



Air pollution abatement by process gas chromatography  
by Terrill Edward Applebury

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

A process gas chromatograph has been developed for the purpose of monitoring the effluent from a Kraft mill recovery furnace. The instrument will analyze in widely varying concentrations of H<sub>2</sub>S, SO<sub>2</sub>, CH<sub>3</sub>SH and higher order sulfur compounds. It is insensitive to the fixed gases and water vapor and performs its analysis in about ten minutes.

The instrument employs a bromine microcoulometric detection cell and is sensitive to H<sub>2</sub>S in as low a concentration as 0.1 ppm and CH<sub>3</sub>SH and SO<sub>2</sub> as low as 0.5 ppm. A central control panel has been built to allow operation from a position remote from the stack. Also included is a system which will allow computer evaluation of the data. It is even possible to have on-line evaluation by the computer.

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

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

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BY PROCESS GAS CHROMATOGRAPHY

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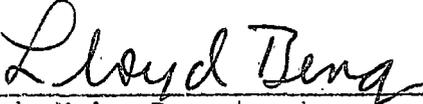
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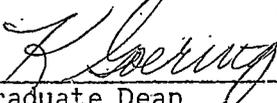
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Approved:

  
Head, Major Department

  
Chairman, Examining Committee

  
Graduate Dean

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## ABSTRACT

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

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

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

## INTRODUCTION

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

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

There are several pollution abatement techniques currently being used. Examples of these are: black liquor oxidation to convert  $\text{Na}_2\text{S}$  to  $\text{Na}_2\text{SO}_4$ , a more stable compound, prior to the direct contact evaporator and thus reduce the amount of sulfur gases formed, scrubbing the stack gases to remove odorous gases, and operating the recovery furnace under controlled conditions.

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

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

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

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

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

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

## RESEARCH OBJECTIVES

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

1. analyze for the concentration of  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_3\text{SH}$ , and other sulfur gases
2. insensitive to fixed gases and water vapor
3. withstand plant conditions
4. require a minimum of maintenance
5. perform automatic analyses in less than ten minutes
6. require a minimum of man hours for efficient operation

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

## SELECTION AND DEVELOPMENT OF DETECTOR

### SELECTION

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

TABLE I. EXPECTED CONCENTRATIONS

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

Adams (4) reported the following information on maximum sensitivity to H<sub>2</sub>S and CH<sub>3</sub>SH of various standard chromatograph detectors:

TABLE II. DETECTOR SENSITIVITY

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

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

Walther and Amberg (16) reported using a thermal conductivity detector sensitive to 10 ppm on all three sulfur gases. The same article, however, reported testing this chromatograph on a recovery furnace stack and finding both  $\text{CH}_3\text{SH}$  and  $\text{SO}_2$  in concentrations below minimum detectability at least part of the time. This, then, does not provide the ultimate answer.

For these reasons we decided to use a coulometric detector. Adams (2) reports sensitivity on this cell as low as 10 ppb on  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SH}$ , and 50 ppb on  $\text{SO}_2$ .

#### DEVELOPMENT

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

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

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

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

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

The cell theory is explained in the Dohrman operational manual (3). Very briefly, this theory can be explained as follows: The sulfur gases separated by the column enter the titration cell through the capillary tube inlet. The sulfur ions react with the  $\text{Br}_2$  in the electrolyte and change the concentration of the  $\text{Br}_2$  in proportion to their quantity. The ion imbalance is immediately sensed by the sensor reference pair of electrodes. The imbalance is the input signal to the microcoulometer's amplifier, which instantly supplies a balancing voltage to the generator electrodes. This balancing voltage generates titrant to restore the electrolyte to its original concentration. The

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

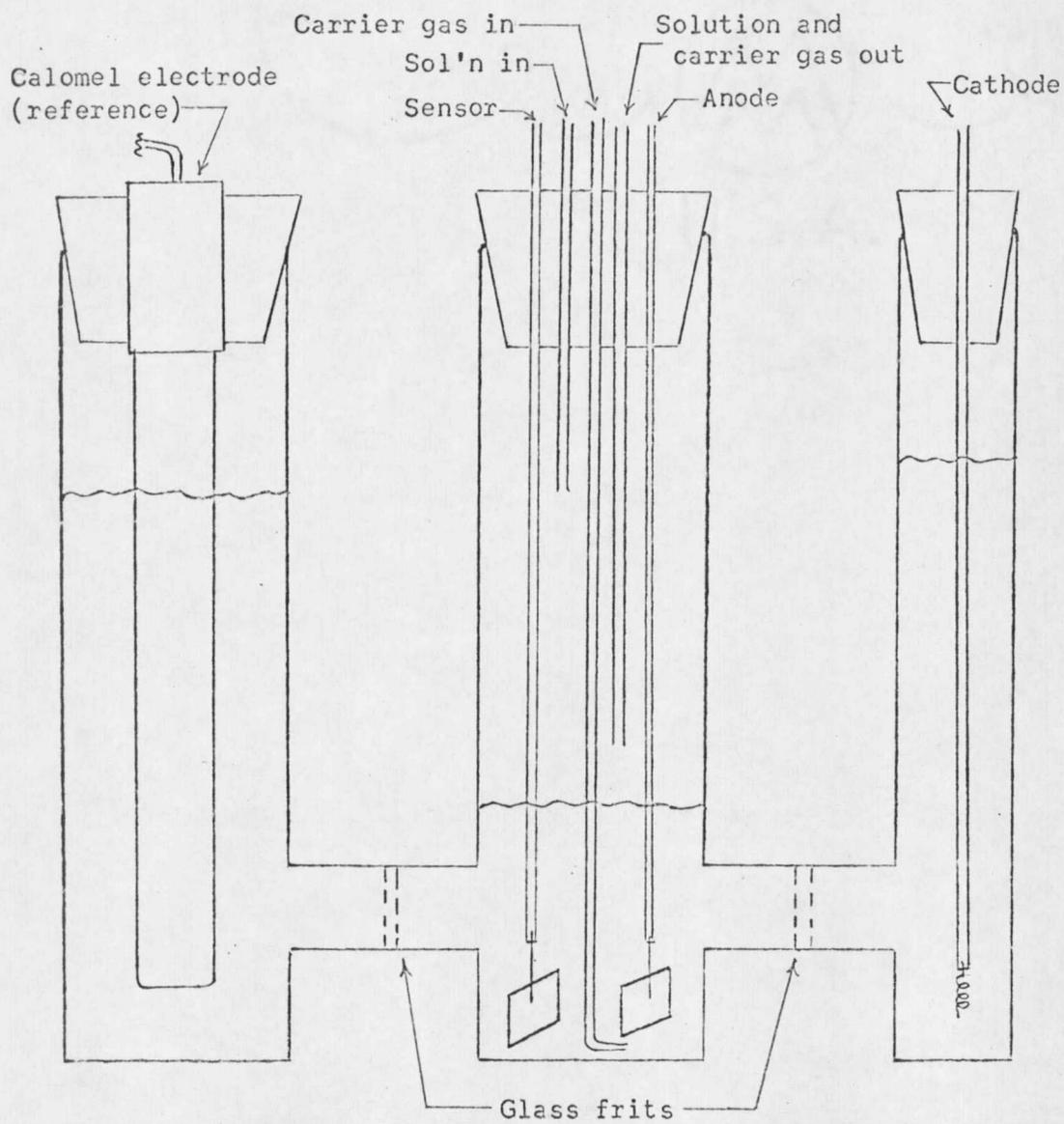


Figure 1. Detection Cell.

















































































