=A(I,IW)
43:      IF(W) 17,22,17
44:      17 IF(IW-1)20,20,18
45:      18 JJ=IW-1
46:      DO 19 J=1,JJ
47:      19 A(I,J)=A(I,J)-W*A(IW,J)
48:      20 JJ=IW+1
49:      DO 21 J=JJ,M
50:      21 A(I,J)=A(I,J)-W*A(IW,J)
51:      A(I,IW)= -W*Z
52:      22 CONTINUE
53:      23 A(IW,IW)=Z
54:      IF (N-IW) 25,25,24
55:      24 IW=IW+1
56:      GO TO 2
57: C      BEGIN WORK ON UPPER OF DIAGONAL ELEMENTS
58:      25 DO 32 IW=2,N
59:      K=IW-1
60:      DO 32 I=1,K
61:      W=A(I,IW)
62:      IF(K) 26,32,26
63:      26 DO 27 J=1,K
64:      27 A(I,J)=A(I,J)-W*A(IW,J)
65:      IF(N-IW)29,28,29

```

```

66:      28 IF(M-N)29,31,29
67:      29 L=IW+1
68:      DO 30 J=L,M
69:      30 A(I,J)=A(I,J)-W*A(IW,J)
70:      31 A(I,IW)=-W*A(IW,IW)
71:      32 CONTINUE
72: C      IF ROWS WERE INTERCHANGED INTERCHANGE THE COLUMNS
73:      JJ=N-1
74:      DO 37 I=1,JJ
75:      IF(INT(I)-1) 33,37,33
76: C      FIND A J GREATER THAN I SO THAT INT(J)=I
77:      33 DO 34 J=I,N
78:      IF(INT(J)-I) 34,35,34
79:      34 CONTINUE
80: C      INTERCHANGE THE ITH AND JTH COLUMNS
81:      35 DO 36 K=1,N
82:      Z=A(K,I)
83:      A(K,I)=A(K,J)
84:      36 A(K,J)=Z
85:      INT(J)=INT(I)
86:      37 CONTINUE
87:      RETURN
88:      END

```

```

1:      SUBROUTINE DLOGCK (K)
2: C SEES IF DATA POINTS ARE REASONABLE
3:      COMMON A(24),DATA(550,50),LINE
4:      COMMON /HILOW/ DMIN(38),DMAX(38)
5:      GO TO(10,20), K
6:      10 DO 2 I=1,20

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7:      2 IF(A(I+4).LT.DMIN(I) .OR. A(I+4).GT. DMAX(I)) WRITE(108,100)
8:      1I,A(2), A(3), A(4)
9:      RETURN
10:     20 DO 4 I= 21,38
11:     4 IF(A(I-16).LT. DMIN(I) .OR. A(I-16) .GT. DMAX(I)) WRITE(108,100)
12:     1I,A(2), A(3), A(4)
13:     100 FORMAT (1H0'LOG SHEET ITEM NO',I3,'EXCEEDS LIMITS ON', F4.0,'/',
14:     1F4.0,'/', F4.0)
15:     RETURN
16:     END

```

```

1:      SUBROUTINE REG( IY,NG,NS,IND, INTX, IN, INX, LAST, L1,KN)
2:      REAL MINI,MAXI,MI,MA
3:      INTEGER S1,01, V1,S2,02, S3, 03,V3
4:      INTEGER SSW1
5:      DIMENSION IND(38),INTX(38)
6:      DIMENSION V(50),SV(50), SSV(50,50) , R(50,50), C (50), STD(50),
7:      1 VBAR(50),SS(50) , IU(49)
8:      DIMENSION MI(39),MA(39)
9:      COMMON A(24),DATA(550,50),LINE
10:     COMMON MAXI(39),MINI(39)
11:     COMMON /WORDS/ LABEL (42,5), NSTA(3,5), NGAS(6,5)
12:     COMMON/REGV/ NR,NC,R,NV,N0BS
13:     EQUIVALENCE (SS,SSV),(V,VBAR) , (C,STD) ,(SV,R)
14:     DATA S1,01,V1, S2,02,S3,03,V3 /'DUE ' , 'TO R','EG ' , 'ABOU',
15:     1'T R', ' ', 'TOTA' , 'L ' /
16:     N8= LAST-1
17:     L9= L1-1
18:     N9 =IY-2
19:     NV = IN + INX/2 +1

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```

20:      NX = NV -1
21:      IF ( NV.GT.50 ) GO TO 729
22:      DO 7 I= 1,NV
23:        SV(I) = 0.
24:        DO 7 J=I, NV
25:          7 SSV(I,J) =0.
26:        NC =0
27:        N0B2 =N0BS
28:        INDV = LAST +KN +3
29:        DO 700 K= 1,N0BS
30:          IF(DATA(K+L9,INDV).EQ.0) GO TO 699
31:          DO 701 I = 1, IN
32:            MA(I) = MAXI(IND(I))
33:            MI(I) = MINI(IND(I))
34:          701 V(I) = DATA( K+L9,3+IND(I))
35:          IF( INX .EQ.0) GO TO 703
36:          DO 702 I= 2, INX,2
37:            MA(IN+I/2)=MAXI(INTX(I-1))*MAXI(INTX(I))
38:            MI(IN+I/2)=MINI(INTX(I-1))*MINI(INTX(I))
39:          702 V(IN+ I/2 ) = DATA (K+L9,INTX(I-1)+3) * DATA(K+L9,3+INTX(I))
40:          703 V(NV) = DATA(K+L9,IY)
41:          MA(NV)= MAXI(LAST+1)
42:          MI(NV) =MINI(LAST+1)
43:          IF(NC ) 705,705,707
44:          705 DO 706 I= 1,NV
45:            706 C(I) = V(I)
46:            NC = 1
47:          707 DO 708 I=1,NV
48:            V(I) = V(I) -C(I)
49:          708 SV(I) =SV(I) + V(I)
50:          DO 709 I=1,NV
51:            DO 709 J=I,NV

