

phlocyanate in the usual way. Ferric sulphate is used as an indicator. In calculating the arsenic present use the proportion :

3 Ag : 1 As : : Weight of silver found : Weight of arsenic present.

The method has been tried successfully with various sulphides such as galenite, pyrite, arsenopyrite, chalcopyrite, sphalerite, etc.; with sulphates like gypsum and anglesite; and with metallurgical products like matte, speiss and flue dust. In the case of analyses of heavyspar the method is not superior to the ordinary fusion with an alkali. The fact that the decomposition with sodium carbonate and zinc oxide has been employed for control and umpire assays upon ores in commercial work for so long a period without objection, is evidence that the results obtained by the method are accurate.

It will be seen that the method for sulphur is a modification of the well known Eschka method, and that for arsenic, is an improvement upon Pearce's method. The advantages of the decomposition described are: (1) that the mass resulting from the heating is not fused, but can be removed readily from the dish and leached with water; (2) the ease and speed with which sulphides, sulphates, arsenates, etc., are decomposed; (3) no time-consuming subsequent evaporations are necessary; and (4) the absence of a large quantity of alkaline and other salts from the solutions in which the precipitations of barium sulphate and silver arsenate are effected.

UNIVERSITY OF UTAH,

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## THE QUANTITATIVE DETERMINATION OF CARBON BISULPHIDE IN A MIXTURE OF BENZENE AND CARBON BISULPHIDE.

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This paper is a preliminary paper to one entitled "The Technical Determination of Carbon Bisulphide in Illuminating Gas," in which determination the carbon bisulphide was separated in the form of potassium xanthate and the carbon bisulphide in the xanthate volumetrically determined by titrating with a standard solution of cupric acetate. In order to calculate the percentage of carbon bisulphide, it is necessary to know the ratio of the copper or cupric oxide to the carbon bisulphide in the copper xanthate formed.

According to the most generally accepted formula of the xanthate formed, it is a cuprous compound with the formula  $(CS.OC_2H_5S)_2Cu$ , in which the ratio of the  $CuO$  to  $CS_2$  is 1.0:0.9561. But Edward S. Johnson<sup>1</sup> found the ratio gravimetrically determined, to vary from 1.0:1.593 to 1.0:1.825, depending upon conditions under which the determination was made. Macagno<sup>2</sup> by a volumetric method found the ratio of  $CuO$  to  $CS_2$  to be 1.0:1.931. Others have found a ratio varying not much from that

<sup>1</sup>This Journal, 28, 1209.

<sup>2</sup>Chem. News, 43, 148.

of Macagno's, indicating a relationship of  $\text{CuO}:2\text{CS}_2$ , and that the copper compound is more probably a cupric xanthate with the rational formula  $(\text{CS}.\text{OC}_2\text{H}_5\text{S})_2\text{Cu}$ .

As the ratios found by Johnson vary so much with slight changes in conditions and differ so widely from those obtained by Macagno, it was necessary to verify either one or the other of these ratios or to establish a new and more correct one. This was done by determining the carbon bisulphide in mixtures of pure benzene and carbon bisulphide by an indirect volumetric method described below.

The quantitative determination of carbon bisulphide in crude benzene and carbon bisulphide preparations presents some difficulties and up to the present time no very satisfactory method has been devised. The principal difficulty seems to be in getting the carbon bisulphide separated in the form of a compound that is stable and quantitative under varying conditions, such as, degree of acidity, excess of precipitants, dilution of solution and quantity of precipitate.

The general principle underlying the methods<sup>1</sup> apparently most widely practised is the separation of the carbon bisulphide by means of absolute alcoholic potash in the form of potassium xanthate and its subsequent determination in the xanthate either gravimetrically or volumetrically. Macagno<sup>2</sup> was the first to suggest a volumetric method for the determination of carbon bisulphide in carbon bisulphide preparations through the medium of the xanthates. This method was also used by Nickels<sup>3</sup> in his work on the purification of crude benzene.

