

# Catalytic Removal Studies at Morgantown

## Methods and Apparatus

Because laboratory work on methods of analysis and removal of organic sulfur was begun before gas was available from the gasification pilot plants, a procedure was developed for utilizing simulated impure synthesis gas in the

laboratory. The use of this simulated gas has continued because the distance between pilot plant and laboratory made supply of gas from the pilot plant impractical and also because the ability to prepare and duplicate a particular gas composition independently of pilot-plant operations has certain advantages. (Preparations are now being made to fill cylinders with gas made in the pilot plants, however.)

The base or carrier gas used in most of the laboratory work was a mixture of carbon monoxide and hydrogen in cylinders supplied by the Matheson Co., Inc. A typical analysis of this gas follows:

	<u>Percent</u>
CO <sub>2</sub> .....	0.6
O <sub>2</sub> .....	.2
H <sub>2</sub> S.....	.9
H <sub>2</sub> .....	49.7
CO.....	44.2
CH <sub>4</sub> .....	.9
N <sub>2</sub> .....	<u>3.5</u>
	100.0

This gas has been found to contain up to 13 grains of organic sulfur per 100 cu. ft.; this organic sulfur is believed to be carbonyl sulfide. The organic sulfur content was found to be advantageous in some of the early work on analytical methods. More recently, the gas purchased has contained little or no sulfur. The gas is purchased at 55:45 hydrogen:carbon monoxide but varies somewhat from that composition, as can be seen from the analysis given.

Organic sulfur compounds - carbon disulfide, ethyl mercaptan, or thiophene, or any desired mixture of these - are added to the gas stream by bubbling the gas through dilute solutions of the organic sulfur compounds in dibutyl phthalate. Dibutyl phthalate, in addition to being a good solvent for the compounds in question, has an extremely low vapor pressure at room temperature, minimizing the possibility of contamination of the catalyst from the solvent.

Figures 8, 9, and 10 give the vapor-pressure or stripping curves of the three organic sulfur compounds from dibutyl phthalate. By using these curves, it is possible to approximate a particular desired concentration up to about 12 grains per 100 cu. ft. and to predict a schedule of additions of organic sulfur to the solution to maintain the desired concentration during continuous operations. Actually, these data are used only as a guide, actual total organic sulfur concentrations at the catalyst inlet being determined by analysis. Use of the curves is necessary in determining the distribution of organic sulfur compounds when more than one type is added at a time, even though the total organic sulfur content is determined by analysis.

Figure 11 is a diagram of the apparatus arrangement used in catalytic removal studies. Gas from a manifold of four cylinders of synthesis gas (A) flows through a wet test meter (C<sub>1</sub>), which is provided to measure total gas flow to the system, through activated carbon (D<sub>1</sub>), for removing carbonyl