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52: 709 SSV(I,J) = SSV(I,J) + V(I)* V(J)
53: GO TO 700
54: 699 N0B2 = N0B2-1
55: 700 CONTINUE
56: IF(N0B2 .LT. 3) GO TO 967
57: C ROW SUMS COMPLETE
58: WRITE(108,7000) NV, N0B2
59: 7000 FORMAT (1H1,'MULTIPLE REGRESSION WITH', I3,' VARIABLES AND' ,I5 ,
60: 1' OBSERVATIONS')
61: WRITE(108, 7100) (NSTA(NS,N4), N4 =1,5)
62: WRITE(108, 7200) (NGAS(NG,N4), N4 =1,4)
63: WRITE (108,363)
64: 363 FORMAT(1H0,'VARIABLES ASSOCIATED WITH CORRELATION COEFFICIENTS'//)
65: 365 FORMAT (1H , 'VAR', I3, ' = ', 5A4 )
66: DO 364 IZ =1, NX
67: IF( IZ-IN ) 3365, 3365, 3364
68: 3365 WRITE(108, 365) IZ, (LABEL(_IND(IZ),LL),LL=1,5)
69: GO TO 364
70: 3364 KKK = 2* (IZ -IN) -1
71: WRITE(108,365) IZ,(LABEL (INTX(KKK),LL), LL=1,5)
72: WRITE(108,3366) (LABEL(INTX(KKK+1),LL) , LL=1,5 )
73: 3366 FORMAT ( 9X, ' * ', 5A4 )
74: 364 CONTINUE
75: WRITE(108,3665) NV
76: 3665 FORMAT( 1H , 'VAR', I3, ' = CONC OF SULFUR GAS')
77: WRITE(108,7001)
78: 7001 FORMAT(1H0,2X1H1,8X 4HMEAN,7X, 13HST. DEVIATION , 5X8HVARIANCE ,
79: 13X14HSUM OF SQUARES ,4X,'MAXIMUM',7X,'MINIMUM')
80: 756 FN =N0B2
81: RN =1./FN

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82:      FN1 = N0B2-1
83:      RN1 = 1./FN1
84:      D0 757 I=1, NV
85:      SS(I) = SSV(I,I) - SV(I) * SV(I) * RN
86:      VBAR(I) = SV(I) * RN + C(I)
87:      VAR = SS(I) *RN1
88:      STD(I) = SQRTF(VAR)
89:      WRITE (108, 7003) I, VBAR(I), STD(I), VAR, SS(I),MA(I),MI(I)
90:      757 CONTINUE
91:      7003 FORMAT (1H , I3, 2X 6E15.8 )
92: C  COMPUTE CORRELATIONS AND STORE IN SSV ARRAY
93:      WRITE(108,7004)
94:      7004 FORMAT(1H0, 8H I J K, 4X 'CORRELATIONS OF VARIABLES I WITH VAR
95:      1IABLES J THROUGH K')
96:      7009 NR = NV-1
97:      D0 719 I =1,NR
98:      IP = I+1
99:      D0 716 J =IP, NV
100:      SCP = SSV(I,J) - SV(I)* SV(J) * RN
101:      716 SSV(I,J) = SCP /SQRTF(SS(I) * SS(J))
102:      KS =IP
103:      D0 719 K = IP, MV, 8
104:      KL = KS +7
105:      IF(KL -NV) 718,718,717
106:      717 KL = NV
107:      718 WRITE(108,7005 ) I,KS, KL, (SSV(I,J) , J=KS,KL )
108:      7005 FORMAT(1H , I2, 2I3, 8F11.6)
109:      719 KS =KL +1
110:      WRITE(108,7000) NV, N0B2
111:      WRITE(108,7100) (NSTA(NS,N4),N4=1,5)
112:      7100 FORMAT( 1H0,30X, 'RESULTS ',5A4)
113:      WRITE(108,7200) (NGAS(NG,N4), N4 =1,4)
114:      7200 FORMAT(1H ,35X, 'FOR GAS ',5A4 /)

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115: 721 IF(NX +1 = NV) 733,730, 729
116: 729 WRITE(108,728) NX
117: 728 FORMAT(1H0,'TOO MANY INDEPENDENT VARIABLES ',I3 )
118: RETURN
119: 730 J =1
120: IY=NV
121: DO732 I= 1,NV
122: IF( I- IY). 731,732,731
123: 731 IU(J) =I
124: J=J+ 1
125: 732 CONTINUE
126: 733 DO 738 J= 1,NX
127: IF ( IU(J) -IY) 734,736,737
128: 734 IR = IU(J)
129: R(1,J+1) = SSV(IR, IY)
130: R(J+1,1) = SSV(IR, IY)
131: GO TO 738
132: 736 WRITE (108,735) IY, J
133: 735 FORMAT( 1H0,'DEPENDENT AND INDEPENDENT VARIABLES ARE SAME',I3,I4,
134: 1/1H , 'PROBLEM IGNORED' )
135: RETURN
136: 737 IC = IU(J)
137: R(1,J+1) = SSV(IY,IC)
138: R(J+1,1) = SSV(IY,IC)
139: 738 CONTINUE
140: R(1,1)= 1.
141: K =NX -1
142: DO739 I= 1,K
143: IR = IU(I)
144: IP = I+1
145: R(IP,IP) =1
146: IF(NX-1) 899,899, 898

