

None of these methods was found to be entirely satisfactory for low concentrations. Further work might make better reproducibility possible, but investigation was terminated because of the much greater suitability of the platinum spiral method.

### Catalytic Conversion to Hydrogen Sulfide

#### Method of Field and Oldach

The method of Field and Oldach<sup>18/</sup> for conversion of organic sulfur to hydrogen with subsequent determination of the hydrogen sulfide was investigated. This method employs activated alumina as catalyst at 900° C; and utilizes the hydrogen content of the gas to effect destructive hydrogenation. The results obtained were always somewhat lower than values obtained by the combustion method. There was evidence that hydrogen sulfide was retained by the catalyst. One industrial laboratory that used this method advised the authors that it was necessary to saturate the gas with water vapor, although Field and Oldach state in their publication that this is unnecessary.

Jilk's method,<sup>19/</sup> which is essentially the same method except that a temperature of 500° C, is employed, specifies that the gas must be saturated with water vapor.

It is understood that raising the temperature to 900° C, was intended to eliminate the necessity of saturating the gas, as well as making oxygen removal unnecessary. (Jilk's method requires that the gas be free of oxygen before entering the catalyst.)

Work in the Bureau's laboratory was carried out using a hydrogen-carbon monoxide mixture (55:45) without adding water vapor. Since the gas was from high-pressure cylinders, it was essentially dry. Saturation with water vapor might have given correct results. However, because of the much greater convenience of the platinum spiral method, further work was abandoned.

#### Platinum-Spiral Method

Lusby's method<sup>20/</sup> employed a hot platinum spiral as a catalyst and utilized the hydrogen content of the gas to effect conversion of organic sulfur compounds to hydrogen sulfide. The hydrogen sulfide was then determined iodimetrically, using a Tutwiler burette. Some other laboratories have used this method but have absorbed the hydrogen sulfide in cadmium chloride, followed by iodimetric titration.

Lusby found that his method, while accurate enough for some purposes, left much to be desired. Among the difficulties were the requirement of considerable time to attain equilibrium between the gas and the platinum wire, the high results due apparently to reaction of iodine with organic

<sup>18/</sup> Field, E., and Oldach, C. S., Conversion of Organic Sulfur to Hydrogen Sulfide for Analysis: Ind. Eng. Chem., anal. ed., vol. 18, 1946, pp. 668-669.

<sup>19/</sup> Jilk, L. T., Proc. Am. Soc. Testing Materials, 1939, Preprint 89.

<sup>20/</sup> Lusby, O. W., Quantitative Determination of Organic Sulfur: Proc. Am. Gas Assoc., 1937, pp. 752-754.

compounds in the gas, and the lack of a satisfactory method for accurate determination of hydrogen sulfide in the order of 0.1 grain per hundred cubic feet. Lusby estimated very low concentrations of hydrogen sulfide by means of lead acetate paper tests.

Since the Morgantown laboratory had developed an improved method for determining low concentrations of hydrogen sulfide in gas which eliminated iodimetric titrations and use of lead acetate paper, it was believed that one of the objections to the original Lusby method might be eliminated. Accordingly that method was thoroughly investigated.

At first, the Lusby apparatus was duplicated exactly. It soon became evident, however, that it would be desirable to lengthen the glass tube to place the rubber stoppers farther from the hot spiral, since the stoppers became softened by the heat. Such lengthening eliminated any serious effect of heat on the stoppers. The necessary lengthening of the copper leads, however, increased the time required to attain equilibrium between spiral and gas. Sulfiding of the copper was evident, and it was decided to replace the copper leads with others made from aluminum rod. This eliminated all trouble due to delay in attainment of equilibrium; equilibrium could now be attained within 15 minutes, even when the concentration of sulfur in the gas was reduced from 25 grains per 100 cu. ft. to 0. Figure 6 shows a sketch of the Bureau's form of the platinum spiral apparatus. It should be noted that the rubber stoppers used are a sulfur-free type.

