

I. INFORMATION OF TECHNICAL VALUE

REASONS FOR USING GASHOLDERS
(Item 10, frames 60-65)
(Marked "Secret")

Summary

It can be said that it is possible in many cases to eliminate gasholders. Since decreased safety of operation is a consequence of the elimination, precautions regarding losses of gas, gasoline, etc., and increased need for reliable operating personnel must be considered. In addition, as these disadvantages resulting from these operable innovations appear, the future will provide experience and indicate possible improvements. It is quite possible that operation without gasholders may become so reliable and simple that it will be used in many cases, even under normal conditions.

Gasholders serve:

1. For the equalization of large differences between production and withdrawal of gases.
2. For the equalization of variations in gas volume of a gas-filled system (at atmospheric pressure).
3. For the storage of gas for temporary and occasional use.

In connection with these three types of operation, cases in which gasholders can be eliminated and the necessary considerations will be investigated in the following text.

1. Gasholders for the equalization of differences between production and withdrawal of gases.

It is of decisive significance whether the production and the withdrawal of the gases concerned are uniform or nonuniform (discontinuous). In uniform operation, it is to be understood that changes in the gas mixture occur only now and then, according to conditions of operation, and that large sudden fluctuations appear only with a breakdown. Furthermore, one must bear in mind that a discontinuous production or withdrawal becomes practically uniform, if a sufficiently large number of individual units (e.g. water gas generators) are in operation.

On the basis of these principles, it can be said that in most cases a gasholder can be eliminated if production as well as withdrawal is uniform. On the other hand, if one of the two is nonuniform, it becomes of primary importance whether only a few or a sufficiently large number of single units are in operation. In the first case, the necessity for a gasholder is evident; in the second case one can manage without a gasholder. If, however, production as well as withdrawal is nonuniform, a gasholder becomes necessary for safe operation, even if a comparatively large number of units is in use both for production and for withdrawal. This principle is especially valid when combustible or explosive gases are involved. In comparison with uniformity or nonuniformity of operation or withdrawal, the nature of the gas (combustibility, toxicity, etc.) is of secondary importance and is a decisive factor only in doubtful cases.

The given fundamental lines of reasoning will be examined in more detail for hydrogenation plants and, in general, in connection with all plants in which these problems exist in similar form.

a. Hydrogen Production

Since hydrogen is almost always handled in fairly large quantities, the withdrawal is to be considered in almost all cases as uniform. It is true that the production occurs in many cases by means of a discontinuous process (water gas generators); however, in most cases the number of generators is so large that the production can also be regarded as uniform. The case in which generators are used in small number only to supplement another main hydrogen source (e.g., Hygas-cracking plant) constitutes an exception. In this case, a gasholder could be dispensed with only with difficulty without involving greater danger (sucking in of air), especially since the production changes in the cracking plant in many cases are not very uniform because of unforeseeable frequent changes in the amount and the density of the raw gas. The production of water gas by the Winkler process, by the Pintsch-Hillebrand, and by the Schmalfeld processes can be called uniform in the sense described above.

For hydrogen generation, on account of the interconnection of blowers, two gasholders have always been used: one for the raw water gas, between the generators and the blowers, and a second for the contact gas, between the blowers and the compressors. According to the above considerations, in special cases both holders could be dispensable; in general, at least one could be eliminated.

Knowledge of operation in hydrogen generation by water gas-coke generators without gasholders has not hitherto been available. Oppau has the most extensive knowledge concerning the elimination of at least one gasholder. In Belitz the plant was operated for several days without the contact gasholder, in which case, however, only the water gas plant was in operation, and the Hygas cracking plant produced no hydrogen. The hydrogenation unit itself did not get into operation. Experience indicates, however, that, in principle, this method of operation will probably be feasible.

Bruex has already been operated for a short time without any gasholder. The results were satisfactory. In that connection, it should be borne in mind that a uniform hydrogen production was obtained with the Winkler generators.

b. Fuel Gas Production

Fuel gas production is to be considered uniform in practically all cases. Even if the fuel gas is produced by mixing several different gases, e.g., Hygas with carbon dioxide, the fluctuations in the supply of the individual gases usually need not be so great that one must consider the production to be nonuniform. Any decision, however, must depend on the individual case. In general, in connection with fuel gas, the gasholder can be eliminated. Furthermore, withdrawal, although it is distributed among an entire series of withdrawal points, can almost always be considered to be uniform.