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147:      898 DO 739 J = IP, NX
148:          IC = IU(J)
149:          R(IP, J+1) = SSV(IP, IC)
150:          R(J+1, IP) = SSV(IR, IC)
151:      739 CONTINUE
152:      899 NR = NX + 1
153:          NC = NR
154:          R(NR, NR) = 1.
155:          CALL IV5050
156:          IF ( R (1,1)) 740, 740, 741
157:      740 I = 1
158:          GO TO 744
159:      741 R1 = R(1,1)
160:          CSQ = 1. - 1./R1
161:          CM = SQRT (CSQ)
162:          D = NOB2 - NX - 1
163:          SE = STD(IY) * SQRT((FN-1)/(D*R1))
164:          WRITE(108, 7611)
165:      7611 FORMAT(1H0, ' INDEPENDENT VARIABLE = CONC OF SULFUR GAS')
166:          WRITE(108, 766)
167:      766 FORMAT(1H, 25X, 'MULTIPLIER', 6X, 'RANGE (+OR-)', 3X, 'T-STATISTIC')
168:          BN = VBAR(IY)
169:          BC = -STD(IY)/R1
170:          DO 747 I = 2, NR
171:              J = IU(I-1)
172:              B = BC * R(1, I) / STD(J)
173:              IF (R(I, I)) 744, 744, 745
174:      744 WRITE(108, 743) I
175:      743 FORMAT(1H0, 'DIAGONAL ELEMENT', I2, ' IS NEGATIVE OR ZERO. PROBLEM IG
176:          1NORED')
177:          RETURN
178:      745 RP = - R (1, I) / SQRT(R(I, I) * R1)
179:          SB = B * SQRT(( 1 - RP * RP) / D) / RP

```

```

180:      T = B/ SB
181:      IF( J .GT. IN ) GO TO 7772
182:      WRITE(108,772) (LABEL(IND(J) , J4),J4=1,5),B,SB,T
183:      772 FORMAT(1H ,2X,5A4, 2E16.8, F10.2)
184:      GO TO 747
185:      7772 KK = 2*(J-IN)-1
186:      WRITE(108,772) (LABEL(INTX(KK), LL) ,LL =1,5),B,SB,T
187:      WRITE(108,7782)(LABEL(INTX(KK+1), LL ) ,LL=1,5)
188:      7782 FORMAT(1H , 1X,'* ' , 5A4 )
189:      747 BN = BN -B * VBAR(J)
190:      J=0
191:      WRITE (108,872) BN
192:      872 FORMAT (1H ,2X,'CONSTANT COEFF',6X,E16.8)
193:      WRITE(108,775) CM,CSQ,SE
194:      775 FORMAT(1H ,9X11HMULTIPLE R= F6.4,11H, R SQUARE=
195:      1F6.4,3X 16HST ERROR OF EST= E16.8)
196:      WRITE(108,776)
197:      776 FORMAT(1H ,2X6HSSOURCE,6X,2HDF, 8X2HSS, 14X2HMS, 13X1HF )
198:      SSR = CSQ * SS(IY)
199:      XN= NX
200:      RMS = SSR/XN
201:      SSA = SS(IY) - SSR
202:      AMS = SSA /D
203:      FR = RMS/AMS
204:      WRITE(108, 780) S1,01, V1, NX, SSR, RMS, FR

```

```

205: 780 FORMAT(1H , 2A4, A2, I6, 2E16.8, F10.2 )
206: K = NOB2 -1 -NX
207: WRITE(108,780) S2,02,V1, K, SSA, AMS
208: K = NOB2 -1
209: WRITE(108,780) S3, 03, V3, K, SS(IY)
210: GO TO 989
211: 967 WRITE (108,977)
212: 977 FORMAT(' NO OBSERVATIONS--NO REGRESSION ANALYSIS')
213: 989 RETURN
214: END

```

```

1: SUBROUTINE DMCK(ND, MO)
2: C CHECK DATE FOR MONTH CHANGE -WONT WORK ON LEAP YEAR
3: IF(ND .LE. 28) RETURN
4: IF(ND.GT.28 .AND. MO.EQ.2) GO TO 10
5: IF(ND.GT.30.AND.(MO.EQ.4.OR. MO.EQ.6 .OR. MO.EQ.9 .OR.MO.EQ.11))
6: GO TO 20
7: IF(ND .GT.31) GO TO 30
8: RETURN
9: 10 ND =ND-28
10: GO TO 40
11: 20 ND=ND-30
12: GO TO 40
13: 30 ND=ND-31
14: 40 MO=MO+1
15: RETURN
16: END

```

