glycerol. For it has already been shown by Freund[1] that trimethylene glycol is, in fact, one of the principal fermentation products of that substance. It is moreover highly probable that the glycol was present in the fat before saponification by the alkali, as the fermentation can hardly have taken place in the soap lye, both on account of its saline character, and on account of the short time intervening between the saponification and the recovery of the glycerol. It had probably been produced in the fat by spontaneous saponification and subsequent fermentation of the glycerol.[2] Refuse house fat formed a considerable part of the soap stock.

The presence of the glycol in glycerol used for making nitroglycerol might be a source of danger, since it reacts with nitric acid with explosive violence. Its presence would be detected in the usual examination by a low specific gravity accompanied by a high oxidation equivalent as shown by the bichromate titration.

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THE EVOLUTION METHOD FOR THE DETERMINATION OF SULPHUR IN WHITE CAST-IRON.[3]

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THIS method is based upon the assumption that when iron is dissolved in an acid any sulphur that may occur in the iron unites with the escaping hydrogen, forming hydrogen sulphide. In the usual mode of conducting the process the impure hydrogen evolved is led into a suitable absorbent and the sulphur finally determined, either by oxidation and precipitation as barium sulphate, or by a volumetric method. In applying the process Fresenius[4] directs that the iron be dissolved in *dilute* hydrochloric acid. Von Reis[5] and Blair[6] concur in this recommendation, as does also Dudley in

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[1] Monatsh. Chem., 2, 638.

[2] Mr. E. Twitchell of Cincinnati informs us that he has found the glycol present in considerable quantity in the "tank liquor" separating from the fat before saponification.

[3] Read at the Springfield meeting.

[4] Quant. Analyse, *1877*, 428.

[5] Stahl-eisen, *1894*, 963.

[6] Chemical analysis of Iron, p. 54.

the published directions for the determination of sulphur in cast-iron, issued by the Pennsylvania Railroad Company.

For the absorption of the hydrogen sulphide various reagents have been recommended. Johnson[1] proposed the use of a bromine solution. Blair absorbs the hydrogen sulphide in an alkaline solution of lead acetate, oxidizes the resulting lead sulphide, and precipitates the sulphuric acid as barium sulphate. According to the usage at many iron works the gases are led into an ammoniacal cadmium chloride solution which is afterwards acidulated and the sulphur determined volumetrically by standard iodine. In order to complete the expulsion of the hydrogen sulphide from the solution of ferrous chloride a stream of carbon dioxide has been generally employed. Blair uses for this purpose a current of hydrogen, while Dudley states that neither gas has any advantages over air used in a slow stream. In iron-works laboratories it is a generally recognized fact that in the use of the evolution method for certain cast-irons, notably those containing a high percentage of combined carbon, an error is liable to occur, and in cases where great accuracy is required the aqua regia method is usually preferred.

It is common to find that during the solution of cast-iron in an acid there is produced a considerable quantity of strong smelling gaseous hydrocarbons. The interior surface of the flask becomes coated with minute drops of an oily liquid which adheres to the glass and is not miscible with water. There can be little doubt that the loss of sulphur which often results in its determination by the evolution method is dependent largely upon the formation of these organic compounds during the solution of the iron.

It is common to find that the white irons dissolve in acid leaving a nearly white silicious residue of a somewhat flocculent character. This residue contains a varying amount of sulphur, which is insufficient, however, to account for the low results sometimes obtained in the determination.

It has been attempted to explain the error on the hypothesis that sulphur exists in iron in more than one modification, that that portion of the sulphur which occurs in the ordinary form

[1] *Ztschr. anal. Chem.*, *1874*.

passes readily into hydrogen sulphide on its elimination from the iron by the action of the hydrochloric acid, while another portion existing in some unknown modification, is not converted into hydrogen sulphide, but remains passively in the residue and is thus lost in the determination.

Such an assumption involves a difficulty. It is not usually considered necessary in order to explain the chemical changes undergone by the elements of a compound to suppose that the atoms of carbon, hydrogen or sulphur exist in the compound in forms different from those in which we know them in other compounds. Of the six hydrogen atoms in alcohol one differs from the others as to its behavior towards oxidizing agents. The supposition that there are two allotropic forms of hydrogen in alcohol would hardly be accepted, however, for it is commonly believed to be the mode of linking of the atoms rather than the occurrence of the elements in allotropic forms in the compound that determines the nature of chemical changes. The fact that a portion only of the sulphur in white cast-iron is liberated as hydrogen sulphide by an acid suggests that the molecule of cast-iron does not contain all its sulphur linked in the same manner. In the present paper I have described some experiments undertaken in order to study the reactions of the evolution method more fully. For the purpose in view a white iron containing 0.17 per cent. of sulphur, as found by the aqua regia method was used.

