An Apparatus and Method for Determining Hydrogen Sulphide. *Subject* in Illuminating Gas.

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An Apparatus and Method for Determining Hydrogen Sulphide in Illuminating Gas.

The apparatus herein described was designed as a means of testing the efficiency of a set of gas purifiers, such as are used in the manufacture of coal gas or carburetted water gas for illuminating purposes. It combines the accuracy of the gravimetric cadmium chloride method and the rapidity of the Tutwiler Method.*

The apparatus consists of a bulb (A) of 300 cc. capacity, about 18 cm. long and 5 cm. in diameter, sealed at the lower end and contracted at the top to 13 mm. To the contracted end is fused the tube (G) terminating in a Greiner and Friedrichs stop-cock (D), to which is fused burettes (B) and (C), each having a capacity of 10 cc. Burette (B) is 20 cm. long and 13 mm. in diameter, calibrated in the middle portion (C) is 34 cm. long and 10 mm. in diameter graduated into 10 cc. and reading to tenths of one cc. Both (B) and

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(C) are fitted with stoppers. To one side of bulb (A) at (L) 14 cm. from the base of (A), is attached tube (T), 7 mm. in diameter and terminating at (M), bearing a stop-cock (F) 25 mm. from (L), a U tube (J), a bulb (O) of 10 cc. capacity and a bulb (P) 2 cc. in capacity. To the opposite side of bulb (A), at (H) 12 cm. from the base of (A), is fused tube (K), 7 mm. in diameter, beginning at (I) and extending into the bulb and terminating at (N) 20 mm. from its base. (K) bears the stop-cock (E), 30 mm from (H). (S) is a clamp which supports the apparatus. When passing gas through the apparatus, it is supported by placing it in a hole in a block of wood.

In making a determination, from 100 to 150 cc. of strong solution of cadmium chloride (28 grams per liter), is run into bulb (A), stop-cock (F) being open and (E) closed. The apparatus is then tilted in such a position that 5 or 6 cc. of the solution pass into bulb (O) which acts as a seal and indicator, preventing traces of hydrogen sulphide from escaping unabsorbed, and indicating when the cadmium chloride solution in (A)

is nearly spent. Bulb (P) prevents traces of solution in (C) from being carried from the apparatus.

Burette (C) is filled with a standard solution of iodine, two solutions of different iodine strengths being used, one containing 4.828 grams of iodine per liter and another one-tenth as strong. The strong solution is of such a strength that 1 cc. is equivalent to 10 grains of hydrogen sulphide per 100 cu. ft. when one-tenth of a cu. ft. of gas is used in the determination and is used in testing the crude gas while the weaker solution is used in testing partially purified gas. Stop-cock (D) is closed and (A) is connected at (M) with the meter and at (I) with the gas supply cock by means of rubber tubing. The meter is read, (E) is opened and the flow of gas so regulated that from 1 to 1.50 cu. ft. pass through the apparatus per hour. When a color appears in bulb (O) the gas is shut off by closing stop-cock (E) and the meter reading taken. In testing partially purified gas when no color has appeared in (O) after 1/10 cu. ft. of gas has passed, but when a

perceptible precipitate has formed in (A), the gas supply is cut off. If a perceptible precipitate has not appeared in (A) after 1/10 cu. ft. has passed, the flow is continued until one does appear.

The apparatus is disconnected from the meter and gas supply, removed from its support, (D) opened and then so tilted that the solution in (C) runs back into (A). Wash water is drawn in through (M) by applying suction at top of (B) and through (K) by opening (E), closing (F) and applying suction at top of (B). The gas above the solution in (A) is removed by opening (F) and applying suction at top of (B). (D) is closed and fresh starch solution run into (B), then (D) is opened and the starch solution run into (A). (E) and (F) are closed and the air in (A) placed under diminished pressure by applying suction at top of (B). (D) is then closed and (B) is filled with concentrated hydrochloric acid which is allowed to pass slowly into (A) until the precipitate of cadmium sulphide is completely dissolved. A little excess of hydrochloric acid is then run in and (D) closed.

The hydrogen sulphide thus liberated in (A), under diminished pressure and out of contact with air is titrated with the iodine solution. Burette (C) is read and the iodine solution introduced intermittently cy carefully opening (D), the apparatus being shaken after each addition. When the starch-iodo blue color persists for one half minute, the end point in the titration has been reached. (The pink or violet color which first appears in the solution must be distinguished from the starch-iodo blue which is the correct end point). (C) is then read. The apparatus is then emptied, rinsed with water and a blank test run to determine the amount of iodine solution necessary to produce the permanent starch-iodo blue color. In making this test the same amount of starch solution and the same volume of water as is used in the determination is used and the whole acidified with hydrochloric acid. From the amount of gas and the volume of iodine solution used in the determination and in the blank, the number of grains of hydrogen sulphide per 100 cu. ft. of gas is calculated. For control work

the volume of gas used need not be reduced to its corresponding volume at standard conditions of temperature and pressure.