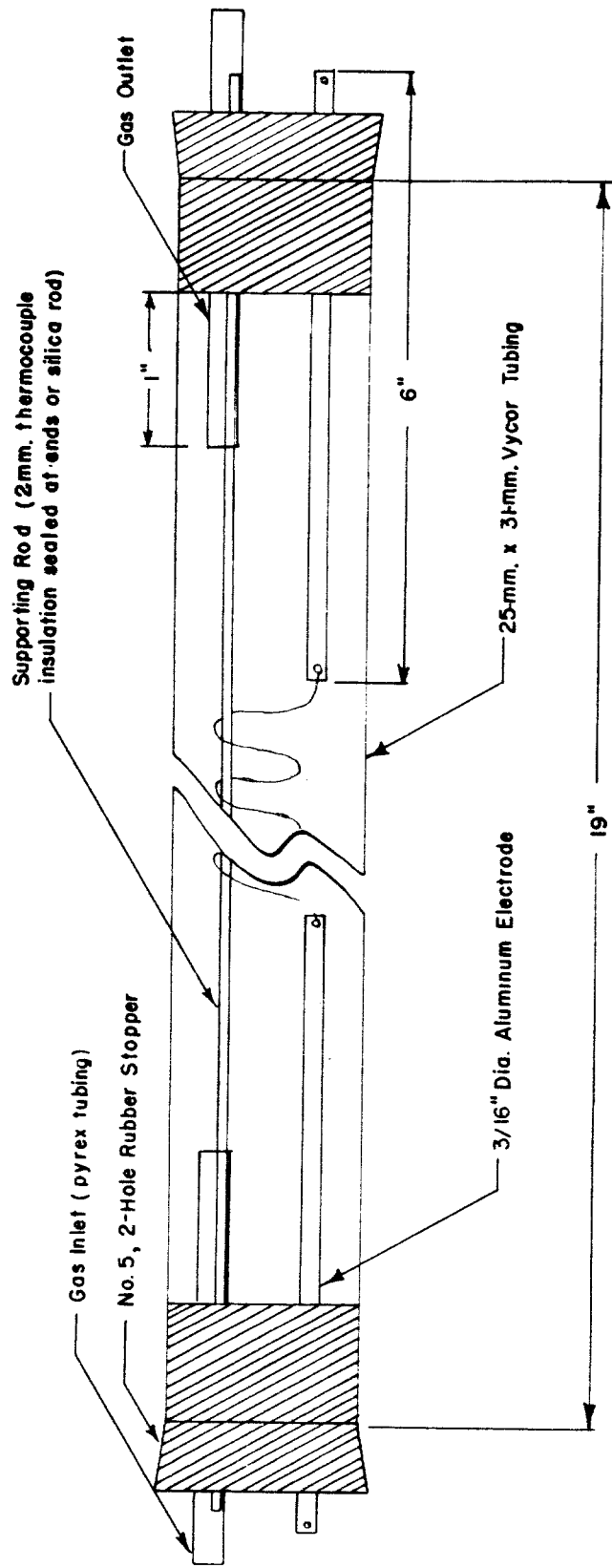
To eliminate any possible difficulties due to sulfur being absorbed or given up by the rubber stoppers, an all glass apparatus was developed. This is shown in figure 7. Difficulty was experienced with this apparatus, in that the glass cracked around the ground-glass joints due to thermal stresses. Laboratory investigation proved that the all-glass type had no advantages over the form in which rubber stoppers are used, so the apparatus shown in figure 6 has been adopted as standard in the Morgantown laboratory.

