



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
© Copyright by Robert James Robertus (1971)

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 H₂S, SO₂, and CH₃SH in the following ranges: H₂S 1 to 1500 parts/million volume/volume SO₂ 10 to 2000 ppm CH₃SH 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 H²S 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.

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

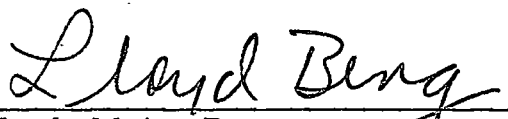
of

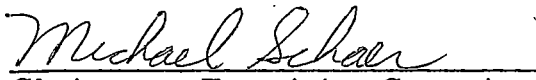
DOCTOR OF PHILOSOPHY

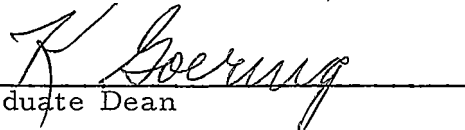
in

Chemical Engineering

Approved:


Head, Major Department


Chairman, Examining Committee


Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

March, 1971

ACKNOWLEDGMENTS

The author wishes to thank the entire staff of the Chemical Engineering Department of Montana State University, and in particular, Dr. Michael J. Schaer who directed this research, for their suggestions which led to the completion of this project.

Thanks, too, are due to Arlan Huso who helped in construction and maintenance of equipment used in the project.

The author also wishes to acknowledge the United States Public Health Service for their financial support given this project.

TABLE OF CONTENTS

PART I

ABSTRACT	xiii
INTRODUCTION	1
RESEARCH OBJECTIVES	5
EQUIPMENT	6
Design of Instrument	6
Operation	8
Probe Design	9
Separation Chamber	12
Detection Cell	15
Theory of Operation	15
Cell Development	17
Electronics	35
Microcoulometer	35
Control Circuit	39
Recorder	42
Calibration Device	42
Mult-Stack Sampling Accessory	46
Miscellaneous	48
RESULTS	50

TABLE OF CONTENTS (continued)

DISCUSSION OF RESULTS	52
Column Packing	52
Interpretation of Data	59
Multi-Stack Sampling	60
SUMMARY	63
RECOMMENDATIONS FOR FUTURE STUDY	64
APPENDIX	65
Related Information	67
Continuous Chromatographic Analyzer- Operations Manual	68
LITERATURE CITED	107

PART II

ABSTRACT	111
INTRODUCTION	112
EXPERIMENTAL PROCEDURE	120
Data Collection	120
Data Analysis	121
RESEARCH OBJECTIVES	122
RESULTS	123
DISCUSSION OF RESULTS	125
Mathematical Technique Used	125
Cautions	127
Variables Considered	129
Comments About Data	130
Computer Output	133
Explanation of Results	134
Final Comments	142
CONCLUSIONS	144
RECOMMENDATIONS FOR FUTURE STUDY	145

PART II (continued)

APPENDIX	146
Program Description.	147
Program Listing	149
Program Output	175
LITERATURE CITED	190

LIST OF FIGURES

PART I

1. Six-Way Linear Sampling Valve	10
2. Stack-Sampling Probe	10
3. Separation Chamber	13
4. Mark 0	21
5. Mark I	21
6. Mark II	24
7. Mark III	24
8. Mark IV	28
9. Mark V	28
10. Mark VI	33
11. Microcoulometer Schematic	38
12. Control Circuit Diagram	40
13. Spinning Syringe Calibrator	45
14. Automatic Sampler Wiring Diagram	47
15. Automatic Sampling System Tubing Connections	47
16. H ₂ S Calibration Data--With Packed Column	53
17. Calibration Data For H ₂ S w/o Packed Column	55
18. Sample of Plant Data Taken	61
19. Final Instrument	66

PART II

20. Process Flow Diagram of a Typical Pulp and Paper Mill	113
21. Black Liquor Piping System Direct Contact Evaporator to Furnace	116