Experience was gained in Poelitz in the production and withdrawal of fuel gas having a calorific value of 157 Btu per cubic foot at 1,236,000 cubic feet per hour. The gases (residue water gas, 219 Btu per cubic foot; blow-off gas, 450 Btu per cubic foot; waste gas from a plant, 1,742 Btu per cubic foot) normally going into the fuel gas were only partially mixed; the periodically accumulated residue water gas was especially deficient. Pressure and heating value fluctuated within suitable operable limits.

c. Hydrogenation Off-Gas

In general the hydrogenation off-gas issues from the chambers intermittently; otherwise a gas holder ahead of the Hygas compressor could be eliminated. Moreover, in this case the extremely high hydrogen sulfide content of the gas is to be considered, which is a hindrance to the discharge of surplus gas to the atmosphere. Likewise, the danger exists, in this case, that, with gas discharge to the atmosphere, heavy hydrocarbons will sink to the ground, and gas pocket explosions could occur. Finally, the hydrogenation off-gas in most cases serves simultaneously as a protective gas atmosphere for the intermediate product tanks, so that the gasholder operates simultaneously as a breathing gasholder for these tanks.

d. Hydrogen Sulfide Gasholders

In plants in which hydrogen sulfide from sulfur-purification units accumulates and must be treated further in a Claus furnace, a gasholder would formerly have been considered necessary. In this connection, a consideration of the utmost importance is that, when the flow to the Claus furnace is nonuniform, the output suffers greatly. If one disregards this relation, a gas holder can be dispensed with in this case also. In Poelitz the circumstances are such that some fuel gas must be passed continually into the Claus furnace. (Not every fuel gas was suitable for this purpose.) Therefore, the hydrogen sulfide piping system shunted with the fuel gas piping system is to be tested. Sufficient gas should be supplied to the Claus furnace that, in addition to the hydrogen sulfide from the two alkazide plants, a certain quantity of fuel gas is always present. Fluctuations in hydrogen sulfide given off then are so adjusted that correspondingly more or less fuel gas goes along into the furnace. Should the gas supply to the furnace suddenly fail (e.g., by stoppage of the air blowers), the alkazide plants will not be disturbed, since the hydrogen sulfide then flows over into the fuel gas piping system until the trouble is corrected. Likewise, this is an advantage as compared with the possible manner of proceeding wherein the accumulating quantities of hydrogen sulfide simply flow off into the completely opened entrance valves in the Claus furnace and the addition of air is adjusted to the fluctuations as well as possible. Of necessity, in order to be able suddenly to take gas away from the Claus furnace, a discharge line must be present, through which hydrogen sulfide can escape. Although the gas cannot be burned in the flare during the war, it is dangerous to discharge it to the atmosphere on account of the toxicity. It is better to return it to the hydrogen-rich gas ahead of the sulfur purification step. In accordance with local conditions, the question of returning it to the raw water gas or the fuel gas would be considered.

e. T52 and AT Plants

The generation of the production gas used in the cracking furnace, as well as the withdrawal by the compressors is to be considered as uniform; therefore, one gas-holder probably can be eliminated. The two-stage Borsig compressors usually used in the above-mentioned plants are, however, sensitive to high intake pressure. It would, therefore, be desirable to develop an automatic pressure controller.

For the circulation of coolant butane in the AT plant, operation without gasholders was at first provided, with the help of suitable regulator contrivances, which caused no difficulties at Leuna (turbo-compressors). This operation, was also apparently carried out without difficulty at Scholven (piston-type compressors).

f. Inert Gas

In most plants, the carbon dioxide released from the water of the carbon dioxide wash, was brought to a definite pressure by means of blowers or compressors and used as inert gas or for chemical purposes. Since, almost always, only a part of the carbon dioxide released was needed, the supply to the blowers or compressors is uniform. A gasholder can, therefore, be dispensed with in an emergency. In Reultz, since the destruction of the carbon dioxide receiver, a 0.5-atm and an 8-atm carbon dioxide piping system was operated in this manner without a gasholder (up to about 283,000 cubic feet of carbon dioxide per hour).

In the production of nitrogen by the combustion of hydrogen or fuel gas and the like, according to the experiments made in Reultz, which were given, the gasholder can be eliminated if somewhat more gas is always produced in the combustion furnace than the nitrogen compressor removes. This excess is discharged to the atmosphere.

To the statements under a to f, several additional general viewpoints should be added, which, according to previous experience and considerations, are to be observed in operation without gasholders.