Macagno obtained the carbon bisulphide in the form of potassium xanthate and titrated the cold aqueous solution slightly acidified with acetic acid with N/10 copper sulphate, determining the end point with potassium ferrocyanide. In applying his method to preparations of known carbon bisulphide content, Macagno found the ratio of  $\text{CuO}$  to  $\text{CS}_2$  in the copper xanthate formed to be 1.0:1.931. This method gives a ratio approximate to that found by the writers. A probable disadvantage in this method is the use of an external indicator and the obscuring of the copper ferrocyanide by the yellow copper xanthate which does not readily settle making the end point difficult to ascertain. A source of error lies in the instability of the potassium xanthate in a cold acetic acid solution unless the precipitant is added at once and in slight excess.

Nickels<sup>4</sup> was the first to gravimetrically determine carbon bisulphide

<sup>1</sup> A. Vogel, *Ann. Chem. Pharm.* **85**, 369; A. Loir, *Ibid.*, **87**, 369; Hofmann, *Ibid.*, **95**, 293; E. A. Grete, *Ber.*, **62**, 122.

<sup>2</sup> *Chem. News*, **43**, 138.

<sup>3</sup> *Ibid.*, **43**, 148.

<sup>4</sup> *Ibid.*

in benzene by means of the xanthates. He weighed potassium xanthate directly<sup>1</sup> and converted it by means of cupric sulphate into a copper xanthate and weighed this. Sources of errors in weighing the potassium xanthate lie in its instability on exposure to the air and the impossibility of removing the alkali by washing with ether. Errors in weighing the copper xanthate arise from its instability and the impossibility of obtaining a constant weight on drying.

Edward S. Johnson<sup>2</sup>, determined carbon disulphide in a mixture of benzene and carbon bisulphide gravimetrically by separating it in the form of potassium xanthate, precipitating this with cupric sulphate in an acetic acid solution, igniting the copper xanthate formed and weighing the residue, as cupric oxide. By this method he found the ratio of CuO to CS<sub>2</sub> to vary from 1.0:1.593 to 1.0:1.1:82 5.258, the variation depending, as he states, upon the quantitative relation of the xanthate formed to the alcoholic potash used, the excess of copper sulphate and the dilution of the solution at the time of precipitating the copper xanthate.

The writers of this paper tried at first, modifications of Macagno's volumetric method. The slightly ammoniacal aqueous solution of potassium xanthate was titrated cold with a standard solution of dilute copper sulphate with the purpose of determining the end point by the appearance of the ammoniacal copper blue. The end point, however, was obscured by the yellow copper xanthate, which would not readily collect. The xanthate was also slightly soluble in the ammonia solution. Petroleum ether and ethyl ether were then used, respectively, to dissolve the copper xanthate immediately upon forming, hoping thus to obtain a distinct end point, but these proved unsatisfactory, due to the slow solution of the precipitate and to the absorption of some of the solution by the ether.

The following method was then devised. It appears to give quantitative results, is easy of manipulation, rapid, and fairly short.

The process in detail is as follows: In obtaining the potassium xanthate the method as used by Johnson (see following article) was closely followed. From 0.1 to 0.17 g. of carbon bisulphide (purified by redistillation and kept in a dark place) is accurately weighed, using a small weighing tube with a tightly fitting ground glass stopper and freed from the weighing tube under the benzene in a 250 cc. flask. From 60-70 cc. of pure benzene absolutely free from carbon bisulphide are used and a variable amount of absolute alcoholic potash added, about 15 cc. for each gram of carbon bisulphide present. The solution in the flask is allowed to stand about one half hour, being frequently agitated and then extracted in a separatory funnel successively, with 30-40 cc. portions of

<sup>1</sup> Allen, *Comm. Organ. Anal.*, Vol. II, Part 2, p. 180.

<sup>2</sup> This Journal, 28, 1209.

cold water and 1 cc. of absolute alcoholic potash until the benzene is freed from all carbon bisulphide in the form of potassium xanthate. The water and the alcoholic extractions are diluted to 500 cc. and 200 cc. portions taken for precipitation with titration. These portions are acidified in the cold with acetic acid and a distinct excess of the standard cupric acetate immediately added. The precipitate is frequently stirred from five to ten minutes, filtered, and washed three or four times with 10-15 cc. portions of cold water to remove all cupric acetate. To the filtrate is added about 3 g. of finely pulverized potassium iodide and after standing for about three minutes the free iodine is titrated with a standard solution of sodium thiosulphate whose strength in terms of the cupric acetate is known.