Experiment 1.—Four grams of this iron were dissolved in hydrochloric acid of 1.12 sp. gr. As the process of solution became retarded the acid was heated gradually to the boiling-point. The escaping gas was led into a solution of bromine. A small quantity of a heavy oil collected in the bromine solution. This oil was decanted, introduced into a platinum boat and burnt in a porcelain tube in a current of nitrous oxide gas. The gas escaping from the tube was led into bromine water, which on treatment with barium chloride in the usual way yielded a precipitate of barium sulphate, showing that the original oil had contained sulphur.

Experiment 2.—The oil collected in an experiment similar to the preceding was digested with concentrated nitric acid. The mixture, contained in a glass-stoppered bottle, was kept at a temperature of 100° C. for two hours. On one evaporation to dryness, re-solution of the residue in water, and addition of barium chloride no precipitation occurred. The solution was then evaporated again to dryness with addition of some barium nitrate, and the residue heated to redness. On re-solution in water a precipitate of barium sulphate appeared. This experiment showed that the oil contained sulphur but in a form not easily oxidizable directly to sulphuric acid by bromine water or concentrated nitric acid. The fact that.a precipitate of barium sulphate was not obtained by mere evaporation with strong nitric acid, but was quickly produced on ignition of the evaporated residue and re-solution in water, indicated the possible presence of a sulphur ether of the type $(CH_3)_2S$.

Experiment 3.—That the oil condensed in the bromine flask was not a pure sulphur compound was evident from the following experiment: A few drops of the oil were warmed in a flask with an alcoholic solution of potassium hydroxide. The escaping gas was found to yield a red precipitate in an ammoniacal solution of cuprous chloride, indicating acetylene. From this it seemed probable that the oil found in the bromine solution consisted mainly of ethylene dibromide, which on treatment with the alcoholic potash had yielded acetylene by the reaction

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

Experiment 4.—The flask which had been used for a sulphur determination by the evolution method, and which exhibited minute oil drops on its inner sides, was rinsed with alcohol and with chloroform. The combined liquids were evaporated in a platinum boat in which a minute quantity of a residue was left. On strongly heating in nitrous oxide and passing the products into bromine water a precipitate of barium sulphate was obtained after the usual treatment with barium chloride.

Experiment 5.—The silicious residue left from the solution of the iron in hydrochloric acid in the determination of sulphur by the evolution method was found on fusion with alkaline carbonate and nitrate to yield a small quantity of barium sulphate when treated in the usual manner for the determination of sulphuric acid. It seemed still to be of importance to ascertain whether the sulphur in this residue existed as a metallic sulphide or as an organic compound. The possibility of the presence of free sulphur seemed to be excluded, inasmuch as air had been expelled from the flask during the solution of the iron by a stream of carbon dioxide. Accordingly, the silicious residue from a sulphur determination was dried at a gentle heat and extracted after the fashion of an ordinary fat extraction process by boiling alcohol and afterwards by boiling chloroform. The extract, on evaporation, left a trace of a yellow oil. This oil, on being burnt in nitrous oxide, gave indications of the presence of sulphur when tested in the manner already described.

The silicious residue, after extracting with alcohol and chloroform, was found, on fusion with alkaline carbonate and separation of the silica, not to contain sulphur. From this it appeared that the silicious residue contained an organic sulphur compound, but did not contain a metallic sulphide.

The acid solution of ferrous chloride left in the evolution flask was filtered, agitated with a few cc. of chloroform. The chloroform on evaporation, ignition of the residue in nitrous oxide, and the usual treatment, was shown to contain sulphur.

The following determinations were made in the manner indicated. The percentages of sulphur are based upon the weight of the iron dissolved.

	Per cent.
1. Sulphur from oil collected in bromine solution....	0.008
2. Sulphur obtained from alcohol and chloroform rinsings of flask..................................	0.010
3. Sulphur extracted from silicious residue...........	0.013
4. Sulphur obtained by *fusion* of silicious residue after extracting by alcohol and chloroform......	0.000
5. Sulphur obtained by agitation of the filtered ferrous chloride solution with chloroform, representing therefore organic sulphur compounds held in solution......................................	0.009
Total...	0.040

This total represents sulphur occurring in difficultly volatile organic compounds and does not include that which is evolved in more volatile compounds. It is not impossible that a loss by volatization occured in evaporating the chloroform extracts preparatory to combustion in nitrous oxide. It seemed very desirable to learn more of the nature of these organic sulphur compounds and accordingly the following experiment was tried with a larger quantity of iron.