In the piping system lying between the gas production and the take-off, the pressure rises or falls with variations in the production or withdrawal of gas. When it starts to fall, it must be held constant by a corresponding increase in the speed of the production blowers or of the gas blowers; when it starts to increase, it must be held constant by a corresponding return or blow-back to the suction side of the blower. The introduction of pressure fluctuations into the system through use of a second method of regulation must be unconditionally avoided. For example, the blow-back from the compressors must not be connected to the suction side of the compressors but to the suction side of the gas blowers, inasmuch as these draw from a gasholder. Also, if a gasholder is not present, it is necessary under certain circumstances to discharge the blow-back from the compressors to the atmosphere. If this point is not observed, both systems oppose each other, and the operation procedure becomes exceedingly troublesome and difficult.

By incorporation of a suitably large exhaust, care is to be taken that, upon a sudden falling off of the total take-off (e.g., through partial falling off of the stream), the gas can be discharged to the atmosphere until the blowers are brought back into operation; or all the safety relief valves present in the system in question can be set so high that they do not operate at the highest pressure which the blowers can deliver.

During shut-down periods (e.g., total circulation) it must be possible to maintain the system concerned under a fixed excess pressure so that intake of air will be avoided. Under these circumstances, it is possible to connect the gas-piping system concerned by opening a cross-connection to a second gas piping system in which there is a gasholder. Also, maintenance under pressure by automatic feed from a stored supply of inert gas is to be considered.

2. Gasholders for the Equalization of Variations in the Gas Volume of a System Filled with Protective Gas (Breathing).

In connection with hydrogenation plants, the following discussion relates to breathing tanks (containing protective gas) for:

- a. Finished gasoline.
- b. Raw and intermediate products of hydrogenation.

With finished gasoline, if the tanks breathe to the air, explosive mixtures can be formed as, e.g., by the rapid emptying of a tank. However, since the finished gasoline contains no sulfur and, therefore, cannot form pyrophoric iron sulfide in the tanks, the explosion hazard is diminished. In the petroleum industry, finished gasoline tanks have, therefore, frequently been allowed to breathe against the atmosphere. Consequently, for avoiding large loss of gasoline, the tanks were connected with each other by gas equalization pipes and the breathing occurred only at one place in a small gas-holder. In connection with the momentary fire hazard caused by the finely balanced action, such breathing, however, appears to be dangerous. Even if one would be able to avoid the advance of fires and explosions from one tank to another through the equalization pipes by allowing the tanks to breathe separately, the danger of the progress of fires and explosions from radiant heat would probably still be too great. Hence, a protective gas appears advisable under these circumstances. Since the refined gasoline should not be permitted to become contaminated, nitrogen and carbon dioxide freed of hydrogen sulfide were at first considered. The solubility of carbon dioxide in gasoline would probably not be objectionably high. The maintenance of a protective gas atmosphere is attained most simply by the use of a gasholder. It is also possible, however, to provide the tanks with inert gas from the inert gas piping system, by means of pressure regulators, without a gasholder. In filling the tanks, the surplus protective gas then would be forced through relief valves to the atmosphere. The gasoline loss entailed by such an arrangement must be taken into consideration. It is to be observed that the regulator and the inlets must be designed sufficiently large that even during a very sudden contraction of the gas volume, e.g., during a cold local rain in the summer, sufficient protective gas can flow in.

The intermediate products of hydrogenation contain practically all the light gaseous constituents; therefore, in operations involving these products, explosive mixtures can develop during breathing. In addition, these products contain sulfur, as a result of the presence of which, pyrophoric iron sulfide is formed, which, upon admittance of air, causes the mixtures to burn or explode. In view of the nonuniform formation of the intermediate products, a protective gas is therefore necessary. In general, the hydrogenation off-gas itself is used for this purpose. Since, according to the statements under 1c, a gasholder is appropriate, a second separate protective gasholder is not necessary.

Crude-oil tanks are suitably fed from an inert gas conduit by means of a regulator, as was described for the finished gasoline. Since the risk of losses is not so great in this case, a small continuous inert gas stream can be passed through the tanks. One can also fill the tanks intermittently with carbon dioxide and allow them to breathe; care must then be taken, however, that the content of carbon dioxide does not get below a fixed percentage. The same principle applies to tanks filled with heavy oil, in which, under normal circumstances, at low temperatures, explosive mixtures do not develop.