LIST OF TABLES

PART I

I. Detector Sensitivities	8
II. Design Specifications for the Various Detectors	18

PART II

III. Process Variables	131
IV. Computer Program Listing	149
V. Results Before Black Liquor Venturi for Gas SO_2	175
Va. For all 39 Variables	176
Vb. For 22 Selected Variables	178
Vc. For 17 Selected Variables	179
VI. Results Before Black Liquor Venturi for Gas H_2S	180
VIa. For all 39 Variables	181
VIb. For 22 Selected Variables	183
VIc. For 17 Selected Variables	184
VII. Results After Black Liquor Cyclone for Gas H_2S . . .	185
VIIa. For all 39 Variables	186
VIIb. For 22 Selected Variables	188
VIIc. For 17 Selected Variables	189

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 H₂S 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 H₂S 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.

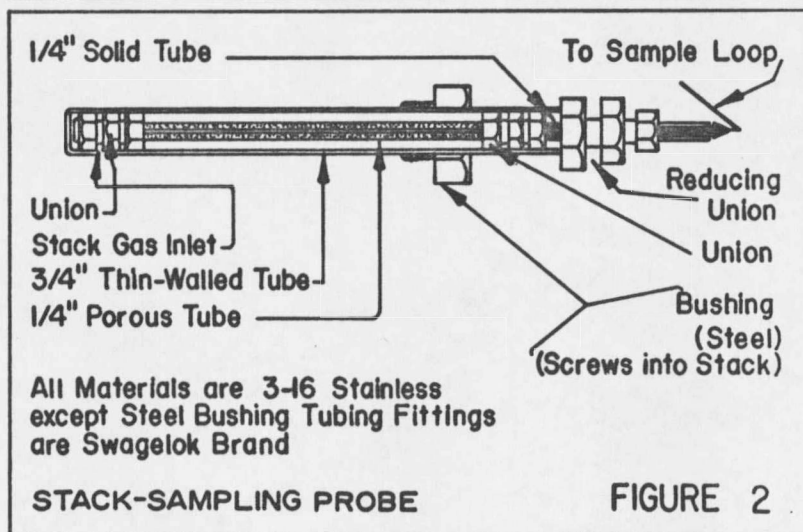
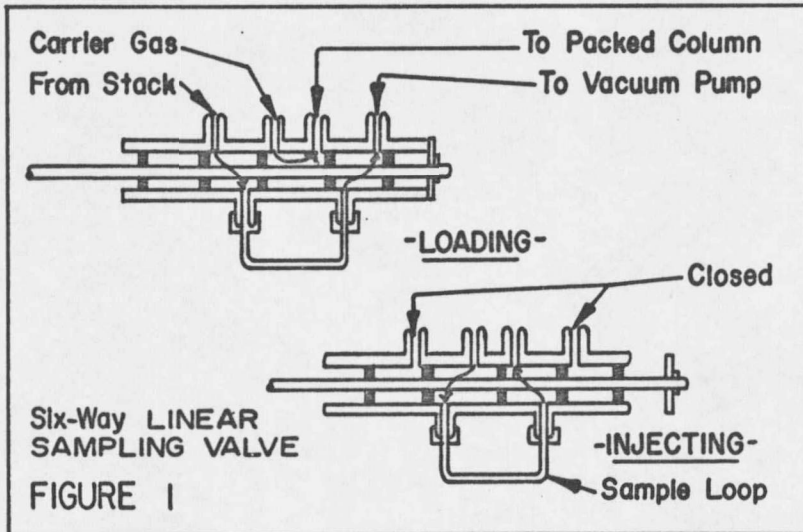
Six minutes later the vacuum pump is switched off, the six-way valve closes, and the carrier gas sweeps the gas sample into the packed column. The column separates the various sulfur compounds and admits them one by one into the detector. The detector (plus associated electronics) will give a peak on 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

