THE DETECTION AND ESTIMATION OF MINUTE QUANTITIES OF
SULPHURETTED HYDROGEN IN COAL-GAS.

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OWING to a recent proposal to modify the test for sulphuretted hydrogen as used on the London gas supply, it became necessary to ascertain, as no published data could be found on the point, what was the best means of estimating small quantities of sulphuretted hydrogen in coal-gas, and what degree of delicacy could be attained in its detection.

The apparently sensitive colour reaction between sodium nitro-prusside and an alkaline sulphide was examined, but it was found that the sensitiveness was more apparent than real, a much larger quantity than is ever likely to be present in purified coal-gas being required to produce any colour.

Recourse was therefore had to the coloration of lead salts, which is the system at present in use. Although it is well recognised that this reaction is a very delicate one, it is somewhat surprising to find how extraordinary its delicacy is; in fact, instead of there being any difficulty in detecting minute traces, the difficulty is to modify the test so that infinitesimal traces are not detected.

An attempt to produce a titrateable solution of a lead salt by passing through it gas containing sulphuretted hydrogen was unsuccessful, owing to the colour which was also produced by tarry matters in the gas. The coloration of paper soaked in a solution of a lead salt was next examined, papers soaked in various strengths of lead salts in solution being compared. From the results of this comparison it was decided to adopt a paper prepared by moistening with an approximately 12 per cent. solution of lead acetate, the paper whilst still wet being placed for a few minutes in an atmosphere of ammonia gas. Papers prepared in this way are used in London for testing the purity of the gas supply.

For several reasons it was found preferable to use these papers dry, considerable difficulty being found in distinguishing when the colour first appeared on a wet paper, and also because when wet they were unworkably sensitive.

The apparatus employed for preparing the sulphuretted hydrogen-contaminated gases consisted of a glass reservoir of known capacity, into which measured quantities of sulphuretted hydrogen could be introduced. As soon as the sulphuretted hydrogen had thoroughly diffused the contaminated gas was examined by expanding a toy balloon inside the reservoir, and thus forcing the gas through a small bore tube, so arranged that the gas as it issued from it impinged on a lead paper prepared as already described. The following illustration shows the apparatus employed.

The reservoir, the capacity of which is 15,500 c.c. when the balloon is deflated, is fitted at the neck with an I.R. stopper pierced with three holes, one fitted with a cock of sufficient bore to pass at least ten feet of coal-gas per hour under the ordinary gas-supply pressure; the second with a glass tube, reaching about one-third down the reservoir, to the end of which is fitted gas-tight an I.R. balloon capable of being expanded so as to fill the reservoir; and the third with a narrow bore glass tube leading to the apparatus where the examination is made.

This consisted of a bell-jar standing in a mercury seal, and fitted at the top with a glass tube, which provides a secondary gas supply, and a cock and a burner, which gives a jet flame. By means of a cock or screw-clip on the inlet tube the height of the flame can be adjusted in this burner so that the gas burns at half a foot per hour.

At the bottom of the reservoir two tubes are fitted through an I.R. stopper, one of which connects with the gas-supply, and the other, which is of small bore, is fitted with a cock or clip.

To ascertain what amount of sulphuretted hydrogen could be detected in a coal-gas, a known volume of sulphuretted hydrogen was introduced through the capillary tube at the bottom of the reservoir, and allowed to diffuse through the gas. This, as

a rule, took from thirty to forty-five minutes. When diffusion was complete, the balloon was partially inflated, thus forcing some of the gas into the apparatus containing the lead paper, which was fixed in such a way that the gas impinged directly on it. In order to insure the thorough diffusion of the sulphuretted hydrogen a second test was always made with the apparatus connected to the bottom of the reservoir and the spots on the two slips of paper compared.

If sulphuretted hydrogen was in this way detected, a measured volume of the contaminated gas was withdrawn from the reservoir and the remainder washed out by a current of coal-gas, the gas being burnt from the cock at the top. As soon as the gas in the reservoir was free from sulphuretted hydrogen, the measured volume of contaminated gas was replaced, diffusion allowed to take place, and the contents again examined. By this means it was possible to detect, within a reasonable time,

one volume of sulphuretted hydrogen in 1,000,000,000 of coal-gas, equivalent to approximately 1 grain of sulphuretted hydrogen in 600,000 cubic feet of coal-gas.

Having thus found the limit to which it could be detected by this means, an attempt was made to produce a standard set of colours corresponding to varying proportions of sulphuretted hydrogen.

Owing, however, to the extremely evanescent nature of the colour-spot, and to the difficulty of being sure the colours matched, this was abandoned in favour of what was found to be a more certain method.

By regulating the lead paper to a known distance from the nozzle, where the gas issues, and passing the gas at a half-foot per hour, it was found that the time required for the production of a colour was a constant for that proportion at that distance.

DIAGRAM SHOWING TIME REQUIRED TO DETECT VARYING QUANTITIES
OF H_2S IN COAL-GAS.

The following table gives some of the mean results obtained by this method at different distances. The variation by different tests in any result was but slight.

