[Contribution from the Department of Gas Engineering, Johns Hopkins University]

THE DETECTION AND ESTIMATION OF TRACES OF CARBON DISULFIDE IN SMALL GAS VOLUMES[1]

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Coal gas and carburetted water gas contain as a normal constituent sulfur in organic combination. This is chiefly carbon disulfide[2] and the formation of this compound places an important limitation upon the use of high-sulfur coals and oils for gas-making purposes.

In commercial coal carbonization, the chemical and thermal conditions are so complex that it is difficult to determine those which assist or minimize the formation of this undesirable compound. Accordingly, a study of carbon disulfide formation under laboratory conditions, using 5 g. of coal, was projected. This quantity will ordinarily yield less than 2 liters of gas, and this, if comparable with commercial coal gas, may be expected to contain approximately 1 mg. of "organic sulfur."

For the detection and determination of carbon disulfide in small quantities of gas, the method of Harding and Doran[3] appears to be the most convenient, because the requisite chemicals are readily available, the cupric xanthate is specific for carbon disulfide, and the precipitation of the carbon disulfide appears to be quantitative, thereby making the method apparently applicable to small quantities of this compound.

To test its suitability more fully, a number of preliminary tests were made using air volumes of from 1 to 4 liters containing approximately from 1 to 6 mg. of sulfur in the form of carbon disulfide.

Although the method of Harding and Doran was observed in all essential details[4] no precipitate was obtained, even when the solutions were allowed to stand overnight. Tests were then made with Baltimore city gas known to contain carbon disulfide. Although from 2 to 4 liters of gas was passed slowly through the absorbent train, no precipitate of cupric xanthate could be obtained. When the two test-tubes were treated separately the first one in the series showed a pale green by transmitted light, but remained clear, while the second tube gave the same light blue that was transmitted by a blank.

It was, therefore, necessary to study the conditions governing the pre-

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[1] Read before the Gas and Fuel Section of the American Chemical Society, at the 69th Meeting, Baltimore, Maryland, April 6 to 10, 1925.

[2] Hutton and Thomas, *Gas Age*, **47**, 88 (1921).

[3] Harding and Doran, This Journal, **29**, 1480 (1907).

[4] The only modification made was in the substitution of cupric sulfate for the cupric acetate. Since the test solution contained an excess of potassium acetate, this substitution did not constitute an essential change in the conditions of the test.

cipitation of small amounts of cupric xanthate. Accordingly, a weighed quantity of pure carbon disulfide was dissolved in a known volume of alcohol, so that one drop of the solution represented 0.2 mg. of carbon disulfide. This solution was dropped into absolute alcohol saturated with potassium hydroxide, the alkali was neutralized with glacial acetic acid, copper sulfate solution was then added, and the whole diluted and allowed to stand. A series of tests was made in which the quantities of carbon disulfide, alcoholic potassium hydroxide, acetic acid, and copper sulfate were varied among themselves, and diluted to various volumes.

These tests showed that small quantities of cupric xanthate (for example that corresponding to about 0.4 mg. of carbon disulfide) can be precipitated at once only by maintaining a small total volume (about 6 cc.) and only a slight excess of acetic acid. The precipitation is aided by the use of an excess of cupric ion. When the total volume or acidity or both are too high, the cupric xanthate apparently forms a sol which coagulates only very slowly if at all.

The colloidal properties of cupric xanthate here indicated probably account for the doubt which has been thrown upon its constitution[5] and may explain the analytical errors attributed to methods which employ it.[6]

With the tests mentioned above as a guide, a number of additional tests were made upon small volumes of illuminating gas, and upon small volumes of air containing added traces of carbon disulfide. Finally, the following procedure was adopted for their analysis.