. Comparative determinations of hydrogen sulphide were made by the gravimetric cadmium chloride, the Tutwiler and the volumetric cadmium chloride methods. In these determinations the meters used were dry meters checked against each other. The samples were taken simultaneously and the volume of gas used reduced to corresponding volume at standard conditions of temperature and pressure by means of the following formulae:

$$V = v \frac{17.64\ (h-a)}{460 - t} \qquad n = \frac{17.64\ (h-a)}{460 - t}$$

$V = v\ n$ where

V = volume of gas at 60° F and 30" pressure.

v = observed volume

t = observed temperature in Fahrenheit degrees.

h = observed barometric pressure

a = tention of aqueous vapor at t.

n = correction factor for t and h.

The following results in grains per 100 cu. ft. were

obtained:

COAL GAS.			WATER GAS		
Grav. $CdCl_2$	Vol. $CdCl_2$	Tut	Grav. $CdCl_2$	Vol. $CdCl_2$	Tut
2.72	2.93	31	0.59	0.55	16
0.53	0.46	22	0.26	0.23	8
0.89	0.79	27	0.40	0.36	11
1.58	1.54	38	0.15	0.13	5
1.00	0.92	24	0.34	0.31	12
2.68	2.65	30			
1.31	1.25	23	Crude Coal Gas.		
2.35	2.26	29			
1.81	1.72	27	225	220	360
0.88	0.84	18	190	188	310
4.86	4.76	110			
2.73	2.69	65			
1.22	1.18	25			
2.72	2.61	28			
1.65	1.59	30			
1.30	1.26	26			
1.09	1.04	24			

The uniformly higher results obtained by the gravimetric method may be due to the absorption of sulphur compounds other than hydrogen sulphide, a much larger volume of gas and cadmium chloride solution being used in the gravimetric method than in the volumetric method.

The principle advantage of Tutwiler's method is its rapidity. A test can be made in about three minutes. Its chief disadvantage is its inaccuracy. The results obtained are only approximate especially on the

partially purified gas, the error varying from 1000 to 4000 per cent as shown by the comparative tests above. This error is due to the titration of the gas with the iodine solution, the unsaturated hydro-carbons, cyclo-pentadiene* and probably sulphur compounds other than hydrogen sulphide reacting with the iodine. Results on the crude gas are less inaccurate, the error amounting to about 15 per cent. This is of course due to the much greater ratio between the amount of hydrogen sulphide present and the other compounds with which the iodine reacts. McMillar states in the original publication of Tutwiler's method that 15 grains of hydrogen sulphide per 100 cu. ft. of gas could escape detection. In the writer's experiments, in no case did the Tutwiler show less than 10 grains per 100 cu. ft. on clean coal gas nor less than 4 grains per 100 cu. ft. on clean water gas.

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* London Journal of Gas Lighting 4/5/10. P. 41;
4/12/10 P. 18.

The gravimetric cadmium chloride method is the most accurate in use at the present time. The great objection to this method, however, in control work is the length of time required to make a determination. The purifying boxes foul quite rapidly and in determining their efficiency tests should be made rapidly and as near ly simultaneously at inlet and outlet of purifier as possible. A method which requires hours for a test becomes impracticable. The large bulk of cadmium chloride solution used allows absorption of other sulphur compounds than hydrogen sulphide, which when oxidized with the bromine give too high results. Another objection is the large amount of cadmium sulphide precipitate required to produce an amount of barium sulphate which can be readily and accurately weighed. When a sample of 0.1 cu. ft. of gas is taken, each milligram of $BaSO_4$ is equivalent to 2.252 grains of sulphur per 100 cu. ft. Thus for partially purified gas containing but a fraction of one grain of hydrogen sulphide per 100 cu. ft., a number of cu. ft. of gas must be used in order to obtain a weigh-

able precipitate.

The volumetric cadmium chloride method has several advantages over the gravimetric method. Accurate results are obtained on a much smaller volume of gas; a smaller volume of cadmium chloride solution causes less absorption of sulphur compounds other than hydrogen sulphide; the method is much more rapid, requiring for a determination instead of hours, from seven to ten minutes, depending upon the purity of the gas.

The advantages of the volumetric cadmium chloride method over the Tutwiler are several. Twenty-eight times as much gas is used in the average determination as is used in the Tutwiler; the burette readings are one-tenth those of the Tutwiler and much more accurate results on gas of low hydrogen sulphide content are obtained. A test can be made in from seven to ten minutes.

Instead of using a meter, a graduated cubic foot bottle may be used for measuring the volume of gas used.

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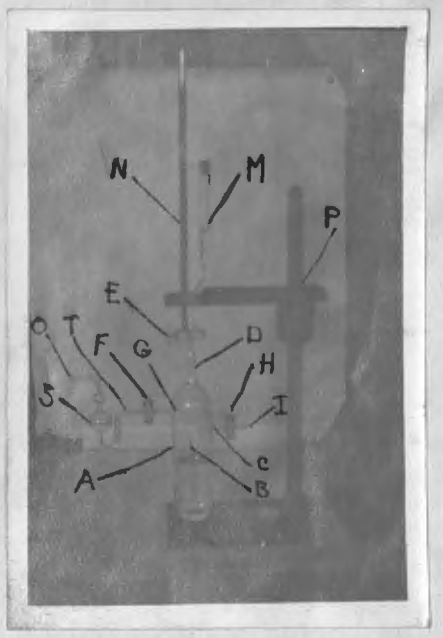

Bibliography of Methods Used for Determining Hydrogen Sulphide in Illuminating Gas.