```

1:      SUBROUTINE RANK (L,LO, N)
2: C  SORTS DATA ACCORDING TO ITEM SPECIFIED BY N
3:      DIMENSION DUM(50)
4:      COMMON A(24),DATA(550,50),LINE
5:      L3 = LO -1
6:      IF( L.GT. L3)RETURN
7:      DO 800 K =L,L3
8:          L2 = K+1
9:          DO 800 J=L2,LO
10:             IF( DATA(K,N) .GE. DATA(J,N)) GO TO 800
11:             DO801 I= 1,50
12:                 DUM (I) = DATA (K,I)
13:                 DATA (K,I) = DATA (J,I)
14:             801 DATA (J,I) = DUM (I)
15:             800 CONTINUE
16:             RETURN
17:             END

```

Program Output

The output shown in the following tables is only a part of the output generated by the computer program just shown. The rest is, however, considered confidential and is omitted from this report.

Table V. Results Before the Black Liquor
Venturi for Gas SO₂

Table Va. For all 39 Variables.

MULTIPLE REGRESSION WITH 39 VARIABLES AND 121 OBSERVATIONS

RESULTS BEFORE B.LIQ. VENTRI
FOR GAS SO2

DEPENDENT VARIABLE = CONC OF SULFUR GAS			
	MULTIPLIER	RANGE (+OR-)	T-STATISTIC
STEAM DRUM PRESS	-.23562841E 01	.27854118E 01	-.85
STEAM TEMP--DEG F	.14969902E 01	.17743206E 01	.84
STEAM FLOW	.34905577E 01	.34330082E 01	1.02
WATER PRESS	-.13116875E 01	.13820391E 01	-.95
WATER FLOW	-.56904955E 01	.30950260E 01	-1.84
PRIM AIR FLOW	.44357872E 01	.98446293E 01	.45
SEC AIR FLOW	.70369549E 01	.98243246E 01	.72
TERT AIR FLOW	.45996151E 01	.15354144E 02	.30
TOTAL AIR FLOW	-.93155174E 01	.52124138E 01	-1.79
AIR TEMP	.26412964E 01	.38935308E 01	.68
LIQUOR SOLIDS CNTNT	.47148697E 02	.32134796E 02	1.47
LIQUOR TEMP AT NOZ	-.18828583E 02	.80633602E 01	-2.34
LIQUOR FLOW	.76379471E 01	.71400251E 01	1.07
NOZZLE SIZE	.00000000E 00	.00000000E 00	.00
NOZZLE PRESS	.18664948E 02	.28845062E 02	.65
SALT CAKE FLOW	.23473072E 01	.11117172E 01	2.11
GR LIQ ALKALINITY	.13396507E 03	.58743713E 02	2.28
BOILER EXIT GAS TEMP	.11477175E 01	.96319044E 00	1.19
CYC EXIT GAS TEMP	.25189028E 01	.86987782E 01	.29
ECON EXIT GAS TEMP	-.11049404E 01	.86026931E 00	-1.28
PRIM AIR--IN. H2O	.22405655E 02	.57202423E 02	.39
SEC AIR-IN. H2O	-.38490356E 02	.59723419E 02	-.64
TERT AIR-IN. H2O	.11272228E 02	.40134430E 02	.28

FURNACE DRAFT	.10411888E 02	.52140884E 02	.20
SCRN & S.H. DRAFT	-.12832442E 02	.16439317E 03	-.08
FAN R.P.M.	.12431564E 01	.83636218E 00	1.49
ECONOMIZER DIFF DRAFT	.31738739E 01	.70168638E 01	.45
VENTURI DIFF DRAFT	.13142641E 02	.19393219E 02	.68
CYCLONE DIFF DRAFT	.59075027E 02	.64498917E 02	.92
I.O. FAN DRAFT	.13938663E 02	.21415039E 02	.65
BRINE CYC DRAFT	-.61961746E 01	.10607262E 02	-.58
BRINE PH	.57490707E 02	.15256094E 03	.38
BRINE DENSITY	-.75570972E 03	.69218628E 03	-1.09
VIBRATION FAN BEARING	-.80497360E 01	.13798011E 02	-.58
BRINE VENTURI PRESS	-.18764740E 02	.22536682E 02	-.83
VENTURI HDR PRESS	-.61367025E 01	.85732889E 01	-.72
CYCLONE HDR PRESS	.14099243E 02	.26290146E 02	.54
TDS BOILER WATER	.13596606E 00	.18437016E 00	.74
CONSTANT COEFF	-.87612476E 03		

MULTIPLE R = .8725, R SQUARE = .7613 ST ERROR OF EST = .10608954E 03

SOURCE	DF	SS	MS	F
DUE TO REG	38	.29429940E 07	.77447187E 05	6.88
ABOUT REG	82	.92291000E 06	.11255000E 05	
TOTAL	120	.38659040E 07		

Table Vb. For 22 Selected Variables.

MULTIPLE REGRESSION WITH 22 VARIABLES AND 121 OBSERVATIONS

