Conversion of Organic Sulfur to Hydrogen Sulfide for Analysis

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Organic sulfur compounds are quantitatively converted to hydrogen sulfide by passing with hydrogen over alumina at 900° C. The technique has made possible the analysis of traces of organic sulfur compounds in gases or liquids when used in conjunction with sufficiently sensitive methods for hydrogen sulfide analysis.

MODERN catalytic processes require raw materials possessing a high degree of purity. Even traces of hydrogen sulfide or organic sulfur compounds in gases or liquids are detrimental to many catalytic reactions. In order to control and eliminate these catalyst poisons, highly sensitive analytical devices are essential. Several satisfactory procedures for hydrogen sulfide determinations are available, such as the colorimetric methods described in a recent paper from this laboratory (*2*), or the lead acetate–impregnated tape method of Moses and Jilk (*5*). For specific organic sulfur compounds there is the highly sensitive isatin test for thiophene (*1*) and the ultraviolet absorption technique for carbon disulfide (*7*). However, the commonly used combustion technique for total organic sulfur, involving converting the sulfur to sulfate followed by gravimetric or turbidimetric analysis (*3, 6*), is very difficult to apply in the region of extremely low sulfur content where the reagents may contain more sulfate than the sample being analyzed.

The purpose of the present study has been the development of a technique for complete conversion of all volatile organic sulfur compounds present to hydrogen sulfide, after which any sufficiently sensitive procedure for hydrogen sulfide can be applied. A modification of the method presented by Jilk (*4*) was selected after a survey of various alternative procedures. In Jilk's method the gas containing organic sulfur compounds is freed from oxygen, humidified, and passed over activated alumina at 500° C. By raising the catalyst temperature from 500° to 900° C. as much as 1% oxygen in the gas was found to have no effect on the results. Humidification of the gas was not necessary, and complete conversion of methyl mercaptan and thiophene to hydrogen sulfide was obtained, whereas at 500° C. only 60 and 20% conversions were obtained, respectively. At 900° C. carbonyl sulfide, carbon disulfide, methyl mercaptan, thiophene, methyl thiocyanate, and sulfur dioxide were tested and found to be completely converted to hydrogen sulfide when passed over activated alumina in the presence of excess hydrogen. No other sulfur compounds were tested.

PROCEDURE FOR GASES

The gases, containing organic sulfur and excess hydrogen, are passed over 6 ml. of 14- to 20-mesh alumina (desulfurized Alorco Grade A, or gel prepared by precipitation from aluminum nitrate solution with ammonia) in a 10-mm. inside diameter quartz or Vycor tube heated to 900° in a vertically mounted split electric furnace. All connecting lines are glass; rubber joints, where unavoidable, are boiled in caustic to remove sulfur, and a minimum of rubber surface is exposed since rubber reversibly absorbs sulfur compounds. Gas rates up to 0.6 liter per minute were found permissible. To avoid errors caused by absorption on the catalyst, it is desirable to equilibrate the catalyst with the gas for at least 30 minutes; with small samples the catalyst may be purged with pure hydrogen for one hour before the analysis, and the adsorbed sulfur removed by another 1-hour purge to conclude the analysis. The hydrogen sulfide–bearing gas from the converter passes through a Milligan bubbler containing 6% caustic solution. The hydrogen sulfide absorbed is analyzed colorimetrically as described in an earlier paper from this laboratory (*2*).

PROCEDURE FOR LIQUIDS

The liquid to be analyzed is placed in a suitable bubbler and sulfur-free hydrogen is passed through it at a rate of approximately 0.6 liter per minute. The volume of liquid is adjusted to give a suitable quantity of hydrogen sulfide for subsequent analysis. The temperature of the bubbler is chosen to give a convenient rate of evaporation, and hydrogen is passed through it until the sample is completely volatilized. The gas stream is passed over alumina at 900° C. and the hydrogen sulfide collected in caustic, just as in the procedure for gases. The hydrogen stream is continued for another hour to flush the system and recover all sulfur adsorbed by the catalyst. Alternatively, nonvolatile or high-boiling liquids can be stripped of their volatile sulfur content with hydrogen by prolonged bubbling without complete vaporization of the liquid. In this case the analysis would necessarily be for volatile sulfur only. The time required is best determined by experiment, since it depends on the volatility of the sulfur compounds present.