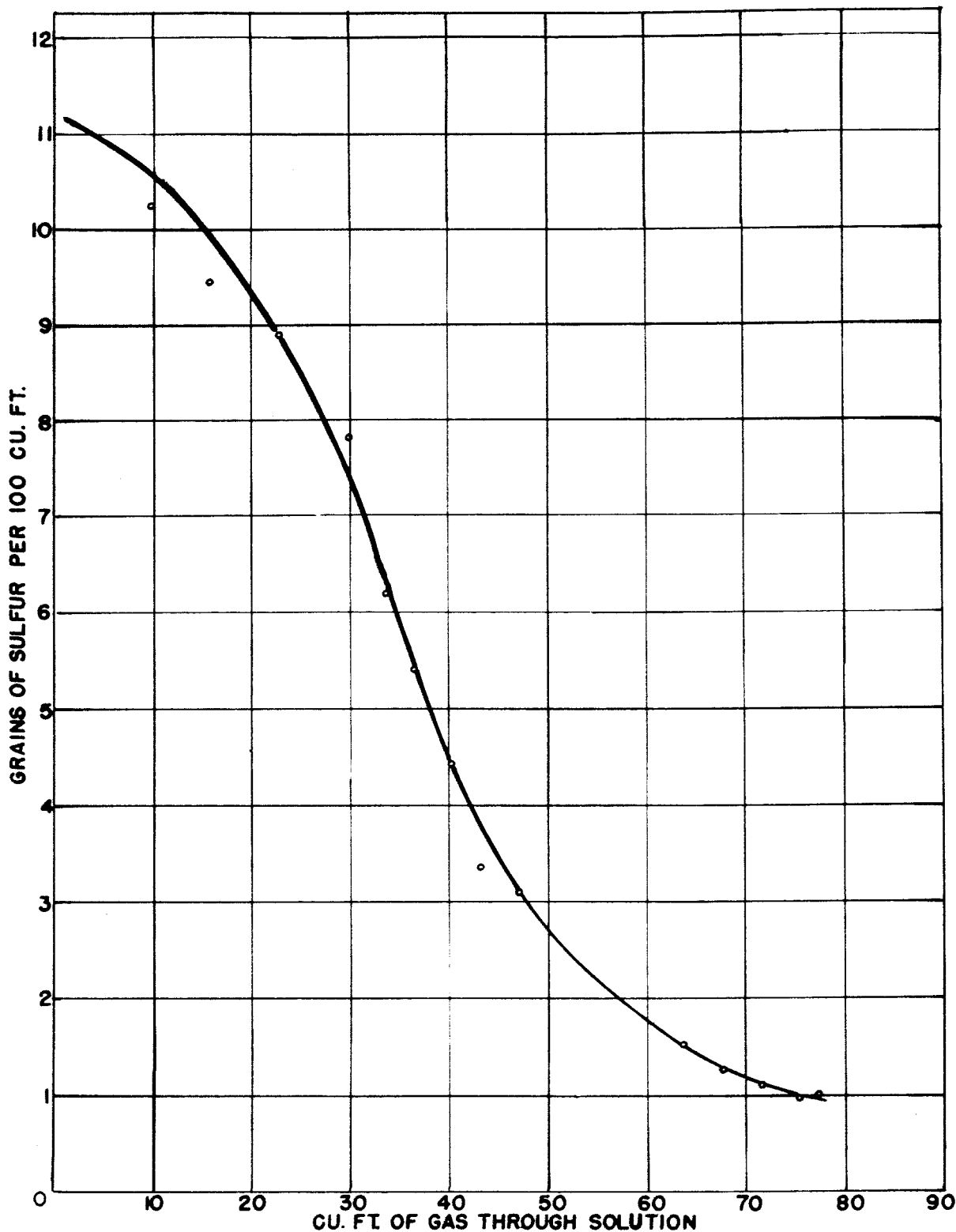


Figure 8. - Vapor pressure of  $C_2H_5SH$  over  $C_2H_5SH$  - dibutyl phthalate mixture at  $23^{\circ}C. \pm 1^{\circ}C.$  6000 ml of dibutyl phthalate having an initial concentration of 0.010%  $C_2H_5SH$  (by weight).