An absorption bulb, designed to bring the gas into intimate contact with two 1cc. portions of the alcoholic potassium hydroxide solution, was prepared by drawing down 18mm. glass tubing into a number of constrictions so as to form a series of five pears, each of which measured about 40 mm. from constriction to constriction. Pieces of 6mm. glass tubing were then sealed to each end and extended to a length of about 25 mm. The whole was then bent and tied with a glass rod as shown in Fig. 1, G. The operations at the blast lamp require only a short time and no great skill. The resulting bulb proved very satisfactory, not only because it brought two 1cc. portions of the solution in series into intimate contact with the gas stream, but also because it required only a small quantity of washing liquid, thus making it possible to precipitate the cupric xanthate in a small total volume. Available bulbs of other forms such as, for example, the Geissler bulb, may require as much as 16 cc. of scrubbing liquid and more rinsing liquid, and were therefore not considered satisfactory for the purpose at hand.

The gas was first passed through about 40 cc. of 5% potassium hydroxide solution contained in a bubbling tube (Fig. 1, C) whose enlarged portion was approximately 25 mm. in outside diameter and 225 mm. in length. This removed most of the carbon dioxide. To effect a more complete removal, the gas was then passed through a second tube containing about 6 cc. of the 5% potassium hydroxide solution. This tube was

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[5] Harding and Doran, THIS JOURNAL, **29**, 1476 (1907). Johnson, *ibid.*, **28**, 1209 (1906). Macagno, *Chem. News*, **43**, 148 (1881).

[6] See, for example, Spielmann and Jones [*J. Soc. Chem. Ind.*, **38**, 185 (1919)], and also Allen's Organic Analysis, Blakiston Co., **1910**, fourth ed., vol. 3, p. 228.

about 14 mm. in diameter and about 100 mm. long (Fig. 1, D). The gas was then dried by passing it through about 25 cc. of concd. sulfuric acid contained in a tube whose enlarged portion measured about 25 mm. in diameter and about 160 mm. in length (Fig. 1, E). The forms of C, D and E, Fig. 1, were chosen because they minimized the use of rubber stoppers and rubber connections, yet provided an apparatus that could easily be made and used by the average technical worker. Their dimensions may of course vary within wide limits. In order to secure small bubbles, and a minimum of pulsation, a small amount of broken glass was introduced into C, D and E, and the gas flow was regulated by the pinch clamp between G and H.

From the sulfuric acid, the gas was next passed through glass wool to remove spray if present, then through the freshly prepared alcoholic potassium hydroxide and finally to waste. In order to avoid loss of carbon disulfide by leakage the entire system from gasometer Bottle B on was maintained under a slight vacuum by placing Bottle I on the floor. The tubes in Bottles A, B and H were arranged as shown in order to give Mariotte bottle effects and so minimize the changes in rate of flow due to changes in head.