The procedure employed in using this method for determining organic sulfur in gas follows:

The gas is passed through an iron oxide-sawdust mixture to remove any initial hydrogen sulfide and then over the platinum wire heated to a yellow heat by means of electric current. Gas rates up to 2 cu. ft. per hour have been used with complete conversion of organic sulfur. The gas leaving the spiral apparatus is bubbled through 50 ml. of 2 percent zinc acetate solution and then metered by means of a wet test meter. The zinc acetate bottle is equipped with a bypass containing iron oxide-sawdust mixture, which protects the wet test meter from any hydrogen sulfide when samples are not being taken. The zinc sulfide suspension is analyzed by the Bureau's methylene blue method.<sup>21/</sup> Because of the sensitivity of this method (0.00001 grain of

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<sup>21/</sup> Sands, A. E.; Grafius, M. A. Wainwright, H. W., and Wilson, M. W.,  
Determination of Low Concentrations of Hydrogen Sulfide in Gas by the  
Methylene Blue Method: Report of Investigations 4547, 1949, 19 pp.



Note: Spiral made from 36" length of 28 gage platinum wire, with loops of 1/2" to 3/4" diam.

Electrodes are machined aluminum welding rods.

Figure 6. - Platinum-spiral apparatus for determining organic sulfur in gas.