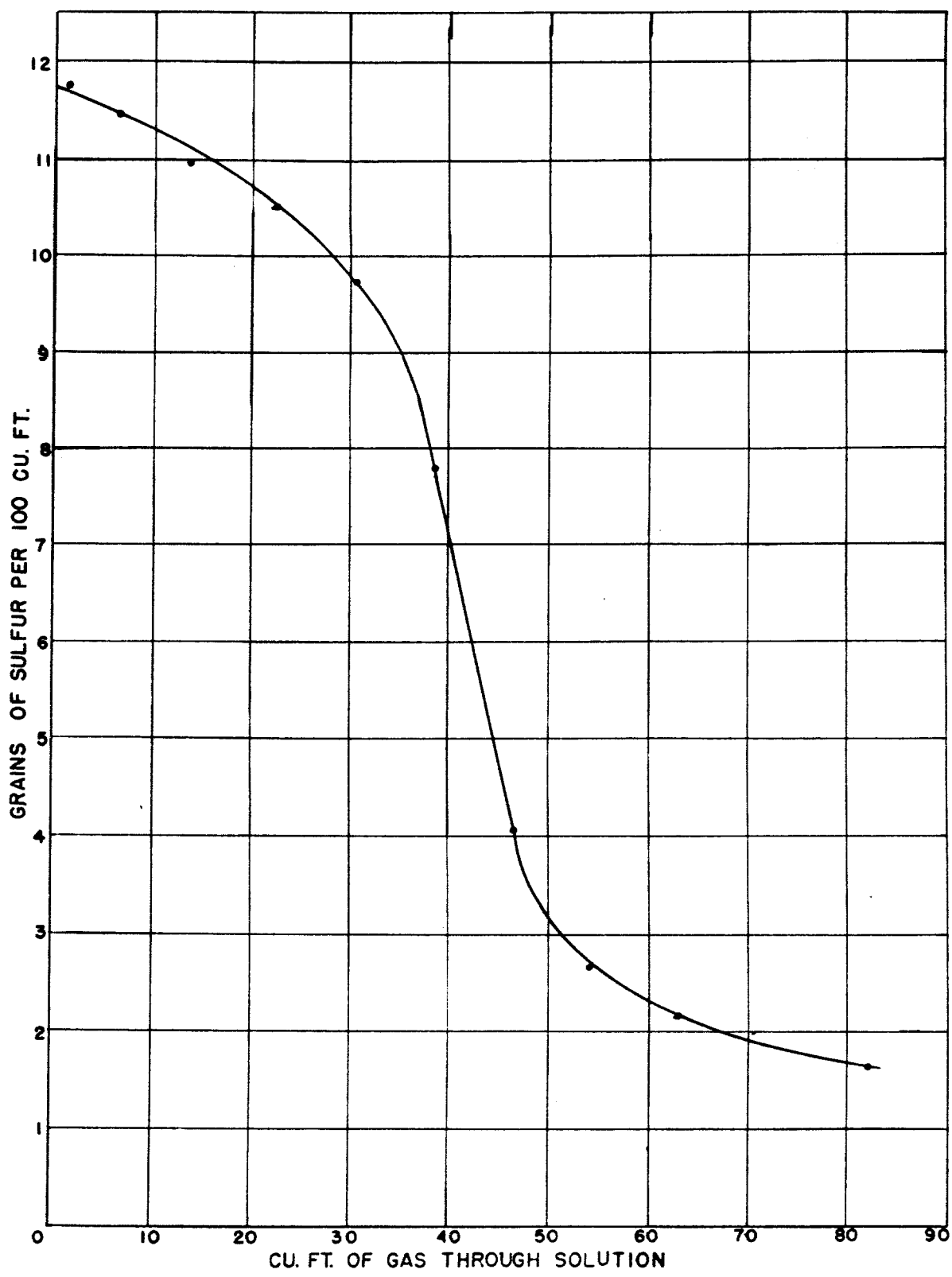


Figure 9. - Vapor pressure of CS<sub>2</sub> over CS<sub>2</sub> - dibutyl phthalate mixture at 23°C. ± 1°C. 6000 ml of dibutyl phthalate having an initial concentration of 0.0086% CS<sub>2</sub> (by weight).