Jour. Cham. Ind. 1884. P. 13.

Hydrogen Sulphide in Coal Gas.

A. Wanklyn.

Gas in 1/10 cu. ft. bottle. Lead acetate solution run in. Gas tested for complete removal by means of lead acetate paper. Calculations made from amount of lead acetate solution required.

Jour. Chem. Ind. 1889. P. 136.

P. Behrend & H. Kast.

Bunte Method. 100 C. C. of gas taken in Bunte burette. Starch and Iodine solution added. Results checked gravimetrically by passing H_2S and clean coal gas thru acid solution of lead acetate.

Analyst - 1902 - 27 - 219.

Detection and Estimation of minute quantities of H_2S in coal gas.

W. J. Dibbin & R. C. Grimwood.

Lead Acetate paper used. One grain H_2S per 600,000 cu. ft. could be detected. Time to produce stain a measure of amount of H_2S SO_2 interferes. Above 1 part in 2500 renders colorimetric results valueless.

Jour. Gas Lighting, 1910-112-28.

Somerville.

Gas passed into I_2 solution and starch, until color disappears. H C N acts on I_2. Determined in separate experiment by means of $PbCO_3$.

Jour. Für Gasbeleuchtung, 43-792-793.

A. Muller.

The Estimation of Hydrogen Sulphide in Coal Gas.

The reagents required are a strong acetic acid solution of cadmium acetate, and a sulphuric acid solution of copper sulphate. Gas passed at moderate rate than 25 C.C. of first solution in erlenmeyer flask. Second solution added, heated to 50 or 60° C. Precipitate of Cu) filtered off, washed, calcined, weighed.

H_2S calculated from weight of CuO.

Jour. Gas Lighting 1900 - 76, - 1265.

H. L. Greville.

Gas passed into strong NH_3, then distilled water, contained in Harcourt flasks. Lead Acetate paper at outlet of second. Wash tubes into basin, titrate with ammoniacal solution of copper sulphate 1 C. C. = .05 Grs. of H_2S. .4 to .6 Cu. Ft. passed per hr. without paper showing.

Zeit. Anal. Chem. 1906-XIV P. 541-551.

O. Brunck.

The Iodometric determination of H_2S.

"Direct titration of H_2S with I_2 (exposed to air) invariably yields low result even when made rapidly. Correct results by modification of Fresenius method in which the dilute solution of H_2S is run into an insufficient amount of I_2 solution, then rest of I_2 solution.

Jour. Gas Lighting. 1908. Vol. 103-P 167-168

F. Carpenter.

Estimation of Minute Quantities of H_2S in Coal Gas.

Papers prepared from 12% Lead Acetate Solution.

5% Glycerol added to some. NH_3 to some.

Dry limit 1 : 1 million.

Moist limit 1 : 10 million.

Hempels Gas Analysis.

Dupasguier Method- Measured amount of gas drawn thru I_2 solution in KI to which starch paste is added. Gas stopped when solution is colorless.

Hempels Gas Analysis.

Gas drawn thru Bromine water pt H_2SO_4 with $BaCl_2$. Weigh $BaSO_4$.

Bunsen. In gas with H,N,CO_2, Hydrocarbons, with balls of MnO_2 covered with solution of phosphoric acid.

In Royle.

Wanklyn bottle (1/10 cu. ft. capacity). Titrate gas with I_2 sol and starch indicator. "Results at the best are only very approximate be-

cause undoubtedly the sulphur compounds other than H_2S have an effect on the iodine causing an incalculable error".

Zeit Für Chemie. 10 - 75.

R. Fresenius.

Gas passed over pumice, covered with $CaSO_4$ gravimetric method.

Jour. Am. Chem. Soc. Vol. 23, P. 173.

C. C. Tutwiler.

Abstracted in paper.

London Jour. of Gas Lighting 4/5/10-p 41;4/12/10 p. 18.

Ross & Race.

Effect of Cyclopentadiene on I_2 solution.

J. C. S. of London, Vol. 43-1883. T. P 267.

L. Wright.

H_2S in Coal Gas.

Di-Tri-Ortho phosphate used. (Na_2HPO_4 & $CuSO_4$ Reagent placed in two U tubes. Cotton wool at either end. Necessary to first saturate with clean coal gas.

NH_3 absorbed in tube of Pumice and Phosphoric acid. $CaCl_2$ tube at inlet and outlet. Weigh tubes before and after passing gas. Increase in weight shows H_2S.

Gravimetric Cadmium Chloride Method.

Abstracted in Paper.

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