The following tabulation shows the results obtained by this method in establishing the ratio of CuO to CS<sub>2</sub> in the copper xanthate found.

Grams CS <sub>2</sub> taken	Excess of Cupric Acetate	Ratio CuO : CS <sub>2</sub> .
0.09825.....	large.....	1.0 : 1.925
0.09825.....	moderate.....	1.0 : 1.926
0.09825.....	slight.....	1.0 : 1.929
0.13360.....	large.....	1.0 : 1.924
0.13360.....	moderate.....	1.0 : 1.930
0.13360.....	slight.....	1.0 : 1.931
0.16826.....	large.....	1.0 : 1.926
0.16826.....	moderate.....	1.0 : 1.925
0.16826.....	slight.....	1.0 : 1.929
Average ratio = 1.0 : 1.927		

This ratio is slightly lower than that obtained by Macagno and much higher than that found by Johnson. It approaches nearest to the ratio of cupric oxide to carbon bisulphide in cupric xanthate which has the rational formula (CS.OC<sub>2</sub>H<sub>3</sub>S)<sub>2</sub>Cu and in which the ratio of CuO to CS<sub>2</sub> is 1.0 : 1.9126. This tends to strengthen the belief that the compound formed is *cupric* xanthate.

Cupric acetate in acetic acid solution is an ideal precipitant giving a better formed precipitate to handle than cupric sulphate. Precipitation except in very dilute solutions is complete in five to ten minutes. Filtration is rapid and the filtrate showed no further precipitation on standing. Three or four washings with cold water are sufficient to remove all cupric acetate from the precipitate. The determination of the excess of cupric acetate by the quantitative freeing of iodine from potassium iodide, and titrating with a standard solution of sodium thiosulphate, using a starch solution as indicator, is extremely accurate.

The sodium thiosulphate solution used was standardized both against C. P. copper foil and a known weight of pure iodine free from potassium iodide by means of a standard solution of potassium bichromate.

A blank titration was run on the cupric acetate alone, using the same amount as was used in the precipitation. The difference in the two readings gives the sodium thiosulphate equivalent to the CuO in the copper xanthate.

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## THE TECHNICAL DETERMINATION OF CARBON BISULPHIDE IN ILLUMINATING GAS.

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No satisfactory working method for the determination of carbon bisulphide in gaseous mixtures has been found by the writers in the accessible literature.

Sutton<sup>1</sup> in his "Volumetric Analysis" mentions a method proposed by Gastine in which the gas is dried, the carbon bisulphide absorbed by concentrated alcoholic potash, the potassium xanthate solution acidified with acetic acid, an excess of sodium carbonate added, and the xanthate then titrated with a standard iodine solution. Sutton also mentions that the gas may be passed through an alcoholic potash solution, the carbon bisulphide absorbed as potassium xanthate, the potassium xanthate solution acidified with acetic acid and titrated with a standard solution of cupric sulphate. This reference in all probability is to Macagno's<sup>2</sup> method for determining carbon bisulphide in carbon bisulphide preparations.

Butterfield<sup>3</sup> mentions a method, probably also Macagno's method referred to above, which consists in separating the carbon bisulphide as potassium xanthate, acidifying the xanthate solution with acetic acid and titrating with standard cupric sulphate.

The triethylphosphine qualitative test appears never to have been used for a quantitative determination of carbon bisulphide.

In the above methods no mention is made of getting rid of the carbon dioxide previous to the absorption of the carbon bisulphide by the alcoholic potash. Unless this is done the potash soon becomes neutralized and ineffective, the carbon dioxide ranging from 2% to 3% and even higher in illuminating gas, depending upon the purifying efficiency of the plant. The difficulty of titrating directly the potassium xanthate in an acetic acid solution with cupric sulphate was made apparent in the preceding paper. It takes some time to precipitate the xanthate in a dilute acetic acid solution and unless the cupric sulphate is added at once, the precipitate slightly dissolves. The acetylene present in the gas might also, under certain conditions, cause serious errors in

<sup>1</sup> Sutton, Vol. Anal., p. 367.

<sup>2</sup> Chem. News 43, 138.

<sup>3</sup> Chemistry of Gas Manufacture, p. 175.