RESULTS BEFORE B.LIQ, VENTURI
FOR GAS SO2

DEPENDENT VARIABLE = CONC OF SULFUR GAS

	MULTIPLIER	RANGE (+OR-)	T-STATISTIC
STEAM DRUM PRESS	-.43186106E-01	.24016352E 01	-.02
STEAM TEMP--DEG F	-.88581276E 00	.12797050E 01	-.69
STEAM FLOW	.35088396E 01	.29879179E 01	1.17
WATER PRESS	-.11241370E 00	.11534996E 01	-.10
WATER FLOW	-.69486666E 01	.27749081E 01	-2.50
PRIM AIR FLOW	.99284124E 01	.61718798E 01	1.61
SEC AIR FLOW	.37032070E 01	.71518927E 01	.52
TERT AIR FLOW	-.67422113E 01	.11641673E 02	-.58
TOTAL AIR FLOW	-.83163424E 01	.27533150E 01	-3.02
AIR TEMP	.11896601E 01	.25024376E 01	.48
LIQUOR SOLIDS CNTNT	.41930252E 02	.24799515E 02	1.69
LIQUOR TEMP AT NOZ	-.19025192E 02	.64182425E 01	-2.96
LIQUOR FLOW	.99322529E 01	.57550230E 01	1.73
NOZZLE PRESS	.44300308E 02	.21998535E 02	2.01
SALT CAKE FLOW	.28567743E 01	.95919299E 00	2.98
GR LIQ ALKALINITY	.13627281E 03	.50557220E 02	2.70
BOILER EXIT GAS TEMP	.83721364E 00	.74133432E 00	1.13
CYC EXIT GAS TEMP	-.64130936E 01	.70643082E 01	-.91
ECON EXIT GAS TEMP	-.22417283E 00	.70112133E 00	-.32
I.D. FAN DRAFT	.10885938E 02	.17542725E 02	.62
VENTURI HDR PRESS	-.35510197E 01	.57362804E 01	-.62
CONSTANT COEFF	-.72022675E 02		

MULTIPLE R= .8513, R SQUARE= .7246 ST ERROR OF EST= .10369467E 03

SOURCE	DF	SS	MS	F
DUE TO REG	21	.28013970E 07	.13339981E 06	12.41
ABOUT REG	99	.10645070E 07	.10752594E 05	
TOTAL	120	.38659040E 07		

Table Vc. For 17 Selected Variables.

MULTIPLE REGRESSION WITH 17 VARIABLES AND 121 OBSERVATIONS

RESULTS BEFORE B.LIQ. VENTRI
FOR GAS SO2

DEPENDENT VARIABLE = CONC OF SULFUR GAS

	MULTIPLIER	RANGE (+OR-)	T-STATISTIC
PRIM AIR FLOW	.88941383E 01	.58988199E 01	1.51
SEC AIR FLOW	-.39549017E 01	.57192507E 01	-.69
TERT AIR FLOW	-.18233490E 02	.95988379E 01	-1.90
TOTAL AIR FLOW	-.51058083E 01	.29029026E 01	-1.76
AIR TEMP	-.42133164E 00	.22850666E 01	-.18
LIQUOR SOLIDS CNTNT	.26763580E 02	.22629013E 02	1.18
LIQUOR TEMP AT NOZ	-.18737488E 02	.60877724E 01	-3.08
LIQUOR FLOW	.11740944E 02	.55588665E 01	2.11
NOZZLE PRESS	.40708954E 02	.19466049E 02	2.09
SALT CAKE FLOW	.31303949E 01	.93666875E 00	3.34
GR LIQ ALKALINITY	.12777605E 03	.49533463E 02	2.58
BOILER EXIT GAS TEMP	.10005836E 01	.68823373E 00	1.45
ECEN EXIT GAS TEMP	-.64370763E 00	.68377793E 00	-.94
VENTURI DIFF DRAFT	.15358491E 02	.15987096E 02	.96
I.D. FAN DRAFT	-.41505604E 01	.16573959E 02	-.25
VENTURI HDR PRESS	-.61340763E 01	.52697859E 01	-1.17
CONSTANT COEFF	-.85084424E 03		
MULTIPLE R= .8399, R SQUARE= .7055 ST ERROR OF EST= .10462830E 03			
SOURCE	DF	SS	MS
DUE TO REG	16	.27274070E 07	.17046294E 06
ABOUT REG	104	.11384970E 07	.10947086E 05
TOTAL	120	.38659040E 07	

15.57

Table VI. Results Before Black Liquor Venturi
for Gas H_2S .

Table VIa. For all 39 Variables.

MULTIPLE REGRESSION WITH 39 VARIABLES AND 147 OBSERVATIONS

RESULTS BEFORE B.LIQ. VENTRI
FOR GAS H2S

DEPENDENT VARIABLE = CONC OF SULFUR GAS	MULTIPLIER	RANGE (+OR-)	T-STATISTIC
STEAM DRUM PRESS	.40381831E 00	.20450419E 00	1.97
STEAM TEMP--DEG F	.24103546E 00	.98677933E-01	2.44
STEAM FLOW	-.27701044E 00	.22741592E 00	-1.22
WATER PRESS	.13054198E 00	.11245894E 00	1.16
WATER FLOW	.34127760E 00	.18966967E 00	1.80
PRIM AIR FLOW	-.18765793E 01	.72527689E 00	-2.59
SEC AIR FLOW	.78343511E 00	.47926259E 00	1.63