Experiment 6. One thousand grams of the same white iron as had been used in the preceding experiments were treated in small portions at a time with hydrochloric acid of 1.15 sp. gr. until the solution was complete. To hasten the process, as the action of the acid became slow, the flask was gently warmed. The escaping gas was passed, first, through a solution of lead acetate supersaturated with sodium hydroxide, and secondly, through a solution of mercuric chloride in alcohol.

1. THE ALKALINE LEAD ACETATE SOLUTION.

In addition to the deposit of lead sulphide which formed in the lead solution, a yellow flocculent precipitate appeared, soluble on shaking in the alkaline fluid. The solution, decanted from the lead sulphide, was slightly acidulated and warmed. The gas produced was found to yield the following reactions with the solutions named:

Ammoniacal cadmium chloride yielded a white flocculent precipitate.

Palladium chloride yielded a cinnamon colored precipitate.

Platinum chloride yielded a yellowish brown precipitate.

Ammoniacal silver nitrate yielded a pale yellow precipitate.

These reactions indicated the presence of a mercaptan. To study the subject more fully the yellow precipitate, produced in a solution of silver nitrate containing an excess of sodium acetate, was subjected to a partial analysis with the following results:

Found.		Calculated for silver mercaptide.	
Silver.	Sulphur.	Silver.	Sulphur.
69.40	20.54	69.63	20.68

From the data so obtained it appears that methyl hydrosulphide was contained in the gas evolved during the solution of the iron in the hydrochloric acid.

2. THE ALCOHOLIC SOLUTION OF MERCURIC CHLORIDE.

This was found to contain a small quantity of a white precipitate which was partly soluble on warming. After cooling again the solution yielded transparent colorless crystals recognized under the microscope as having the form of crystals of the compound $(CH_3)_2SHgCl_2$ which results when methyl sulphide is added to a solution of mercuric chloride. Upon boiling the aqueous solution of the precipitate in the mercuric chloride solution and leading the vapors into palladium chloride solution, orange crystals were obtained which under the microscope were not distinguishable from the compound formed when palladium chloride and methyl sulphide are brought together. The precipitates formed in the solutions of mercuric chloride and palladium chloride being somewhat soluble, the quantity obtained was insufficient for analysis. It is however very probable that methyl sulphide $(CH_3)_2S$ occurred among the gases evolved during the solution of the iron.

It seems important that in the evolution method of sulphur determination the possibility of the presence of these and kindred sulphur compounds should be taken into account. Two modes of procedure suggest themselves for the recovery of that portion of the sulphur which is liable to be lost in the determination.

I. By direct oxidation to sulphuric acid.

II. By convertion into hydrogen sulphide followed by oxidation to sulphuric acid.

I. DIRECT OXIDATION OF ORGANIC SULPHUR COMPOUNDS.

The action of concentrated nitric acid, potassium permanganate and other energetic oxidizing agents in solution tends merely to convert methyl sulphide into its oxides $(CH_3)_2SO$. and $(CH_3)_2SO_2$. Bromine enters into direct union forming $(CH_3)_2SBr_2$.

Under strongly oxidizing influences methyl hydrosulphide merely yields methylsulphonic acid, an acid which is well known to form a soluble and stable barium salt. Hence while it is a characteristic property of hydrogen sulphide to undergo oxidation to sulphuric acid readily, it is equally characteristic of these organic sulphur compounds and their homologues not to change easily into sulphuric acid even under apparently favorable conditions.

It seemed possible that by direct combustion of the gases the complete oxidation of the sulphur to sulphuric acid might be effected.

A great many experiments have been tried in this direction of which the following is a summary.

As the gases are not evolved in sufficient quantity during the solution of the iron to burn steadily from a jet, it was found necessary to conduct through the evolution flask a current of some combustible gas in order to maintain a more constant flame. For this purpose carbon monoxide was used. The gas was burned from a platinum jet in a glass globe through which a current of moist nitrous oxide was caused to flow. Nitrous oxide was used rather than air or oxygen for the reason that during the combustion of any gas in it nitrogen dioxide is continually formed in considerable quantity. The conditions are therefore highly favorable to the oxidation of any sulphur dioxide produced from the flame of the burning gas, and the complete condensation of the resulting sulphuric acid.