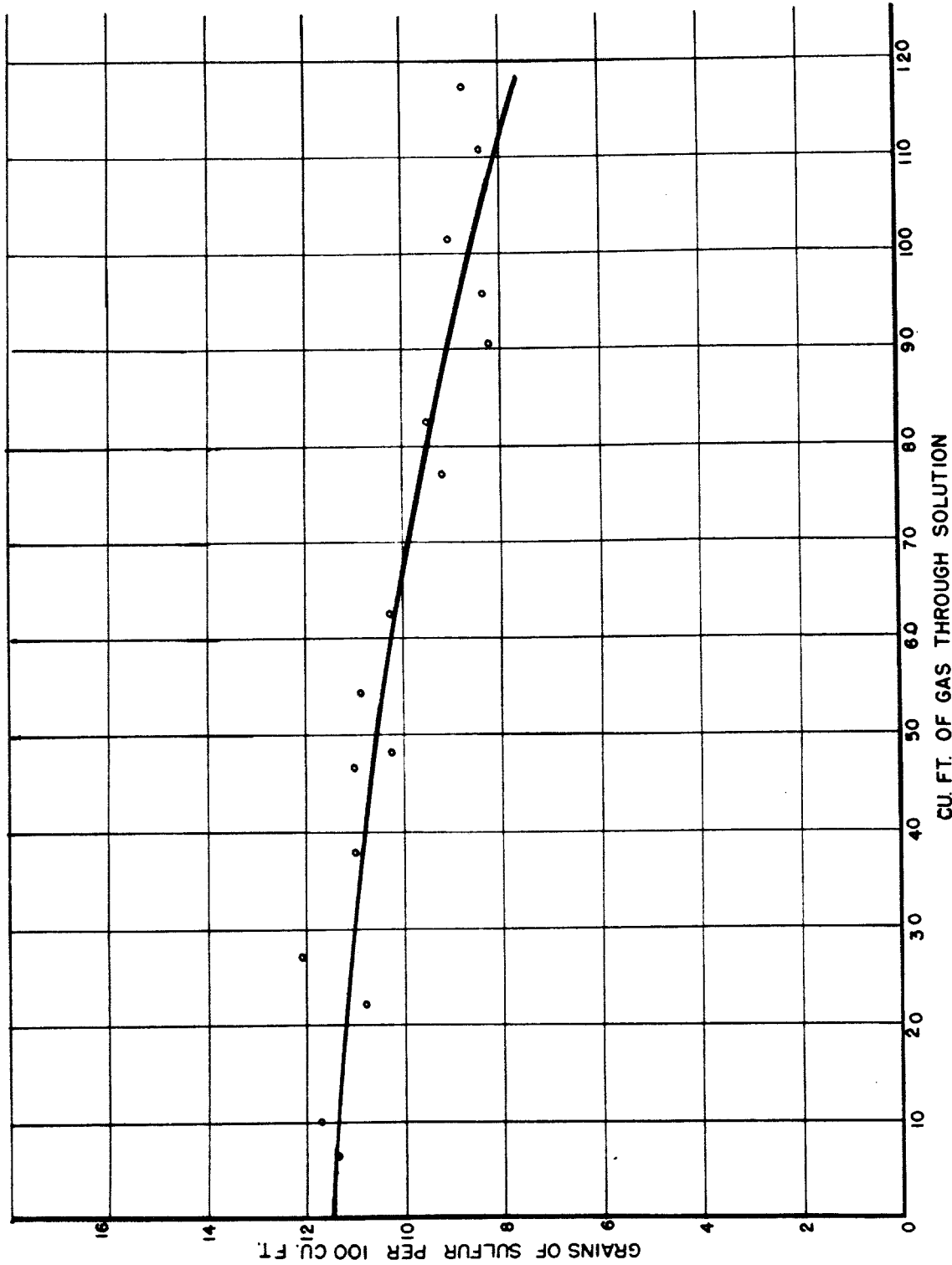