Regarding the danger mentioned, of temperature increase resulting from burning during the attacks (of air upon iron sulfides), whereby explosive mixtures could be formed by evaporation, the use of a protective gas in the form of a continuous small stream of gas passed through the tanks is also recommended.

3. Gasholders for Storage for Temporary and Occasional Use.

For this purpose, decisions can probably be made only on the basis of individual cases. In the hydrogenation plant, such problems may arise only very infrequently.

Stettin-Poelitz
Aug. 10, 1944

INFORMATION ON PASTE PRESSES FOR USE AT 700 ATMOSPHERES
(Item 10, frames 101-108)

I should like to give you some information on paste presses operated at 700 atm.

The presses were ordered at Esslingen in 1936 through the Mineraloel-Baugesellschaft m.b.H., Berlin. The Esslingen Engineering Works constructed them in accordance with the principle of the Leuna presses. Oil-hydraulic drive was used at an oil pressure of 25 atm. The theoretical throughput was 790 gallons per hour for 12 double strokes and a stroke length of 23.6 inches.

The press cylinder is connected by 4 rods to the drive cylinder.

I should like to call attention at this point to a defect in construction, namely, the sharp deformation of the connecting flange at the cylinder itself.

Before operation began, 8-day experiments were conducted on these presses with an extract oil mixture at 302 F. Cast-iron packing (System Esslingen) was used. The plungers were obtained from Mannesmann-Remscheid. The experiments gave satisfactory results. Operation was then begun.

The operation pressure was 620 atm; the temperature was 293 F. The material injected contained about 8 per cent solids. The plungers were cooled with water.

It was soon evident that the cast-iron packing, in spite of many changes and in spite of good lubrication with fuel oil and with lubricating oil, was unsuitable. Each plunger received 13 gallons of lubricant per hour. The cast-iron packing rings broke and damaged the plunger surfaces.

After using the cast-iron packing rings, we changed to bronze packing (60 Brinell, Goetze System), which were found to be comparatively good.

To collect further data, we used plungers with Thermit packing for some time.

Plunger material, as well as type of packing, concerned us, as usual. The Mannesmann plungers were not previously tested. In this connection, the following should be said:

The plungers have an outside diameter of 3.5 inches and a bore 2 inches in diameter and 47 inches long, a yield point of 47,700 psi and an ultimate strength of 65,000 psi for 24 per cent elongation.

The pressure load was 13,200 psi. According to the specifications of the Materialpruefungsanstalt at Ludwigshafen, this load is very high. The material is not suitable for these varying requirements.

All the fractures extend from the inside to the outside. This phenomenon is caused by the fact that the cooling water corrodes the plungers markedly under the severe internal conditions and thus initiates the fractures. The plungers are severely attacked internally and are, for the most part, eccentric.

For several months, we have substituted a drilling-oil emulsion for the cooling water. Nevertheless, fractures of the plungers were still obtained.

Then, at the suggestion of the Esslingen Engineering Works, we used cast plungers. These plungers were made of the material that Esslingen uses for crankshafts in Diesel engines. The low surface hardness of the plungers (245 Brinell) acted detrimentally, although the life was at least as great as that of the Mannesmann plungers insofar as we have been able to ascertain.

In addition, we used nitrated plungers (500-600 Brinell), which, up to the present, have been excellent. We believe that the higher price, about twice that of the cast-iron plungers, will be money well spent.

The lives of the plungers and the packing vary within broad limits, namely, 700 to 2000 hours.

We discovered another very bad feature in the press cylinder itself. After about 3 million cycles, one of the four cylinders burst in a boring on the suction side at a bolt hole. In accordance with the experience of the different supply houses with hydraulic pumps during the last few years, this behavior of these cylinders was to be expected. We detected, after several hours of operation, fractures in four 3-stage press cylinders from Balcke. We are, therefore, forced to change the cylinders of our four presses in succession.

In connection with the construction of the presses, it was further found that the four rods that connected the drive cylinder to the press cylinder were not strong enough. We made some measurements of the deformation of these rods during operation of the presses and found that, as a result of the deformation of the flange of the press cylinder, the connecting rods underwent a deformation of 0.016 inch. This value corresponds to a load of 5680 psi, which does not lie within the allowable range.