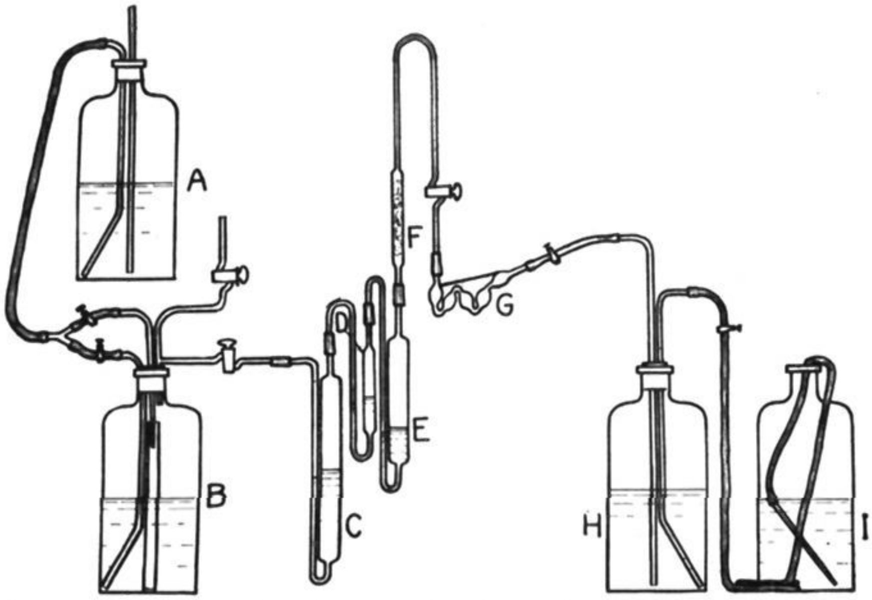

Fig. 1.—Apparatus for the quantitative estimation of traces of carbon disulfide in small gas volumes.*

* This drawing was not made to scale.

About 2 liters of gas was passed through the system in about half an hour. The chain was then swept out with 300–400 cc. of air (free from carbon disulfide), introduced between B and C. The alcoholic potassium hydroxide solution was then transferred to a 50cc. beaker with the aid of a very small quantity of distilled water, so that the total volume of the solution and washings did not exceed 12 cc. The solution was then warmed slightly and stirred to expel gases, cooled, acidified by the addition of 0.7 cc. of glacial acetic acid, and treated with a carefully measured volume of standard 0.01 *N* copper sulfate solution in excess. Usually, exactly 4 or 5 cc. of the copper solution was taken. The whole was then allowed to stand, preferably overnight, to insure complete precipitation of the copper xanthate. The solution, containing the excess of copper, was then filtered off through paper, and the precipitate washed thoroughly with three or four portions of water, measuring 10 to 15 cc. each, until all of the soluble copper was completely removed from the filter.

An attempt was made to estimate the excess of copper in this filtrate by adding to it a gram of finely divided potassium iodide, allowing the solution to stand for a few minutes, then titrating the liberated iodine with a standard 0.01 *N* sodium thiosulfate solution, using freshly prepared starch as an indicator. This, however, proved impossible, as an apparent end-point was reached before the requisite volume of sodium thiosulfate solution had been added. Upon allowing the solution to stand, re-bluing occurred, and a second or a third deceptive end-point might be obtained. Attempts to follow this bleaching and re-bluing to a consistent end-point proved to be without avail.[7]

The iodimetric estimation of copper is considered very accurate. It appears, however, that this is true only when certain conditions are observed, among these being a copper concentration much higher than those obtained in the experiments of the writer, detailed above.

The difficulty with the end-point was overcome by evaporating the filtrate and washings to dryness on a steam-bath, taking up with 5 cc. of hydrochloric acid (containing one part of the concentrated acid to 15 parts of water), adding 1 g. of finely powdered potassium iodide, allowing the solution to stand for three minutes, then titrating with 0.01 *N* sodium thiosulfate solution. As the end-point was approached, 2 cc. of freshly prepared starch indicator (containing 2 g. of soluble starch per liter) was added. The total volume at the end, including that due to the added thiosulfate and starch solution, did not exceed 10 to 12 cc. This procedure gave sharp end-points which re-blued only very slowly.

A convenient buret for this titration can be prepared by cutting the tip from a Mohr pipet calibrated for a total volume of 5.00 cc. in 0.05cc. divisions. A short rubber tube, a pinch clamp, and a special glass tip may then be attached. This glass tip should be drawn to a long capillary, whose length and diameter are such that the full free flow of the buret is only dropwise. With this, a fraction of a drop can conveniently be drawn. This buret is by no means novel, but its use is here described not only because it is desirable in connection with the present problem, but also because it can be applied with profit by the gas and fuels chemist in other procedures such as, for example, in certain methods for the determination of naphthalene in illuminating gas in which small quantities of picric acid are estimated.