Time taken to produce a Colour Spot on Lead Paper by Gas containing One Volume of Sulphuretted Hydrogen in								
Distance of Lead Paper from Nozzle at which Gas issues.	1,000 volumes of Coal-Gas.	10,000 volumes of Coal-Gas. min. secs.	250,000 volumes of Coal-Gas. min. secs.	One million volumes of Coal-Gas. min. secs.	Ten million volumes of Coal-Gas. min. secs.	100 million volumes of Coal-Gas. min. secs.	1,000 million volumes of Coal-Gas. min. secs.	10,000 million volumes of Coal-Gas. mins.
Close to...	at once	0 2	0 5	0 8	1 7	5 0	11 30	more than 30 mins.
$\frac{1}{8}$ inch ...	„	0 4	0 10	0 15	1 30	—	—	„
$\frac{1}{4}$ inch ...	„	0 8	0 15	0 30	1 50	12 0	21 30	„
$\frac{1}{2}$ inch ...	„	0 12	0 18	—	2 20	—	—	„

Two curves have been plotted on the results obtained, the ordinates representing the number of volumes of coal-gas containing one volume of sulphuretted hydrogen and the abscissæ time in seconds. The ordinates are plotted in geometrical progression, it being obviously impossible to plot them as an arithmetical progression, and consequently time is plotted in the same manner. Two curves have been plotted in order to show the importance of the distance factor.

The right-hand curve represents the results found when the lead paper was close to the point of issue of the gas, and the left-hand curve the results obtained when the paper was adjusted to a distance of $\frac{1}{4}$ inch from the nozzle.

DISCUSSION.

Mr. R. ORCHARD said that Dr. Rideal had experimented in a similar way to that described by Mr. Grimwood. In his experiment, using the gas referees' apparatus, Dr. Rideal had found that the delicacy of the official test was such that 1 part of sulphuretted hydrogen in five millions could be detected, passing 5 cubic feet of gas per hour. At first a gold-beater's skin balloon had been used. Subsequently a rubber balloon was tried, but it was found very difficult to free the rubber from sulphuretted hydrogen, and on allowing the apparatus to stand over-night, although on the previous evening the gas was free from sulphuretted hydrogen, after twelve to twenty-four hours a reaction was obtained from the rubber. The use of a rubber balloon had therefore been discontinued. Dr. Rideal had used a carboy with a large gold-beater's skin balloon in it, the carboy holding about 40 litres, and, using the official apparatus with six jets, he had found the minimum delicacy to be one in five millions.

Mr. HEHNER said that the delicacy of the sulphuretted hydrogen test by lead paper was exceedingly great. It was unintelligible why sulphuretted hydrogen must on no account be present in coal-gas, while from 17 to 22 grains per 100 cubic feet of other sulphur compounds were permitted, seeing that the sulphuretted hydrogen would burn into exactly the same product as the other sulphur compounds. The

nitro-prusside test, which was credited with being delicate, was a blunt test compared with the lead acetate test. *P*-amido-dimethylaniline gave a beautiful blue coloration (methylene blue) in the presence of sulphuretted hydrogen and ferric chloride, and had been recommended by Caro as a reagent for sulphuretted hydrogen. He (Mr. Hehner) had convinced himself that it was not nearly so delicate as lead acetate. Lead acetate solution was, again, much inferior to dry lead paper. Discoloration could be observed on the paper long before it was apparent in the solution. The preparation of mixtures of air or coal-gas with minute known amounts of sulphuretted hydrogen and the quantitative removal of the mixture from the vessel for the purpose of making the tests was by no means an easy one, as of course no substance or liquid could be used that might absorb the trace of sulphuretted hydrogen. While Mr. Dibdin had used an india-rubber balloon, by the expansion of which the gas was driven out, Dr. Rideal objected to the india-rubber on account of the difficulty with which the sulphuretted hydrogen that was absorbed by the balloon could again be driven out. Dr. Rideal had used gold-beater's skin instead. He (Mr. Hehner), however, found that the gold-beater's skin rapidly removed, probably on account of the oil with which the skin was prepared, every trace of sulphuretted hydrogen, both from air and from coal-gas, so that after a few hours' contact no H_2S was left. He had found it simplest to withdraw from a large vessel in which the gas mixture had been prepared by crushing calibrated capillary glass tubes filled with sulphuretted hydrogen, after allowing sufficient time for diffusion, some of the gas by the action of an aspirator or pump, measuring the gas thus withdrawn, under ordinary pressure. As to the general results, his experience was entirely in accordance with that of Mr. Dibdin.

Mr. GRIMWOOD, in reply, said that with regard to the question of the absorption of sulphuretted hydrogen by the india-rubber balloons and the subsequent giving of it up again, this has not been their experience.

When the apparatus was first put together they found that the rubber absorbed sulphuretted hydrogen, but after it had once had as much as it would take up, they had no further difficulty with it.

The mode of procedure certainly prevented the possibility of any occluded sulphuretted hydrogen affecting the result, as a blank determination was always made before any sulphuretted hydrogen was introduced into the apparatus.

With regard to the difference in sensibility found by Dr. Rideal and themselves, it must be remembered that two estimations of such difficulty as this cannot be expected to agree unless they are carried out under the same conditions, and it seems most probable that Mr. Hehner's experience of the absorption of sulphuretted hydrogen by the oil dressing of the gold-beater's skin, together with the difference in the two methods adopted, accounts for their want of agreement.