Some vapors—for instance, benzene—deposit carbon on the catalyst. If the deposit becomes heavy the activity of the catalyst is lowered. Should this tendency exist, a very small sample must be analyzed or the catalyst must be regenerated periodically during the determination. Carbon deposits also increase the adsorption of sulfur on the catalyst and make necessary prolonged purging with hydrogen at the end of the analysis. Complete regeneration is accomplished by passing air over the catalyst for 5 minutes at 900° C. The catalyst is purged of sulfur before each regeneration. The regenerating air is by-passed around the absorbing solution to avoid oxidation of sulfide.

DEMONSTRATION OF CONVERSION TO HYDROGEN SULFIDE

Activated alumina (Alorco Grade A) or precipitated aluminum oxide when charged as 14- to 20-mesh granules in a quartz tube was found to give complete conversion at 900° C. at a space velocity of 3000 hours^{-1}. The hydrogenation was demonstrated for carbonyl sulfide, carbon disulfide, methyl mercaptan, methyl thiocyanate, thiophene, and sulfur dioxide, as shown in Table I. The determinations were made by introducing a measured volume of the gas or a weighed amount of the liquid into the gas stream. The actual concentration was therefore indefinite. It was found impractical to make up homogeneous gas samples for this purpose

Table I. Conversion of Organic Sulfur to Hydrogen Sulfide over Alumina at 900° C.

Sulfur Compound	Space Velocity	Average Sulfur Concentration		Carrier Gas	Converted[a] to H_2S
	Hours^{-1}	*Micrograms/liter*	*Grains/100 cu. ft.*		%
COS	2800	1260	55.7	H_2	97
	2800	1260	55.7	33CO-67H_2	96
	2800	500	21.9	H_2	104
	17,000	96	4.2	33CO-67H_2	100
	Empty tube	440	19.4	33CO-67H_2	100
CS_2	3000	530	23.0	H_2	96
CH_3SH	3000	1010	44.5	33CO-67H_2	109
	3000	1260	55.7	H_2	100
CH_3SCN	3000	343	15.0	H_2	100
C_4H_4S	3000	457	20.0	H_2	100
	2500	171	7.5	33CO-67H_2	97

[a] Deviations from 100% are considered within precision of experiments.

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Table II. Determination of Sulfur Content of Liquids

Solvent	Sample	Sulfur Compound	Sulfur	Found[a]
	Ml.		*Micrograms/ml.*	%
No. 30 white oil	25	COS	13.7	92, 92
	25	CH_3SH	14.2	96
	25	C_4H_4S	110	102, 97
Benzene	5	CS_2	640	98, 101, 99
	2	C_4H_4S	8.3	99, 98, 100

[a] Deviations from 100% are considered within precision of experiments.

because the sulfur content dropped fairly rapidly with time when stored either in a water-sealed holder or in a metal cylinder.

Carbonyl sulfide is most readily converted to hydrogen sulfide. As shown in Table I, conversion is completed at 900° C. even in the absence of a catalyst. In the presence of alumina a temperature of 500° C. is sufficiently high to assure complete conversion of carbonyl sulfide and carbon disulfide, provided oxygen is absent from the gas. (Oxygen is automatically converted to water by the catalyst when operated at 900° C.) However, even in the absence of oxygen, thiophene and mercaptans are not completely converted to hydrogen sulfide at 500° C.