Harding and Doran in the article describing their method for illuminating gas give no analyses of gases of known carbon disulfide content, showing instead that analyses of a city gas gave consistent checks. In view of the questions which have been raised concerning the accuracy of xanthate procedures, it seemed advisable to check the above method against a gas containing a known weight of carbon disulfide. Accordingly, a small

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[7] Harding and Doran make no mention of such a difficulty, yet the writer has received from gas and fuel chemists a number of adverse reports upon their method, based chiefly upon the failure to secure a satisfactory end-point.

quantity of pure carbon disulfide was dissolved in a sufficient weight of pure ethyl alcohol to give a solution of known carbon disulfide content (approximately 1%). A known weight of this was vaporized into a known volume of air, the resulting gas mixture was sealed and allowed to stand overnight to permit diffusion, and the gas so obtained was then analyzed. Two tests were made, giving the values reported in Table I.

TABLE I

THE QUANTITATIVE ESTIMATION OF SMALL AMOUNTS OF CARBON DISULFIDE

Gas taken, cc.	CS_2 taken, g.	$CuSO_4$ soln. taken, cc.	Thio. soln. required, cc.	Thio. soln. equivalent to CS_2	CS_2 found, g.	Error G. of CS_2
1960	0.00130	4.00	3.09	0.84	0.00133	0.00003
1960	.00069	4.00	3.49	.44	.00069	.....

One cc. of thiosulfate solution was equivalent to 0.001587 g. of CS_2. Four cc. of copper sulfate solution was equivalent to 3.93 cc. of thiosulfate solution.

These results were calculated on the assumption that the cupric xanthate possessed the normal formula, $Cu(CS_2OEt)_2$. The above method when applied to so small a quantity of material is not sufficiently precise to permit judgment between this ratio and that found experimentally by Harding and Doran under somewhat different conditions.

The chief error in the method appears to lie in the determination of the end-point. Even with the procedure given above, it was difficult for an experienced observer to estimate this accurately to within one-half a drop of 0.01 *N* solution, which represents a possible error of over 5% on the smaller quantity of carbon disulfide taken. Gas volumes sufficient to give a milligram or more of carbon disulfide should therefore be chosen for the quantitative examination.

It seemed desirable to ascertain the minimum amount of carbon disulfide which could conveniently be detected qualitatively, using further refinements in the procedure. Accordingly, an absorption bulb, designed to scrub a gas stream with a few drops of alcoholic potassium hydroxide solution, was prepared by drawing down 6mm. tubing and fashioning this in miniature after the five-pear bulb described above, save that a length of the original tubing was allowed to remain on each end for hose connection, instead of sealing on other tubing. Six to eight drops of freshly prepared alcoholic potassium hydroxide solution were then placed in the bulb so that the gas stream passed through two 3- to 4-drop portions in series. A 100cc. sample of air containing a known amount of carbon disulfide was then examined by passing it first through two 2cc. portions of 5% aqueous potassium hydroxide solution in series, then through 2 cc. of concd. sulfuric acid, then through the small absorption bulb described. Throughout, the system was maintained under a slight vacuum to prevent loss of carbon disulfide. The gas flow was so regulated that it required about 20 minutes to pass the 100 cc. because a more rapid rate carried the alcoholic solution forward through the small bulb. When the sample of gas had been passed forward, the system was swept out with 40 to 50 cc. of air free from carbon disulfide. The alcoholic potassium hydroxide solution was then washed out upon a small watch glass (about 4 cm. in diameter) with the aid of a few drops of water, and evaporated over a water-bath until only a drop or two remained. The watch glass was then cooled, a couple of drops of glacial acetic acid were then added, and finally four or five drops of 0.01 *N* cupric sulfate solution. This test was made upon a number of samples of air containing various amounts of carbon disulfide. With samples containing 0.02 mg. or more of this substance a yellow precipitate of cupric xanthate could be detected immediately after the copper solution was added. If possible, two to three times this quantity of carbon disulfide should be taken.