Ruhrcoel G.m.b.H.
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April 25, 1939

THE APPLICABILITY OF POTASSIUM FERRICYANIDE TO THEQUANTITATIVE DETERMINATION OF HYDROGEN SULFIDE

(Item 10, frames 153-157)

Up to the present time, hydrogen sulfide has been determined industrially by several methods; the method used in any given case has depended on the material to be analyzed (caustic, phenol water, gas sample). Usually the iodometric process was used. In previous work, the development of a single method of determination, applicable to different materials, was sought which would make possible the elimination of the use of iodine and of cadmium. The inaccurate method of titration with potassium ferricyanide already known was investigated and modified to obtain a useful method.

THE MECHANISM OF THE TITRATION OF HYDROGEN SULFIDEWITH POTASSIUM FERRICYANIDE

The potassium ferricyanide acts as an oxidizing agent according to the equation:



In order to detect the end point of the titration, a complex colored compound, which decomposed in an excess of oxidizing agent, thus indicating the end of the reaction, was employed as indicator. The indicator was a mixture of ferrous sulfate, ammonium chloride and dimethylglyoxime in alkaline solution. The following hypothesis for the reaction mechanism of the indicator was confirmed experimentally:

(1) The indicator solution is decolorized by the addition of potassium ferricyanide.

(2) The indicator solution is not destroyed by the addition of potassium ferricyanide.

(3) The addition of sodium sulfide to the indicator solution causes the color to deepen, probably because of the formation of small amounts of colloidal ferric sulfide. During the titration the solution becomes clear again. Thus, sulfide ions do not influence the indicator.

(4) Since ferric ion interferes, the ferrous sulfate solution must be prepared fresh daily.

Possible Errors in the Titration:

(1) The indicator solution loses its color by standing in air. Even ten minutes is enough to cause the color to change from red-violet into a pale orange. Since the oxygen in the air contributes to the color change and, consequently, too little potassium ferricyanide is consumed, it is necessary to control the duration of the titration. The influence of the duration of titration on the results is shown by Curve 1.



Curve 1: Dependence of Potassium Ferricyanide Consumption on Titration Time.

At a constant titration time, agreement of results is obtained, as shown in Table I.

TABLE I

<u>Time, min</u>	<u>Consumption, cc 0.1N $K_2Fe(CN)_6$</u>
2	12.87
3	12.69
3	12.69
3.5	12.52
4	12.45
4	12.39
5	12.18
5	12.23
6	11.97
8	11.85

A sodium sulfide solution was used for the titrations.

(2) The addition of ferrous sulfate after the titration is ended reproduces the colored compound, and thus results in a further source of error. Increasing the ferrous sulfate content causes an increased consumption of potassium ferricyanide. It is, therefore, necessary always to work with the same amount and concentration of ferrous sulfate. A varying consumption of potassium ferricyanide would necessitate the destruction of various concentrations of ferrous ions. Thus, by increasing the addition of ferrous sulfate the following values, for example, were found:

TABLE II

<u>$FeSO_4$, cc</u>	<u>Consumption of 0.1N $K_2Fe(CN)_6$, cc</u>	<u>Titration time, min</u>
1	10.84	4
3	11.12	4
5	11.58	4

After the principles and the sources of error of the potassium ferricyanide method were determined, an experiment was undertaken to compare that method with the iodometric titration of a sodium sulfide solution.

Determination of Hydrogen Sulfide in a Sodium Sulfide Solution by the Iodometric and by the Potassium Ferricyanide Method.

Procedure for the titrimetric determination of hydrogen sulfide with 0.1N potassium ferricyanide solution:

Into a mixture of 100 cc of 20 per cent potassium carbonate solution, 10 cc of 10 per cent ammonium chloride solution, and 5 cc of 5 per cent alcoholic dimethylglyoxime solution, is introduced 2 cc of a freshly prepared 0.56 per cent ferrous sulfate solution, and the solution to be analyzed is added. The titration time is 4 minutes, which is the time calculated from the instant of the addition of ferrous sulfate until the end of the titration. The color change (red violet to yellowish green) should remain for at least a minute (stop watch).

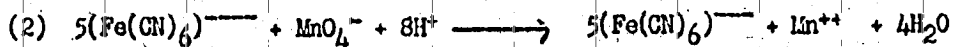
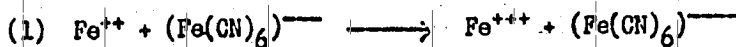
At a titration time of 4 minutes one obtains agreement with the iodometrically obtained values. At shorter titration times, the results are greater than the theoretical values; at longer titration times, the results are less than the values obtained by the iodometric determination.