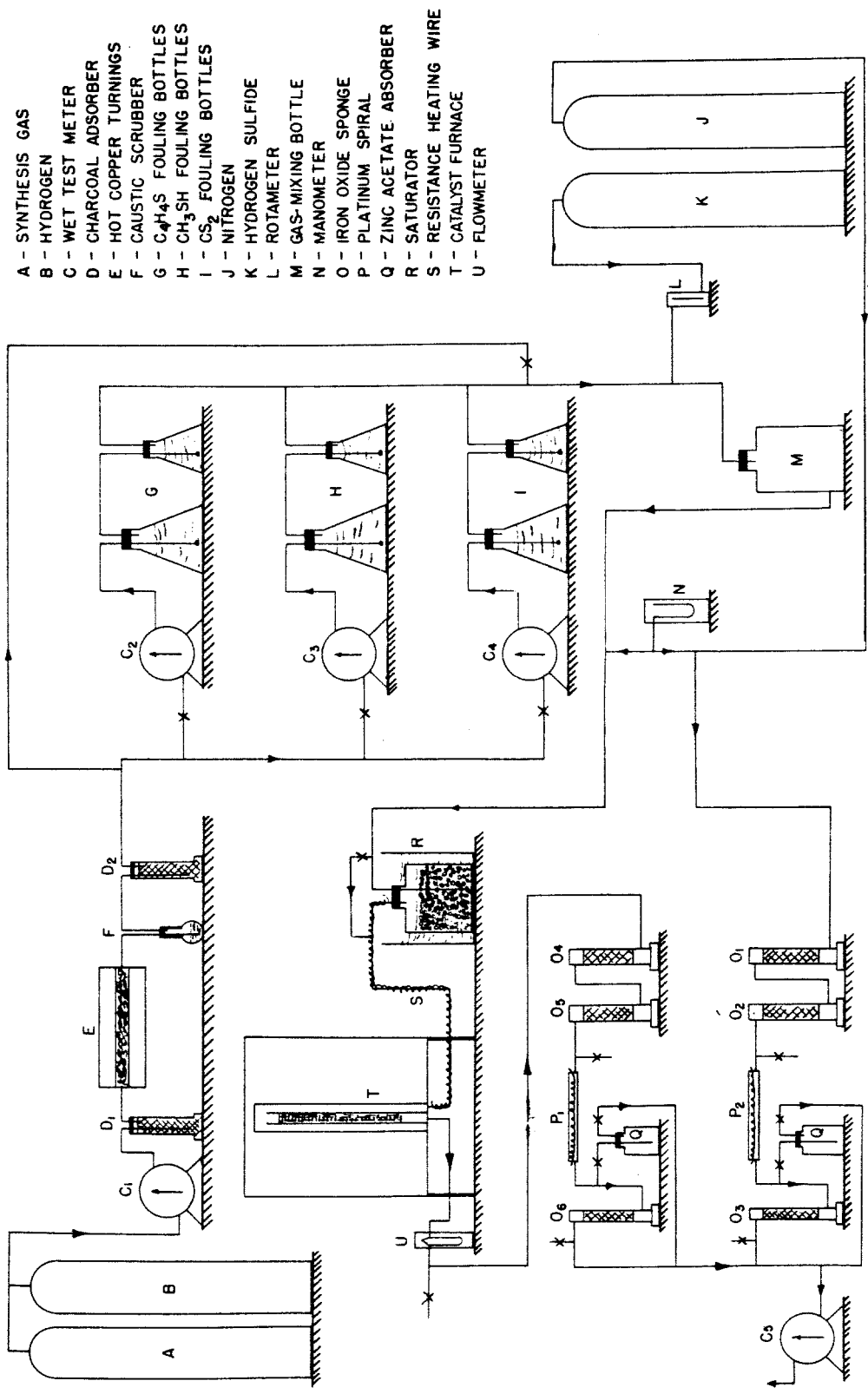