TERT AIR FLOW	-.22124434E 01	.10847244E 01	-2.04
TOTAL AIR FLOW	-.36318332E 00	.33008879E 00	-1.10
AIR TEMP	-.24930906E 00	.20295602E 00	-1.23
LIQUOR SOLIDS CNTNT	.42658186E 01	.21204243E 01	2.01
LIQUOR TEMP AT NOZ	-.33886248E 00	.40564799E 00	-.84
LIQUOR FLOW	-.64582831E 00	.44348907E 00	-1.46
NOZZLE SIZE	.00000000E 00	.00000000E 00	.00
NOZZLE PRESS	.14541607E 01	.18944817E 01	.77
SALT CAKE FLOW	.15419167E-01	.69597244E-01	.22
GR LIQ ALKALINITY	-.68290625E 01	.38572521E 01	-1.77
BOILER EXIT GAS TEMP	-.16019183E 00	.60792621E-01	-2.64
CYC EXIT GAS TEMP	-.20407035E-02	.49258351E 00	-.00
ECON EXIT GAS TEMP	-.84688187E-01	.51649801E-01	-1.64
PRIM AIR--IN. H2O	-.54037390E 01	.38154793E 01	-1.42
SEC AIR-IN. H2O	.56615772E 01	.39403419E 01	1.44
TERT AIR-IN. H2O	-.22315464E 01	.24573469E 01	-.91

FURNACE DRAFT	.83449764E 01	.33376007E 01	2.50
SCRN & S.H. DRAFT	.27294540E 02	.10916997E 02	2.50
FAN R.P.M.	-.36501333E-01	.53282220E-01	-.69
ECONOMIZER DIFF DRAFT	-.73177314E 00	.45928782E 00	-1.59
VENTURI DIFF DRAFT	.14554882E 01	.12058506E 01	1.21
CYCLONE DIFF DRAFT	-.50576115E 01	.46195765E 01	-1.09
I.D. FAN DRAFT	-.41837378E 01	.14061089E 01	-2.98
BRINE CYC DRAFT	.11520777E 01	.61497605E 00	1.87
BRINE PH	.23057053E 02	.80012026E 01	2.88
BRINE DENSITY	-.13834249E 02	.38607071E 02	-.36
VIBRATION FAN BEARING	-.38645244E 00	.88696688E 00	-.44
BRINE VENTURI PRESS	.61415482E 01	.15053263E 01	4.08
VENTURI HDR PRESS	-.57419157E 00	.37215853E 00	-1.54
CYCLONE HDR PRESS	-.33574409E 01	.14145985E 01	-2.37
TDS BOILER WATER	-.98141059E-02	.96134394E-02	-1.02
CONSTANT COEFF	-.68423431E 02		

MULTIPLE R= .9382, R SQUARE= .8802 ST ERROR OF EST= .74625874E 01

SOURCE	DF	SS	MS	F
DUE TO REG	38	.44172762E 05	.11624409E 04	20.87
ABOUT REG	108	.60145508E 04	.55690277E 02	
TOTAL	146	.50187312E 05		

Table VIb. For 22 Selected Variables.

MULTIPLE REGRESSION WITH 22 VARIABLES AND 147 OBSERVATIONS

RESULTS BEFORE B.LIQ. VENTRI
FOR GAS H2S

DEPENDENT VARIABLE = CONC OF SULFUR GAS

	MULTIPLIER	RANGE (+OR-)	T-STATISTIC
STEAM DRUM PRESS	.39476764E 00	.24211550E 00	1.63
STEAM TEMP--DEG F	.14691383E 00	.10228479E 00	1.44
STEAM FLOW	-.13238728E-00	.27331918E 00	-.48
WATER PRESS	.54505028E-01	.12914771E 00	.42
WATER FLOW	.22065121E 00	.22329873E 00	.99
PRIM AIR FLOW	-.58446437E 00	.53134573E 00	-1.10
SEC AIR FLOW	.16430674E 01	.49690980E 00	3.31
TERT AIR FLOW	-.31783209E 01	.94362611E 00	-3.37
TOTAL AIR FLOW	-.10170517E 01	.23040181E 00	-4.41
AIR TEMP	.21576381E 00	.18921918E 00	1.14
LIQUOR SOLIDS CNTNT	.25585337E 01	.24212132E 01	1.06
LIQUOR TEMP AT NOZ	-.21134127E-01	.46149164E 00	-.05
LIQUOR FLOW	.72379965E 00	.50087231E 00	1.45
NOZZLE PRESS	.56392565E 01	.18006191E 01	3.13
SALT CAKE FLOW	-.10837168E 00	.79201102E-01	-1.37
GR LIQ ALKALINITY	-.49452276E 01	.44725513E 01	-1.11
BOILER EXIT GAS TEMP	.33766031E-01	.60472056E-01	.56
CYC EXIT GAS TEMP	-.94458449E 00	.54806077E 00	-1.72
ECON EXIT GAS TEMP	-.77979267E-01	.61521225E-01	-1.27
I.D. FAN DRAFT	-.38222742E 01	.14467258E 01	-2.64
VENTURI HDR PRESS	-.12853165E 01	.37965220E 00	-.3.39
CONSTANT COEFF	-.14865071E 03		

MULTIPLE R= .8722, R SQUARE= .7607 ST ERROR OF EST= .98026142E 01

SOURCE	DF	SS	MS	F
DUE TO REG	21	.38175887E 05	.18178992E 04	18.92
ABOUT REG	125	.12011426E 05	.96091400E 02	