TABLE III

Iodometrically, <u>gm H₂S/l</u>	With K ₃ Fe(CN) ₆ (4 minutes titration time), <u>gm H₂S/l</u>
9.44	9.40
17.25	17.14
3.29	3.38
12.78	12.71

The two methods are equivalent if one works under the specified conditions.

Standardization of Potassium Ferricyanide Solution with Potassium Permanganate. The reaction is indicated by the equations:



Procedure: One hundred cc of about 0.1N potassium ferricyanide solution is diluted with 200 cc of water, made alkaline with potassium hydroxide, heated to boiling, and concentrated ferrous sulfate solution is added. As soon as the reduction is completed, the solution is cooled, diluted to a definite volume (500 cc), and filtered through a dry filter. An aliquot portion of the filtrate is titrated, after dilution and acidification, with 0.1N potassium permanganate solution.

Since the standardization of potassium ferricyanide solution against potassium permanganate is somewhat troublesome, it is found expedient to substitute standardization against sodium sulfide. The concentration of the sodium sulfide solution may be determined iodometrically.

Examples of the Use of the Potassium Ferricyanide Method.

(1) Alkazine solution:

The potassium ferricyanide method for the determination of hydrogen sulfide, as is already known, may be used for analyzing alkazine solution. Results obtained with our method, modified as described above, agreed with results obtained iodometrically.

TABLE IV

<u>By First Method,</u> <u>gm H₂S/l</u>	<u>By Second Method,</u> <u>gm H₂S/l</u>
17.90	18.13
12.41	12.38

First Method: Titration with 0.1N potassium ferricyanide (titration time 4 minutes).

Second Method: Liberation of the hydrogen sulfide by acidification, heating, and absorption by means of 0.1N iodine solution.

(2) Sodium hydroxide:

The 10 per cent sodium hydroxide solution (downstream from the alkazine solution in the process), which contains hydrogen sulfide and which was formerly titrated iodometrically, can be titrated to obtain equally accurate results, when a titration time of 4 minutes is maintained.

TABLE V

<u>Iodometrically,</u> <u>gm H₂S/l</u>	<u>With 0.1N K₃Fe(CN)₆,</u> <u>gm H₂S/l</u>
4.93	4.87
4.95	4.90
5.71	5.77
3.36	3.39

(3) Phenol water:

Hydrogen sulfide in phenol water may also be determined.

TABLE VI

<u>Iodometrically,</u> <u>gm H₂S/l</u>	<u>With 0.1N K₃Fe(CN)₆</u> <u>gm H₂S/l</u>
9.37	9.28
2.15	2.21
12.63	12.61
14.02	14.07

(4) Examination of the hydrogen sulfide from the alkazide plant:

The precipitation of hydrogen sulfide gas by cadmium acetate and the iodometric determination of the cadmium sulfide can be avoided by absorption of the hydrogen sulfide with 1 per cent sodium hydroxide and titration with 0.1N potassium ferricyanide.

TABLE VII

<u>Iodometrically,</u> <u>vol % H₂S</u>	<u>With 0.1N K₃Fe(CN)₆,</u> <u>vol % H₂S</u>
17.85	17.57
23.19	22.95
20.18	20.11

In conclusion, our modified ferricyanide method for the determination of sulfide ions may be accepted as a standard method of analysis and may be substituted for the iodometric method; appreciable quantities of iodine and of cadmium salts may thereby be saved. The method is being used in the Laboratory for Gas and Low Pressure.

Gas Plant and Low-Pressure Laboratory
Bottrop
April 27, 1943

THE QUANTITATIVE DETERMINATION OF CADMIUM SULFIDEWITH POTASSIUM FERRICYANIDE

(Item 10, frames 158-162)

The necessity of limiting the consumption of iodine, imported from abroad, by the introduction of suitable substitute methods, provided in past years the motive for a critical investigation of the already known inaccurate titration of hydrogen sulfide with potassium ferricyanide and for modification of this method to obtain a useful method. As a result of that investigation, a potassium ferricyanide method was developed as a standard alternative method for the determination of sulfide ions. The ferricyanide method was proved to be suitable for replacing the iodometric method, formerly employed for numerous industrial analyses; thus, appreciable amounts of iodine can be saved (Report of April 27, 1943, "The Applicability of Potassium Ferricyanide to the Quantitative Determination of Hydrogen Sulfide").

The Behavior of Cadmium Sulfide toward Potassium Ferricyanide.