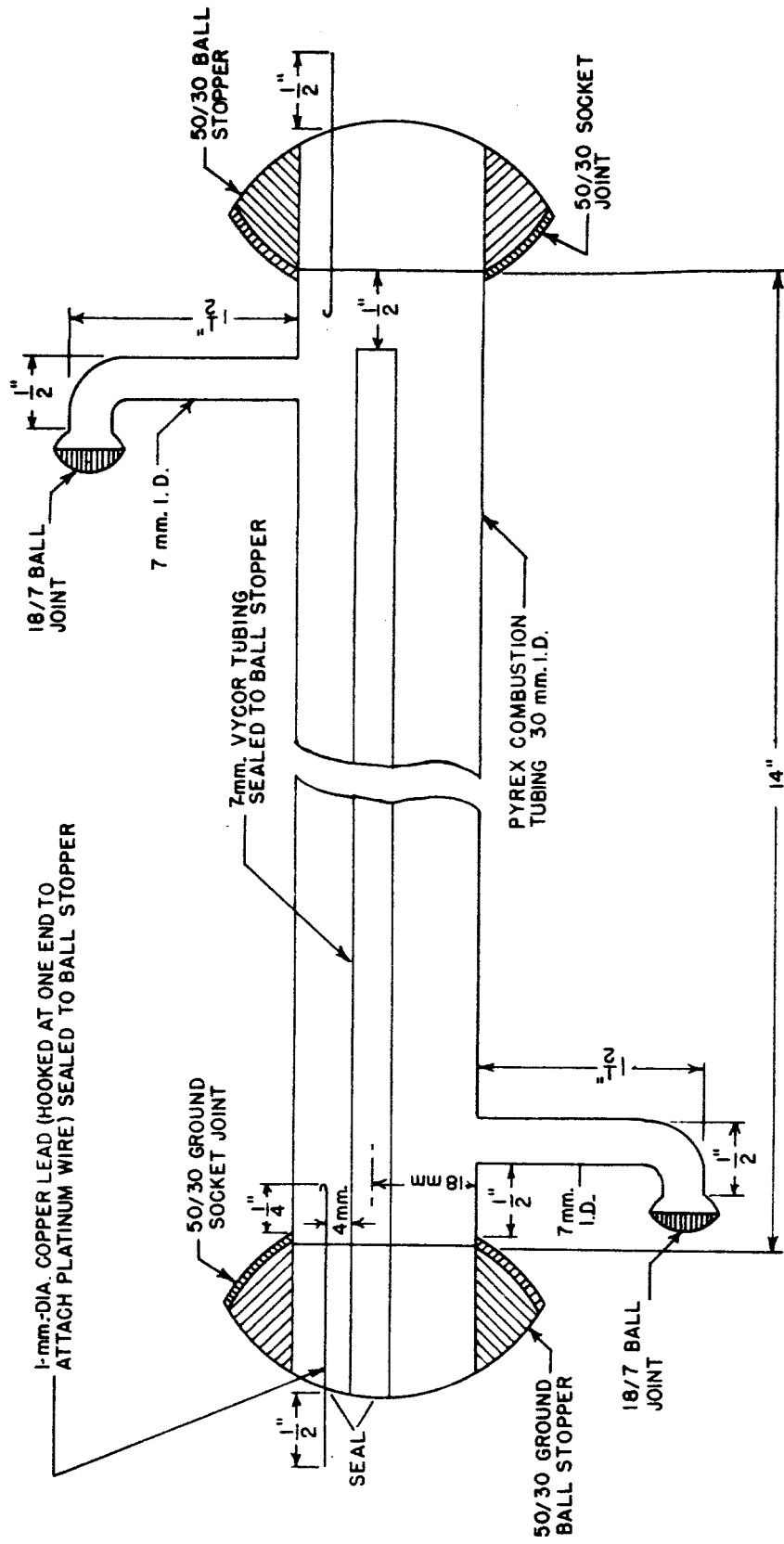


Figure 7. - All-glass platinum-spiral apparatus.

sulfur per 50 ml. of solution), only very small gas samples are required, and a determination can be made in less than one-half hour, including both time for sampling and color development.

Some deposition of carbon may occur on the glass of the spiral apparatus, but this does not affect the accuracy of the results. Formation of carbon can be eliminated by the addition of water vapor to the gas.

The completeness of conversion of organic sulfur to hydrogen sulfide was established by synthetic samples containing carbon disulfide, carbonyl sulfide, ethyl mercaptan, and thiophene. With all of these compounds, at least 99.9 percent conversion was effected. The method is equally satisfactory for sulfur dioxide in gas.

The possibility of substituting nichrome wire (80 percent nickel, 20 percent chromium) for the platinum wire in the spiral was investigated. Since thiophene is generally considered to be the most difficult of the common organic sulfur compounds to convert, that compound was selected for use in these experiments.

To obtain conversions comparable with those obtained by the use of platinum, the gas rate had to be markedly decreased. Thus, the following results were obtained, using a concentration of 6.5 grains of sulfur (as thiophene) per 100 cu. ft.:

<u>Gas rate, cu. ft./hr.</u>	<u>Conversion, percent</u>
1.0	90.0
.6	99.2
.4	Complete

Although nichrome wire has the advantage of lower cost, the higher gas rates possible with the use of platinum make it preferable for work where a large number of samples must be taken at frequent intervals, as in the Bureau's experimental work on removal of organic sulfur.

Actually, the cost of platinum is not too great, since a long life is obtained from a given spiral. Failure of a spiral is not believed to occur except when it is inadvertently overheated. In such cases, a break generally occurs at only one point and may be easily repaired by fusion in an oxy-gas flame without the use of fluxing agent.

Tests were made using a mixture containing varying proportions of hydrogen and carbon monoxide and about 7 grains of organic sulfur (as thiophene) per 100 cu. ft. It was found that a minimum of 28 percent hydrogen was required to obtain complete conversion. A conversion of 90 percent was obtained when the hydrogen content was 17 percent.

Similar tests on mixtures of hydrogen and nitrogen indicate that conversion was complete with a minimum hydrogen concentration of only 15 percent. Comparison of these results indicates the probability of a reverse reaction between carbon monoxide and hydrogen sulfide to yield carbonyl sulfide; the extent of this reaction is reduced, in accordance with the law of mass action,

by increasing the hydrogen concentration. In the absence of carbon monoxide, a lower hydrogen concentration can be used.

Investigation of the method for adaptation to natural gas revealed that when the natural gas contained 10 grains of sulfur (as carbon disulfide), it was necessary to add enough hydrogen to yield a mixture containing 80 percent hydrogen to effect complete conversion. It was evident that a certain amount of cracking of the methane took place; decomposition products apparently give reverse reactions with hydrogen sulfide. Iodimetric determinations gave results which were much too high - additional evidence of the formation of organic decomposition products.

Application of the platinum-spiral method to coke-oven gas in Germany<sup>22/</sup> gave results that were 6.6 percent low; this was probably due to the methane content of the coke-oven gas. On the basis of the Morgantown results, it is believed that, for the analyses of coke-oven gas, or carburetted water gas, 1 volume of pure hydrogen should be added for each volume of gas to overcome the interfering effect of methane. The sensitivity of the methylene blue method for hydrogen sulfide is such that this much dilution with hydrogen would still permit determination of as little as 0.002 grain of sulfur per 100 cu. ft. if a gas sample amounting to 1 cu. ft. is passed over the spiral.