Figure 10. - Vapor pressure of  $C_{12}H_{10}S$  over  $C_{12}H_{10}S$ -dibutyl phthalate mixture at  $23^{\circ}C. \pm 1^{\circ}C.$  6000 ml of dibutyl phthalate having an initial concentration of 0.119%  $C_{12}H_{10}S$  (by weight).



- A - SYNTHESIS GAS
- B - HYDROGEN
- C - WET TEST METER
- D - CHARCOAL ADSORBER
- E - HOT COPPER TURNINGS
- F - CAUSTIC SCRUBBER
- G - C<sub>4</sub>H<sub>4</sub>S FOULING BOTTLES
- H - CH<sub>3</sub>SH FOULING BOTTLES
- I - CS<sub>2</sub> FOULING BOTTLES
- J - NITROGEN
- K - HYDROGEN SULFIDE
- L - ROTAMETER
- M - GAS-MIXING BOTTLE
- N - MANOMETER
- O - IRON OXIDE SPONGE
- P - PLATINUM SPIRAL
- Q - ZINC ACETATE ABSORBER
- R - SATURATOR
- S - RESISTANCE HEATING WIRE
- T - CATALYST FURNACE
- U - FLOWMETER

Figure 11. - Apparatus for studying removal of organic sulfur.

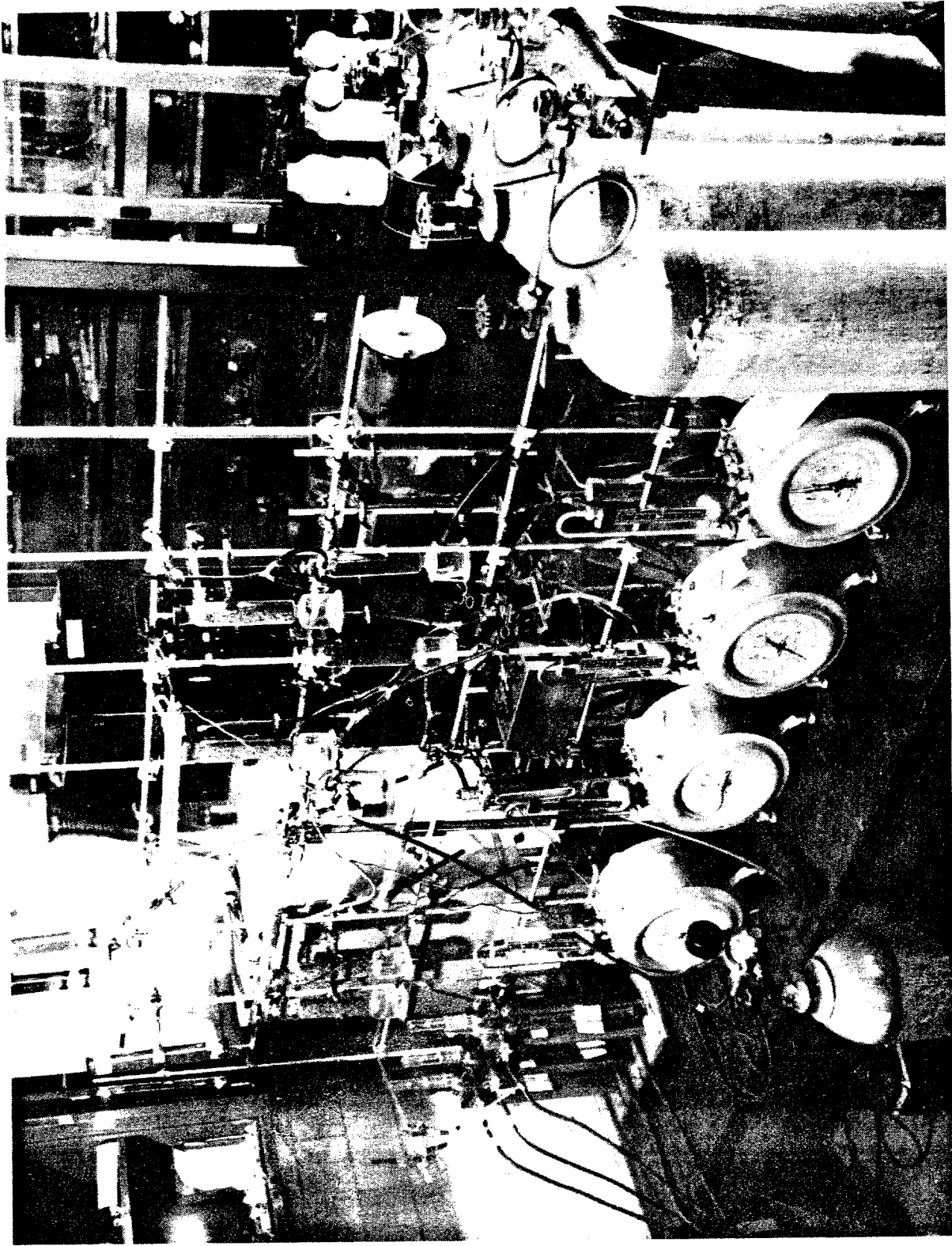


Figure 12. - Experimental apparatus for testing catalysts for the conversion of organic sulfur to hydrogen sulfide.