In the investigation cited it was indicated that the modified procedure was not applicable to industrial analysis on account of the low reactivity of cadmium sulfide toward potassium ferricyanide. On account of the cyanide and sulfur dioxide contents, the precipitation of hydrogen sulfide as cadmium sulfide was necessary. In the analysis of most plant samples containing hydrogen sulfide, the cadmium sulfide precipitation could be eliminated by absorbing the gases in alkazide or in 1 per cent sodium hydroxide.

In previous work, it was also attempted to make possible the quantitative determination of cadmium sulfide precipitate by the potassium ferricyanide method. The theoretically suggested possibility of titration of the hydrogen sulfide (liberated by acidification of a cadmium sulfide precipitate and absorbed in 1% caustic) with potassium ferricyanide was found too complicated, in practical execution, for a plant laboratory. Nevertheless, a suitable analytical procedure was based directly on the above-mentioned low reactivity of cadmium sulfide toward potassium ferricyanide.

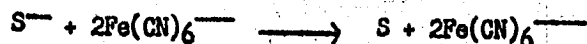
Principle of the Determination of Cadmium Sulfide with 0.1N Potassium Ferricyanide.

By dissolving the cadmium sulfide precipitate, to be determined, in sulfuric acid, a cadmium sulfate solution results, in which the unknown cadmium equivalent of the hydrogen sulfide, after neutralization, is treated with an excess of sodium sulfide solution standardized against potassium ferricyanide. The excess sodium sulfide is determined by back-titration with 0.1N potassium ferricyanide. From this titration, the hydrogen sulfide equivalent of the cadmium sulfide is obtained. In practical use, this sort of cadmium sulfide determination has several difficulties, which are eliminated as described hereinafter.

Removal of the Sources of Error in the Determination of Cadmium Sulfide with Potassium Ferricyanide.

(1) Neutralization of the sulfuric acid-cadmium sulfate solution.

The reaction between ferricyanide and sulfide ions,



must be carried out in a solution made alkaline with soda. The reaction of sodium sulfide with cadmium ions requires a medium as nearly neutral as possible, since the unstable sodium sulfide solution would readily yield hydrogen sulfide in a weak acid solution. Careful neutralization of the cadmium sulfate solution prepared from the cadmium sulfide precipitate is, therefore, necessary.

(2) Indicator for the Neutralization.

In order not to mask the color change from red to yellowish green during the back titration of the excess sodium sulfide with 0.1N potassium ferricyanide, I used, for the neutralization, a mixed indicator which gives a green color in a weakly alkaline medium (pH 7-8).

(3) The Characteristic Color of Cadmium Sulfide.

The characteristic color of cadmium sulfide, especially of large amounts of cadmium sulfide, would make difficult the determination of the end point of the potassium ferricyanide titration. By allowing the bulk of the precipitate to settle in a volumetric flask and pipetting out aliquot parts of the solution this trouble was eliminated. Filtration of the solution was found to be unsuitable, principally on account of the instability of sodium sulfide solution, and on account of excessive time consumption.

(4) Stability of Sodium Sulfide Solution.

According to experience, the stability of sodium sulfide solution is low. In order to avoid loss of standardized sulfide solution by decomposition, I consider it expedient, in addition to the above-proposed procedure, to effect the precipitation of cadmium sulfide at a low temperature (10°C).

The preparation and standardization of the sodium sulfide solution, required daily, would be no additional burden for our control laboratory, since a sodium sulfide solution, standardized daily against potassium permanganate or iodine, is already on hand for the standardization of potassium ferricyanide solution (Report of April 27, 1943, bottom of page 3).

(5) Concentration of the Sodium Sulfide Solution.

The concentration of the sodium sulfide solution is adjusted primarily according to the amount of cadmium sulfide employed in the analysis. In general, it is recommended that about 0.1N sodium sulfide solution be used. Twenty to fifty cc of this solution is sufficient to react completely with the neutralized cold cadmium sulfate solution.

With due consideration of the troublesome factors described and of other experience, I demonstrated the applicability of the method to precise and to industrial analysis.

Examples of Application of the Cadmium Sulfide Determination with Potassium Ferricyanide.

The cadmium sulfide precipitate required for the precise analyses was produced from sodium sulfide solutions of different concentrations, which had been determined with 0.1N potassium ferricyanide. Iodometric analyses of plant samples (Nullgas) were conducted for comparison. The following tables contain a compilation of the results of the comparative analyses.