TOTAL	146	.50187312E 05		

Table VIc. For 17 Selected Variables.

MULTIPLE REGRESSION WITH 17 VARIABLES AND 147 OBSERVATIONS

RESULTS BEFORE B.LIQ. VENTRI
FOR GAS H2S

DEPENDENT VARIABLE = CONC OF SULFUR GAS				
	MULTIPLIER	RANGE (+OR-)	T-STATISTIC	
PRIM AIR FLOW	+ .13184738E 01	.50944734E 00	-2.59	
SEC AIR FLOW	+ .22866039E 01	.42747819E 00	5.35	
TERT AIR FLOW	+ .28779535E 01	.85247171E 00	-3.38	
TOTAL AIR FLOW	+ .62854820E 00	.27690977E 00	-2.27	
AIR TEMP	+ .30505085E 00	.18715549E 00	1.63	
LIQUOR SOLIDS CNTNT	+ .32561283E 01	.22098331E 01	1.47	
LIQUOR TEMP AT NOZ	+ .57935345E 00	.43647027E 00	1.33	
LIQUOR FLOW	+ .53882313E 00	.46875185E 00	1.15	
NOZZLE PRESS	+ .51001139E 01	.16455173E 01	3.10	
SALT CAKE FLOW	+ .11250532E 00	.76825440E-01	-1.46	
GR LIQ ALKALINITY	+ .45500603E 01	.44511766E 01	-1.02	
BOILER EXIT GAS TEMP	+ .36415230E-01	.57431694E-01	.63	
ECON EXIT GAS TEMP	+ .45179646E-01	.59969436E-01	.75	
VENTURI DIFF DRAFT	+ .14080296E 01	.14209471E 01	.99	
I.D. FAN DRAFT	+ .45514469E 01	.13462191E 01	-3.38	
VENTURI HDR PRESS	+ .15762901E 01	.38360035E 00	-4.11	
CONSTANT COEFF	+ .13500143E 03			
MULTIPLE R = .8586, R SQUARE = .7371 ST ERROR OF EST = .10073484E 02				
SOURCE	DF	SS	MS	F
DUE TO REG	16	.36995535E 05	.23122209E 04	22.79
ABOUT REG	130	.13191777E 05	.10147520E 03	
TOTAL	146	.50187312E 05		

Table VII. Results After Black Liquor Cyclone for
Gas H_2S .

Table VIIa. For all 39 Variables.

MULTIPLE REGRESSION WITH 39 VARIABLES AND 111 OBSERVATIONS

RESULTS AFTER B.LIQ. CYCL
FOR GAS H2S

DEPENDENT VARIABLE = CONC OF SULFUR GAS	MULTIPLIER	RANGE (+BR=)	T-STATISTIC
STEAM DRUM PRESS	+.14446821E 01	.10778809E 01	+1.34
STEAM TEMP--DEG F	.43521824E 01	.12323532E 01	3.53
STEAM FLOW	+.31344146E 00	.17579899E 01	+.18
WATER PRESS	.81514511E 01	.51500015E 01	1.58
WATER FLOW	+.82125783E-01	.20258589E 01	+.04
PRIM AIR FLOW	.61794329E 01	.76642313E 01	.81
SEC AIR FLOW	+.16651093E 02	.88364592E 01	-1.88
TERT AIR FLOW	+.61933879E-01	.79407148E 01	+.01
TOTAL AIR FLOW	.25634279E 01	.19382696E 01	1.32
AIR TEMP	.41001110E 01	.31675186E 01	1.29
LIQUOR SOLIDS CNTNT	+.18623715E 03	.49916473E 02	+3.73
LIQUOR TEMP AT NSZ	.77410135E 01	.73895931E 01	1.05
LIQUOR FLOW	+.20642548E 01	.46139393E 01	+.45
NOZZLE SIZE	.97761078E 02	.43322571E 02	2.26
NOZZLE PRESS	.00000000E 00	.00000000E 00	.00
SALT CAKE FLOW	+.13697987E 01	.40174131E 01	+.34
GR LIQ ALKALINITY	.11626478E 02	.18360382E 02	.63
BOILER EXIT GAS TEMP	+.11653051E 01	.90394717E 00	-1.29
CYC EXIT GAS TEMP	+.16643848E 01	.35543146E 01	+.47
ECEN EXIT GAS TEMP	+.15585785E 01	.69610351E 00	-2.24
PRIM AIR-IN. H2O	.34535156E 02	.42043213E 02	.82
SEC AIR-IN. H2O	+.10753947E 03	.48483353E 02	-2.22
TERT AIR-IN. H2O	+.51922485E 02	.38282822E 02	-1.36

FURNACE DRAFT	.63322067E 02	.564703732E 02	1.12
SCRN & S.H. DRAFT	.15909419E 03	.18442618E 03	.86
FAN R.P.M.	-.12096405E 01	.60116512E 00	-2.01
ECONOMIZER DIFF DRAF	-.88461212E 02	.12699428E 03	-.70
VENTURI DIFF DRAFT	.13875473E 02	.19066833E 02	.73
CYCLONE DIFF DRAFT	-.42815613E 02	.29471344E 02	-1.45
I.D. FAN DRAFT	-.12662409E 02	.15946468E 02	-.79
BRINE CYC DRAFT	-.22861252E 02	.22262970E 02	-1.03
BRINE PH	.10859036E 03	.20649225E 03	.53
BRINE DENSITY	.11375393E 04	.56145728E 03	2.03