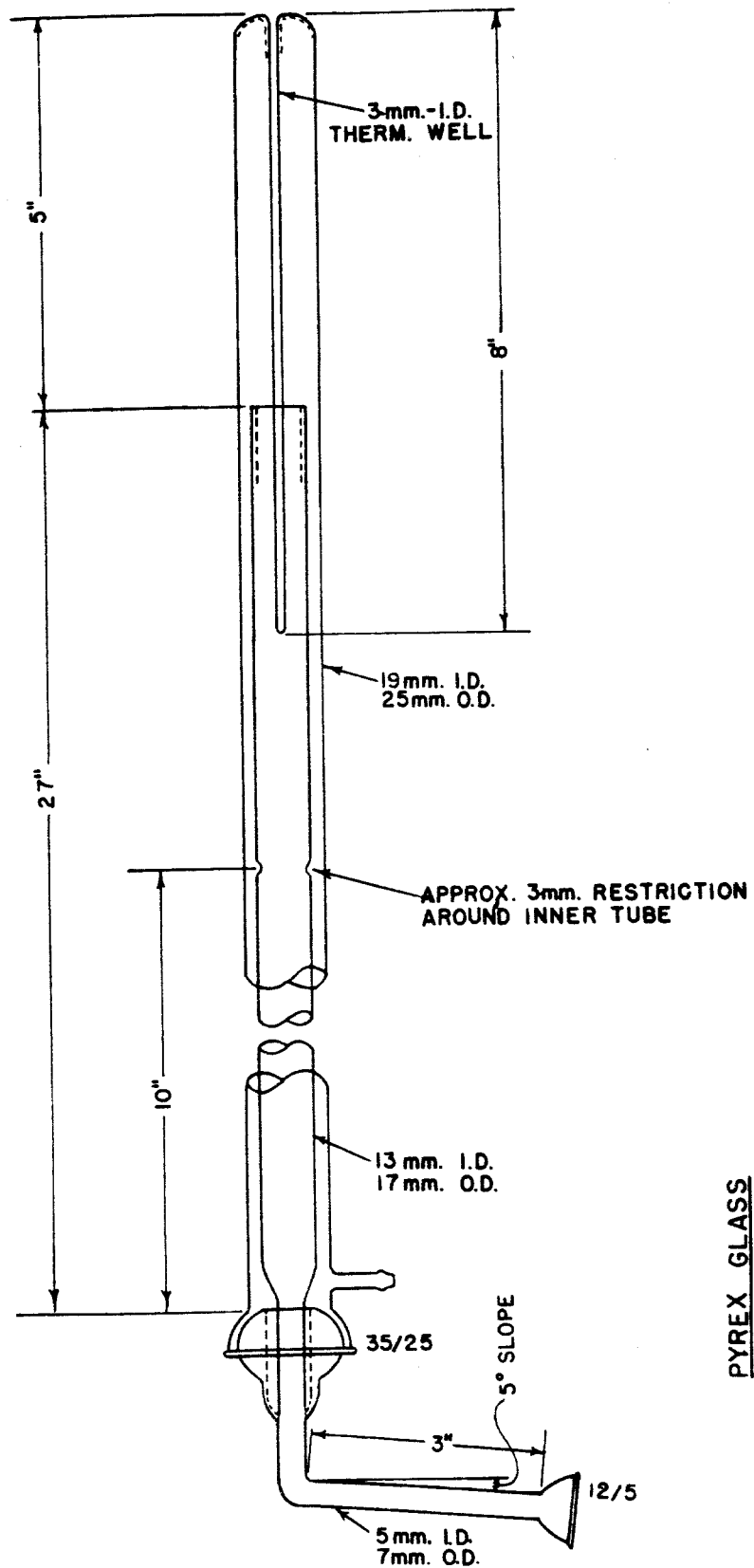


Figure 13. - Catalyst tube used in organic sulfur removal studies.



sulfide and iron carbonyl. Gas then flows through copper turnings (E) heated to 300° C. to remove oxygen, through 20 percent caustic solution (F) to remove any acidic constituents, and thence through a second activated carbon adsorber (D<sub>2</sub>). The gas flow is then split and passed through the organic sulfur fouling bottles (G, H, and I). The parallel streams are supplied with wet test meters (C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>) ahead of the fouling bottles.

The parallel streams are then joined in a manifold, and hydrogen sulfide is added from cylinder (T) through rotameter (L) before entering the mixing bottle (M). Provision is made for sampling gas for hydrogen sulfide immediately after the mixing bottle. Apparatus for determining the inlet organic sulfur concentration consists of two iron oxide towers (O<sub>1</sub> and O<sub>2</sub>), platinum spiral apparatus (P<sub>2</sub>), and zinc acetate absorber (Q) for absorbing hydrogen sulfide formed in the spiral apparatus, gas for this test being measured by wet test meter (C<sub>5</sub>). An iron oxide tower (O<sub>3</sub>) is provided for protecting the wet test meter against hydrogen sulfide.

The main gas stream leaving the mixing bottle (M) is bubbled through a saturator (R) containing water at a thermostatically controlled temperature sufficient to provide the desired water vapor content. A bypass is provided around the saturator for cases when no water vapor addition is desired. The line between the saturator and the catalyst tube (T) is provided with a heating element to prevent condensation of water vapor. Gas