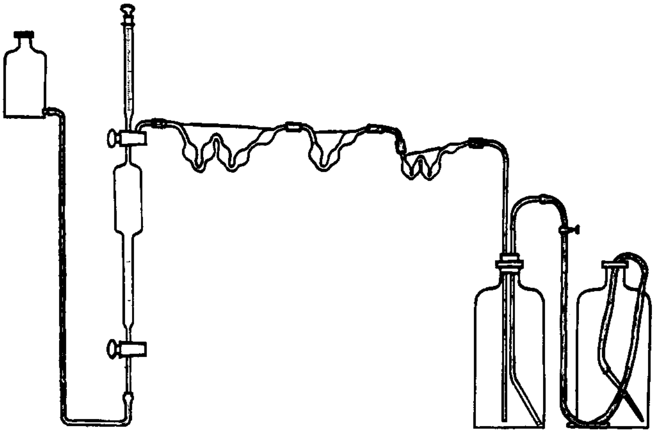

Fig. 2.—Th equalitative detection of traces of carbon disulfide in small gas volumes.*

* This drawing was not made to scale.

Fig. 2 illustrates the set-up of the apparatus used for detecting the carbon disulfide contained in a sample of gas from an ordinary 100cc. Tutwiler buret.

Summary

The need of a method for the detection and estimation of traces of carbon disulfide in small volumes of gases has been indicated, and a qualitative method capable of detecting 0.02 mg. of carbon disulfide in a volume of 100 cc. of gas, and a quantitative method capable of estimating 1 mg. or more of carbon disulfide in a somewhat larger gas volume have been developed and are here reported. This method was developed from a study of the method of Harding and Doran for larger quantities, and like that method, depends upon the formation of cupric xanthate, the excess of copper being determined iodimetrically.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

MIXED AQUO-AMMONOCARBONIC ACIDS. I. AMMONOLYSIS TO AMMONOCARBONIC ACID

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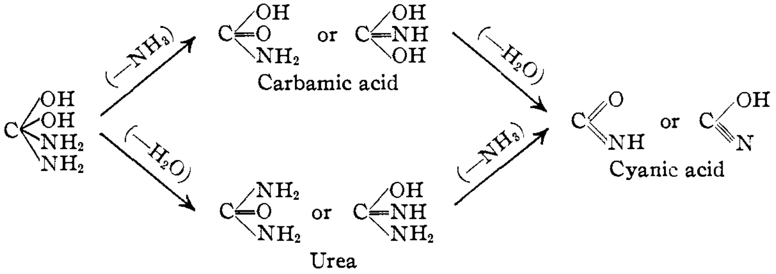
Mixed aquo-ammonocarbonic acids may be defined as substances which are derivatives of both water and ammonia in the sense in which ordinary carbonic acid is a derivative of water, and in which the ammonocarbonic acids[2] are derivatives of ammonia. As such, they may be regarded as desolvation products (that is, formed by loss of water, or of ammonia, or of both) of one of three hypothetical mixed aquo-ammono-orthocarbonic acids: $C(OH)_3NH_2$, $C(OH)_2(NH_2)_2$, or $C(OH)(NH_2)_3$. This may be represented by a scheme such as the following.



Water or ammonia may, furthermore, be lost in such a way as to give rise to mixed aquo-ammonocarbonic acids containing two or more carbon atoms, as in the familiar formation of biuret and of cyanuric acid from urea, $2CO(NH_2)_2 = HN(CONH_2)_2 + NH_3$, and $3CO(NH_2)_2 = (HNCO)_3 + 3NH_3$.

The number of mixed aquo-ammonocarbonic acids which can be formally derived in this manner is very large. There are 65 mixed aquo-ammonocarbonic acids containing three carbon atoms or less, which should theoretically be capable of existence. Of this number 23 have actually been prepared either in the free state, as salts or, most commonly, in the form of esters.

Mixed aquo-ammonocarbonic acids may be conceived as being formed,

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[1] The material in this and the following paper is from a thesis submitted to the Department of Chemistry and the Committee on Graduate Study of Stanford University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1924.

[2] Franklin, THIS JOURNAL, **44**, 486 (1922).