Further work should be done on application of this method to natural, coke-oven, and carburetted water gases, using the hydrogen addition technique.

Although, by suitable dilution with hydrogen, it is believed that the platinum spiral can be applied to other gases, the method is of greatest value when applied to synthesis gas. The ability to take samples at 5-minute intervals and complete analyses inside of one-half hour - as can be done using this method - is of extreme importance in carrying out research on organic sulfur removal from gas. In bench-scale work, many experiments will reveal marked changes in organic sulfur content of purified gas in a short time. Determinations of organic sulfur that require even as little time as 1 hour to obtain a large enough sample may yield misleading results because an average result over a period of time - rather than an instantaneous result - is obtained.

#### REMOVAL OF ORGANIC SULFUR

The work at Morgantown on removal of organic sulfur has thus far been limited to the bench-scale study of catalytic processes operating at elevated temperatures and studies of organic sulfur removal by adsorption on activated carbon.

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<sup>22/</sup> Grimme, W. and Koch, E., [A New Method of Analyzing Organic Compounds of Sulfur in Gases]: Chem. Ztg., vol. 97, 1938, pp. 870-871.

Most of the catalytic processes described in the literature<sup>23,24,25,26,27/</sup> involve cooling the gas leaving the generator, removing hydrogen sulfide by scrubbing in some liquid purification process or by means of iron oxide dry boxes, reheating the gas for catalytic conversion to hydrogen sulfide, and again cooling the gas for removal of hydrogen sulfide.

The German alkalinized iron process<sup>28/</sup> removed organic sulfur by catalytic oxidation and retained the sulfur in the catalyst as sodium sulfate. Thus, in this process, no subsequent cooling or removal of hydrogen sulfide was required, and the gas could be fed to the Fischer-Tropsch converter at the elevated temperature.

Another catalytic process is that of Huff,<sup>29, 30/</sup> wherein both hydrogen sulfide and organic sulfur were removed at 450° C. on various metallic catalysts. The catalysts were regenerated by burning off the sulfur. This process was actually tested by coating or impregnating with catalyst checker brick packed in the superheater of a water-gas set. Although subjected to varying temperatures, tar, oil, and dust, the catalyst gave encouraging results.

In planning the program of work on catalytic removal of organic sulfur at Morgantown, it was desired to avoid the necessity of reheating the gas for catalytic treatment and to make possible utilization of waste heat in gas leaving the waste-heat boiler in the gas plant. This necessitated consideration of a process that would convert organic sulfur before removal of the original hydrogen sulfide content (since most processes for removing hydrogen sulfide are operated at ordinary temperatures) or, better, consideration of a process for simultaneously removing organic sulfur and hydrogen sulfide.

### 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

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- 23/ Key, A., Improved Process for Removing Organic Sulfur Compounds from Gases: British Patent 580,474, 1946.
  - 24/ Booth, N., and Jolley, L. J., Improvement in and Relating to the Purification of Coal Gas: British Patent 574,776, 1946.
  - 25/ Fischer, F., Process for Purifying Gases from Organically-Combined Sulfur: U. S. Patent 1,741,834, 1929.
  - 26/ Groombridge, W. H., and Page, R., Treatment of Gases Containing Sulfur: U. S. Patent, 2,239,000, 1941.
  - 27/ Evans, E. V., Eliminating Sulfur from Oil: U. S. Patent 1,257,829, 1918.
  - 28/ See footnote 3.
  - 29/ Huff, W. J., and Logan, L., The Purification of Commercial Gases at Elevated Temperatures: Am. Gas. Assoc., Inc., New York, 1936.
  - 30/ Huff, W. J., Logan, L. and Lusby, O. W., Purification of Gases: U. S. Patent 1,947,776, 1934.