The results were not satisfactory for two reasons:

1. It was found impossible to prevent the occasional extinguishing of the flame, due to the slight pulsations in the gas stream.

2. It was not possible to expel all of the less volatile hydrocarbon oils from the evolution flask into the combustion globe without boiling the ferrous chloride solution and consequent risk of driving over too much steam which tended to extinguish the flame. These difficulties necessitated the abandonment of the method.

II. CONVERSION OF ORGANIC SULPHUR COMPOUNDS INTO HYDROGEN SULPHIDE.

The precipitates produced by the mercaptans in solutions of metallic salts, are not easily converted into sulphides. From this statement must be partially excepted the lead, silver and copper compounds which may change slowly into sulphides. The cadmium compound, which is often seen as a white precipitate when in the evolution method ammoniacal cadmium chloride is used as an absorbent, is more stable. The white precipitate gradually changes into yellow cadmium sulphide, especially on exposure to light.

The process adopted by Blair—absorption in alkaline lead solution—no doubt possesses an advantage on account of the possible change of the lead compound into lead sulphide, as it in this way may affect the recovery of a portion of the lost sulphur. The compounds of the sulphur ethers of the type $HgCl_2(CH_3)_2S$ are still less prone to change into metallic sulphides under the conditions imposed by the method.

Experiment 7.—The vapor of methyl sulphide largely diluted with carbon dioxide was passed through a red hot porcelain tube. By this treatment the sulphur compound was shown to be readily convertible into hydrogen sulphide, undergoing, however, an intermediate transformation into methyl hydrosulphide, CH_3SH, a gas which is easily recognized by its reactions with various metallic salts in solution.

Based upon the results of these experiments the following modification of the evolution method was tried:

The iron was dissolved in hydrochloric acid of 1.12 sp. gr. added slowly while a stream of carbon dioxide was being transmitted through the flask. Heat was applied as soon as the action became retarded. The escaping gas was led through a porcelain combustion tube heated to dull redness. The porcelain tube contained a roll of platinum foil eight inches long. The delivery tube from the evolution flask was pushed far enough into the porcelain tube to permit any liquid which might distil over to drop into the hot platinum roll. A slow stream of carbon dioxide was passed continuously through the evolution flask and heated porcelain tube. The solution of the ferrous chloride was finally heated to gentle boiling and kept boiling until the oily drops which usually coat the sides of the flask were carried away. This required two hour's boiling or two and one-half hours for the entire process. Inasmuch as organic compounds of high boiling-point are undoubtedly formed, this long-continued boiling is especially important. As an absorbent, bromine dissolved in dilute hydrochloric acid was used. After passing a nitrogen flask containing the bromine solution the gas was conducted to the bottom of an eight liter bottle containing a little of the same bromine solution. Experiments have shown that the use of this large bottle is necessary to the complete condensation of the sulphuric acid. The platinum foil used in the porcelain tube is not essential but protects the porcelain tube from risk of fracture from the dropping of the liquid upon its heated inner surface. Mica may be used instead of platinum but is rapidly corroded by the hot acid vapors. The sulphur was determined by weighing as barium sulphate.

In the following table column II contains the results of some determinations of sulphur by the method described.

Column I contains results obtained by the same method except that no heated tube was used.

Column III contains results obtained by the aqua regia method as described by Blair.[1]

The irons used for the determinations were selected on account of their high percentage of sulphur.

Evolution method. Per cent.	Evolution method. Gases passed through a heated tube. Per cent.	Aqua regia method of Blair. Per cent.
	IRON A.	
0.059	0.096	0.101
0.046	0.095	0.098
0.050	0.104	0.096
0.050	0.104	0.099
0.054	0.099	0.100
0.055	0.100	0.102
....	0.092	0.102
....	0.105	0.104
....	0.098	....
....	0.101	....
Mean 0.052	0.099	0.100
	IRON B.	
0.100	0.183	0.173
0.101	0.178	0.170
0.087	0.175	0.168
0.099	0.181	0.170
0.092	0.177	0.174
0.084	0.188	0.171
Mean 0.094	0.180	0.171

In conclusion, I have to thank Messrs. F. B. Smith and H. C. Beggs for the very great care they have taken in carrying out the determinations by the method described.

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[1] Chemical Analysis of Iron, p. 57.