TABLE I

DETERMINATION OF THE HYDROGEN SULFIDE CONTENT OF
SODIUM SULFIDE SOLUTIONS WITH 0.1N POTASSIUM
FERRICYANIDE DIRECTLY AND AFTER PRECIPITATION AS
CADMIUM SULFIDE

Run No.	Hydrogen Sulfide Found, gm	
	By Titration with 0.1N Potassium Ferricyanide after Precipitation as Cadmium Sulfide	By Direct Titration with 0.1N Potassium Ferricyanide
1	0.0134	0.0136
2	0.0156	0.0155
3	0.0178	0.0172
4	0.0356	0.0349
5	0.0351	0.0349

TABLE II

DETERMINATION OF THE HYDROGEN SULFIDE CONTENT OF SOME
PLANT SAMPLES (NULLGAS) WITH IODINE AND WITH POTASSIUM
FERRICYANIDE AFTER PRECIPITATION AS CADMIUM SULFIDE

Run No.	Hydrogen Sulfide, by Titration with 0.1N Potassium Ferricyanide, gm	Hydrogen Sulfide, by Titration with 0.1N Iodine, gm
6	0.0531	0.0554
7	0.0559	0.0581
8	0.0275	0.0283
9	0.0114	0.0118

Deviations of the results of plant analyses are limited mainly by sampling technique. Two iodometric determinations on samples taken at the same time, for example, showed a deviation of the same order of magnitude as do the results in Table II.

It does not need to be mentioned that the analytical procedure described may be utilized not only for the determination of hydrogen sulfide but also for the determination of cadmium. In our plant the degree of purity of cadmium carbonate produced from a treated cadmium residue was determined by the potassium ferricyanide method.

EXPERIMENTAL PART

Procedure for Determination of Cadmium Sulfide with 0.1N Potassium Ferricyanide.

The freshly precipitated cadmium sulfide is washed thoroughly with weak acetic acid solution in order to remove the adhering cadmium acetate. Then the precipitate and the filter are placed in a 250 cc volumetric flask. The cadmium sulfide is dissolved by heating in 20 to 40 cc of approximately 35 per cent sulfuric acid, and the solution is neutralized (after expulsion of the hydrogen sulfide and cooling) with equally strong sodium hydroxide in the presence of two drops of the mixed indicator (composition of the indicator: 0.50 gm methyl red, 0.12 gm methylene blue, and 50 cc absolute alcohol). The color of the neutralized solution is pale green. The solution is cooled to 10 C; 20 to 50 cc (depending on the amount of cadmium sulfate present) of a sodium sulfide solution of known concentration is added from a pipet, and the solution is diluted to the mark with cold distilled water. After thorough shaking, the bulk of the cadmium sulfide formed settles and 50 cc of the supernatant solution is titrated with 0.1N potassium ferricyanide solution according to instructions previously given (Report of April 27, 1943, page 3, and Report of May 14, 1943).

Experimental Data.

Table III contains the experimental data for the analyses.

TABLE III

EXPERIMENTAL DATA FOR CADMIUM SULFIDE DETERMINATION

WITH 0.1N POTASSIUM FERRICYANIDE

Run No.	Na ₂ S Solution Employed after Neutralization		Back Titration with 0.1N K ₃ Fe(CN) ₆ , cc	H ₂ S Equivalent of CdS Precipitate Found, gm	H ₂ S Content by Direct Titration (T) or by Iodometric Titration (I), gm
	cc	Equivalent 0.1N K ₃ Fe(CN) ₆ , cc			
1	40.00	16.06	8.17	0.0134	0.0136 (T)
2	40.00	18.20	9.00	0.0156	0.0155 (T)
3	50.00	42.50	32.00	0.0178	0.0172 (T)
4	40.00	41.04	20.12	0.0356	0.0349 (T)
5	40.00	41.04	20.38	0.0351	0.0349 (T)
6	50.00	51.35	20.12	0.0531	0.0554 (I)
7	50.00	51.32	18.65	0.0559	0.0581 (I)
8	25.00	31.41	15.22	0.0275	0.0283 (I)
9	25.00	26.80	20.10	0.0114	0.0118 (I)

In Runs 1 to 3, 20 cc of 37 per cent sulfuric acid was used for dissolving the cadmium sulfide precipitate; in Run 4, 40 cc of 37 per cent acid was employed.

Summary.

The present work provides a further step in the saving of iodine. In addition, as a result of the extension of the potassium ferricyanide method to the determination of cadmium sulfide, this method is now generally practicable for hydrogen sulfide analysis, since the indirect method no longer offers difficulty. The possibility of a titrimetric determination of cadmium is also suggested.

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