Examples of sulfur determinations in liquids are shown in Table II. In the case of the white oil solutions the oil was not vaporized over the catalyst; instead, the volatile sulfur was removed by stripping. Some of the sulfur solutions were unstable, as evidenced by a decrease in volatile sulfur with time. The benzene solutions were completely vaporized and passed over freshly regenerated catalyst. The carbon formation from a single analysis was not sufficient to interfere with the analysis.

ADSORPTION OF SULFUR ON CATALYST

Even at 900° C. some sulfur is retained by the alumina catalyst. The amount retained represents an equilibrium value for a given concentration and does not affect conversion. In analyzing a continuous gas sample of fairly uniform composition it is therefore sufficient to operate the catalyst until equilibrium is established (0.5 hour), after which a sample can be analyzed without danger of error due to adsorption. In case sulfur is to be determined in a batch sample of liquid or in a gas of varying composition, the catalyst must be completely purged with hydrogen before starting the analysis and again after all the sample has been treated. With 6 ml. of 8 to 14-mesh alumina at 900° C., complete desulfurization of the catalyst is achieved by passing 28 liters of pure hydrogen over it.

GENERAL APPLICATION

The analytical technique can be applied to a wide variety of gases and liquids. Successful analyses have been carried out on such gases as hydrogen, carbon monoxide, methane, ethylene, nitrogen, and coke-oven gas, and such liquids as methanol, benzene, cyclohexane, tetralin, and white oil. No tests have been made in which the hydrogen content of the vapors passing over the hydrogenation catalyst was less than 30%. The presence of water vapor is not necessary but it is helpful in some cases in reducing carbon deposition. Carbon dioxide does not interfere, provided it is not present in quantities sufficient to neutralize the caustic scrubbing solution. Unsaturated compounds, either initially present or formed over the catalyst, do not interfere. Oils and tars which collected in the scrubber may cause trouble if present in quantity. Should this occur, the scrubber solution can be acidified and the hydrogen sulfide stripped out and reabsorbed. Oxygen in concentrations up to 1% in the gas stream has been found harmless.

LITERATURE CITED

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Identification of Sulfur Compounds in Gas Mixtures

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A sensitive method for identification and quantitative determination of sulfur compounds present in gas mixtures depends on differences in solubility of the sulfur compounds in an inert solvent. A complete analysis usually involves both an absorption and a stripping run in a multiple-plate saturator. The total sulfur content of the gas leaving the saturator is plotted against gas volume. A stepwise curve results, wherein the gas volume at which the sulfur concentration changes abruptly is characteristic of a specific sulfur compound and the magnitude of the change is a measure of the concentration of that compound. As yet an exhaustive evaluation of the method to determine its accuracy has not been made, but identification runs on partially purified manufactured gas and coke-oven gas are presented, the results of which are in general agreement with previous industrial experience.

THE problem of completely removing sulfur compounds from gases is frequently encountered, particularly in catalytic processes. The most suitable means for effecting sulfur removal depends on the types present. Hydrogen sulfide is the most common form of sulfur encountered, but it is usually accompanied by relatively small concentrations of such organic sulfur compounds as carbonyl sulfide, carbon disulfide, and mercaptans. A new method has been developed for identifying and determining the concentration of these organic sulfur compounds when present in concentrations of a few parts per million. The technique is based on differences in solubility in an inert solvent used in conjunction with a highly sensitive analytical method (*1*, *2*). It is applicable not only to sulfur compounds but to any other class of compounds for which a sufficiently sensitive analytical method is available.

The accuracy and reliability of this method of identification have not been demonstrated on gases of known composition. Because of time limitations, the plant tests were made after only qualitative evaluation of the method on known gas mixtures. However, the results obtained on partially purified manufactured gas and coke-oven gas are in sufficient agreement with previous experience in the industry (*4*) to justify presentation at this time.

THEORY

The successful method herein presented is based on the following theory:

Henry's law generally applies to the solubility of gases in inert liquid at low concentrations. This law states that at equilibrium

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