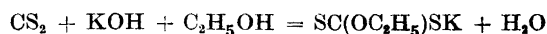


Determination of Carbon Disulphide in Aqueous Solution

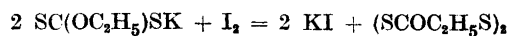
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In connection with an investigation of the carbon disulphide catalyzed iodine-azide reaction (to be published later), it became necessary to be able to — easily and rapidly — determine the concentration of carbon disulphide in an aqueous solution. A survey of the literature concerned showed that there was no suitable method for this purpose. Methods previously used are, for instance, conversion of carbon disulphide to sulphate or silver sulphide followed by a gravimetric determination. For the estimation of small amounts of carbon disulphide in air or in solution, colorimetric methods have been used, *e. g.* the formation of the yellow colour of cupric diethyldithiocarbamate. The best method for the estimation of considerable amounts of carbon disulphide in air or of pure carbon disulphide seems to be the xanthate method. Matuszak¹ has reviewed the literature and has shown that the method is quantitative. By this method, carbon disulphide is absorbed in or mixed with alcoholic potash, whereby a xanthate is formed:



The solution is then acidified with acetic acid until the reaction is acid to phenolphthalein, but still alkaline to litmus, and starch indicator is added. The solution can now be titrated with iodine solution according to the equation:



Matuszak mentions that the presence of water slows up the reaction between carbon disulphide and alcoholic potash. The reaction is instantaneous when absolute alcohol is used, but a solution made from 95 per cent alcohol reacts with sufficient rapidity. From this fact we concluded that the diffi-

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culty in solutions with higher concentrations of water might be overcome by allowing the mixture to stand for some time. Of course, carbon disulphide can be removed from an aqueous solution by aeration, and absorbed in alcoholic potash; but this is a tedious and complicated method. Harrower and Wiley² have, however, used this method when determining carbon disulphide in blood.

PROCEDURE

Into a 300 ml Erlenmeyer flask with glass stopper is introduced 20 ml of alcoholic potash (10 % potassium hydroxide in 96 % alcohol). Into the flask is now pipetted 10 ml of the aqueous solution of carbon disulphide, the stopper is replaced, the flask shaken for a few seconds, and left in darkness for 30 min. The stopper is then removed and washed with a small amount of water. One drop of phenolphthalein is added, and the solution is neutralized by dropwise addition of 60 % acetic acid. An excess of 3–4 drops is added. For the sake of imparting to the solution an adequate reaction, one gram of calcium carbonate, *p. a.*, is added, and the flask shaken for about 15 seconds. 1 ml starch indicator is added, and the solution is diluted with water to 150 ml. It is now ready for the titration with 0.01 *N* iodine. The iodine solution is added to an excess of about 0.5 ml (corresponding to a strong blue colour). The excess of iodine is determined by back-titration with 0.01 *N* thiosulphate.

According to Matuszak¹, it is important that titration of xanthate takes place in a nearly neutral solution. The addition of calcium carbonate to a xanthate solution, acidified with acetic acid, has previously been used by Lehmann³. If the alcoholic potash, used as reagent, is not freshly prepared, it is absolutely necessary to run a blank determination by substituting 10 ml water for the 10 ml carbon disulphide solution. Otherwise the blank determination is carried out exactly as the real determination. According to Harrower and Wiley², it is advisable to dissolve potassium hydroxide in alcohol at low temperature, and to store the reagent in an ice box. Prepared in this way, the reagent has a very small blind value when fresh.

Matuszak¹ titrates the xanthate formed with iodine until the formation of a blue colour. According to our experience, the addition of an excess of iodine and back-titration with thiosulphate seems to yield the most accurate results, especially when rather small amounts of carbon disulphide are to be determined.

EXPERIMENTAL RESULTS

After a few introductory experiments, it seemed most expedient to use 5 or 10 % alcoholic potash. The experiments were carried out in such a way that 10 ml of water were added (in expt. no. 11, 20 ml water were added) to a varying amount of alcoholic potash contained in a 300 ml Erlenmeyer flask. 15–20 mg carbon disulphide were now added (7.613 mg $\text{CS}_2 \sim 10$ ml 0.01 *N* iodine). The carbon disulphide used was of analytical quality and was further purified by distillation. It was weighed out in a capillary tube on a micro balance. The tube was introduced into the alcoholic potash. After replacing

Table 1. Conversion of carbon disulphide to xanthate in 10 % alcoholic potash. The amounts of carbon disulphide added and found are given as the equivalent volumes of 0.01 N iodine. 'Reaction time' is the time allowed for the reaction between carbon disulphide and alcoholic potash. Temperature during the experiments: 16.5–17.0° C.

Expt. no.	Reaction time min	Alcoholic potash, ml	Water added, ml	CS ₂ added	CS ₂ found
1	30	10	10	18.10	17.92
2	30	15	10	21.05	21.03
3	30	20	10	20.21	20.21
4	30	20	10	25.12	25.11
5	30	20	10	14.03	14.04
6	30	20	10	19.71	19.67
7	30	20	10	17.31	17.32
8	30	20	10	23.51	23.49
9	30	40	10	22.12	22.13
10	30	80	10	27.26	27.28
11	30	20	20	23.24	23.07
12	60	20	10	19.01	19.00
13	120	20	10	27.31	27.30
14	20	20	10	22.13	22.10

the stopper, the carbon disulphide could be washed out of the tube by a slight shaking of the flask. The flask was then allowed to stand in darkness for a certain time (reaction time). The capillary tube was then crushed with a spatula, and neutralization and titration accomplished as described above.

From Table 1 it can be seen that, when using 20 ml of alcoholic potash, a reaction time of 30 min. is sufficient for the quantitative conversion of carbon disulphide to xanthate. In the column 'CS₂ added', the amounts of carbon disulphide used is given, — but expressed as equivalents, in ml, of 0.01 N iodine solution. The column 'CS₂ found' gives the corresponding experimental values — also in ml 0.01 N iodine solution. From Table 2 it can be seen that 5 % alcoholic potash may be used, but the reacting solution must be allowed to stand longer, or more alcoholic potash must be used.

SUMMARY

The well known xanthate method for the determination of carbon disulphide has been modified so that carbon disulphide, in an aqueous solution, can be directly titrated, without first separating the carbon disulphide from the water.

Table 2. Conversion of carbon disulphide to xanthate in 5 % alcoholic potash. The amounts of carbon disulphide added and found are given as the equivalent volumes of 0.01 N iodine. 'Reaction time' is the time allowed for the reaction between carbon disulphide and alcoholic potash. Temperature during the experiments: 15.6–16° C.

Expt. no.	Reaction time min	Alcoholic potash, ml	Water added, ml	CS ₂ added	CS ₂ found
15	30	20	10	21.65	21.10
16	40	20	10	27.25	27.20
17	60	20	10	25.12	25.11
18	30	30	10	30.40	30.38
19	30	40	10	20.73	20.73
20	40	30	10	19.01	19.00
21	40	40	10	20.05	20.06
22	30	80	10	24.14	24.16

REFERENCES

1. Matuszak, M. P. *Ind. Eng. Chem., Anal. Ed.* 4 (1932) 98.
2. Harrower, J. R., and Wiley, F. H. *J. Ind. Hyg. Toxicol.* 19 (1937) 486.
3. Lehmann, K. B. *Arch. Hyg.* 20 (1894) 61.

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