leaving the catalyst tube (T) passes through a water-cooled condenser and condensate trap (not shown in diagram) and is measured by a glass flow meter (U) and finally passes through platinum spiral apparatus identical with that already described for the raw gas. Figure 12 is a photograph of the apparatus used for testing three catalysts simultaneously.

The catalyst furnace is of special design provided with three separate heating zones from top to bottom. The temperature of each zone is independently controlled by a Tagliabue six-point temperature indicator-controller. The catalyst tubes are placed in holes drilled longitudinally through a 3-inch-diameter solid-steel cylinder; this insures equal distribution of temperature.

Nitrogen (J) used for purging and hydrogen (B) used for preliminary reduction of catalysts (when required) are provided. A connection (not shown) is provided at the inlet to the saturator for admitting air required for regeneration of certain catalysts.

Figure 13 is a sketch of the catalyst tube used in this work. The tube is equipped with ball-and-socket joints, to eliminate rubber connections, and a thermocouple well. Gas flows up through the annular space, where it is preheated, and passes down through the inner tube containing the catalyst.

Low concentrations of hydrogen sulfide (10 grains per 100 cu. ft., or less) were determined by the methylene blue method.<sup>31/</sup> Higher concentrations of hydrogen sulfide were determined by use of the Tutwiler burette. Organic sulfur in the gas was determined by the platinum spiral method after first removing hydrogen sulfide by means of iron oxide.

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<sup>31/</sup> See footnote 21.