VIBRATION FAN BEARING	.24916702E 02	.13777013E 02	1.81
BRINE VENTURI PRESS	.14809677E 02	.23124588E 02	.64
VENTURI HDR PRESS	.12895914E 02	.41304283E 01	3.12
CYCLONE HDR PRESS	.14684935E 02	.26708069E 02	.55
TDS BOILER WATER	-.22287548E 00	.94369948E-01	-2.36
CONSTANT COEFF	-.12403479E 04		

MULTIPLE R= .9032, R SQUARE= .8158 ST ERROR OF EST= .70631180E 02

SOURCE	DF	SS	MS	F
DUE TO REG	38	.15906000E 07	.41857895E 05	8.39
ABOUT REG	72	.35919200E 06	.49887773E 04	
TOTAL	110	.19497920E 07		

Table VIIb. For 22 Selected Variables

MULTIPLE REGRESSION WITH 22 VARIABLES AND 111 OBSERVATIONS

RESULTS AFTER B.LIQ. CYCL
FOR GAS H2S

DEPENDENT VARIABLE = CONC OF SULFUR GAS

	MULTIPLIER	RANGE (+OR-)	T-STATISTIC
STEAM DRUM PRESS	-.12775068E 01	.11011534E 01	-1.16
STEAM TEMP--DEG F	.48169432E 01	.11463976E 01	4.20
STEAM FLOW	.24087608E 00	.16137981E 01	.15
WATER PRESS	.55733700E 01	.45174446E 01	1.23
WATER FLOW	.16446028E 01	.17742720E 01	.93
PRIM AIR FLOW	.14049057E 02	.54329071E 01	2.59
SEC AIR FLOW	-.17584457E 02	.65711040E 01	-2.68
TERT AIR FLOW	-.40706301E 01	.71620016E 01	-.57
TOTAL AIR FLOW	.15805733E 00	.17989511E 01	.09
AIR TEMP	.82465534E 01	.21107225E 01	3.91
LIQUOR SOLIDS CONTNT	-.90160278E 02	.38951050E 02	-2.31
LIQUOR TEMP AT NOZ	.20629797E 01	.52900219E 01	.39
LIQUOR FLOW	.47822809E 01	.20679646E 01	2.31
NOZZLE PRESS	.00000000E 00	.00000000E 00	.00
SALT CAKE FLOW	.46952181E 01	.29530945E 01	1.59
GR LIQ ALKALINITY	.15660522E 02	.18721237E 02	.84
BOILER EXIT GAS TEMP	-.13373680E 01	.88200885E 00	-1.52
CYC EXIT GAS TEMP	-.65421957E 00	.35551453E 01	-.18
ECON EXIT GAS TEMP	-.12895346E 01	.68422341E 00	-1.88
I.D. FAN DRAFT	-.21143997E 02	.10924782E 02	-1.94
VENTURI HDR PRESS	.82049608E 01	.32630033E 01	2.51
CONSTANT COEFF	-.37088164E 04		

MULTIPLE R= .8550, R SQUARE= .7311 ST ERROR OF EST= .76753906E 02

SOURCE	DF	SS	MS	F
DUE TO REG	21	.14254780E 07	.67879875E 05	11.52
ABOUT REG	89	.52431400E 06	.58911680E 04	
TOTAL	110	.19497920E 07		

Table VIIc. For 17 Selected Variables.

MULTIPLE REGRESSION WITH 17 VARIABLES AND 111 OBSERVATIONS

RESULTS AFTER B.LIQ. CYCL
FOR GAS H2S

DEPENDENT VARIABLE = CONC OF SULFUR GAS

	MULTIPLIER	RANGE (+OR-)	T-STATISTIC
PRIM AIR FLOW	.15905542E 02	.54161263E 01	2.94
SEC AIR FLOW	.19348907E 02	.68892393E 01	2.81
TERT AIR FLOW	.27481346E 01	.74356136E 01	1.37
TOTAL AIR FLOW	.54008782E 00	.18933048E 01	1.29
AIR TEMP	.96869516E 01	.21470833E 01	4.51
LIQUOR SOLIDS CNTNT	.71127777E 02	.40179901E 02	1.77
LIQUOR TEMP AT NOZ	.89224964E 00	.51735878E 01	1.17
LIQUOR FLOW	.65019941E 01	.20108757E 01	3.23
NOZZLE PRESS	.00000000E 00	.00000000E 00	1.00
SALT CAKE FLOW	.51842213E 01	.29840326E 01	1.74
GR LIQ ALKALINITY	.10340135E 02	.19642059E 02	1.53
BOILER EXIT GAS TEMP	.50903291E 00	.91167486E 00	1.56
ECON EXIT GAS TEMP	.13989906E 01	.72771949E 00	1.92
VENTURI DIFF DRAFT	.16160553E 02	.18824203E 02	1.86
I.D. FAN DRAFT	.31269485E 02	.11421211E 02	2.74
VENTURI HDR PRESS	.58541822E 01	.32986021E 01	1.77
CONSTANT COEFF	.20229543E 04		

MULTIPLE R = .8227, R SQUARE = .6769 ST ERROR OF EST = .81866898E 02

SOURCE	DF	SS	MS	F
DUE TO REG	16	.13197860E 07	.82486625E 05	12.31
ABOUT REG	94	.63000600E 06	.67021914E 04	
TOTAL	110	.19497920E 07		

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