must be removed, else ammonium chlorplatinate will be formed.

The decomposition and removal of ammoniacal salts by nitric acid is most applicable here. The process is described in "Crookes' Select Methods," page 32. If hydrochloric acid is present, it is beneficial, as the chlorine which would be liberated also decomposes ammoniacal salts.

THE DETERMINATION OF METHANE, CARBON MONOXIDE, AND HYDROGEN BY EXPLOSION IN TECHNICAL GAS ANALYSIS.

BY W. A. NOYES AND J. W. SHEPHERD.

Received March 7, 1898.

THE determination of carbon monoxide in technical gas analysis with the Orsat apparatus is not very satisfactory, partly because the gas is absorbed so slowly by the cuprous chloride, and partly because the cuprous chloride must be very frequently changed unless two absorption bulbs filled with the reagent are used. These difficulties may be avoided and the carbon monoxide, hydrogen, methane, and nitrogen may be determined by explosion, if the determination is accompanied by a determination of the oxygen consumed in the combustion, by explosion, of a known volume of the gas. For this purpose we have introduced in the Orsat apparatus in place of the fourth bulb an explosion pipette of the form shown in Fig. 1. The pipette has the advantage over that usually supplied with apparatus for gas analysis, that during the explosion the gas is confined by glass stop-cocks on both sides, insuring positively against loss during the moment of high pressure in the apparatus. A little sulphuric acid is added both to the water in the explosion pipette and to that in the measuring burette. This greatly decreases the ionization of the carbonic acid and so lessens the solubility of the carbon dioxide in the water. The results given below demonstrate that the error arising from the solubility of carbon dioxide in dilute acid in the case of mixtures containing six to eight per cent. of the gas must be very small.

Fig. 1.

For the purpose of determining the amount of oxygen remaining after the explosion, we have attached to the outer end of the capillary tube of the Orsat apparatus a small hydrogen generator of the form shown in Fig. 2. The hydrogen is generated from aluminum foil and a solution of potassium hydroxide of sp. gr. 1.27. The lower bulb of the generator should have a capacity of about twenty cc. The stopper bearing the delivery-tube of the generator is pushed into its mouth and covered with water to avoid diffusion of the hydrogen, and the rubber connection with the capillary tube of the Orsat is surrounded with a glass tube filled with water for the same reason. With these precautions, hydrogen, which is almost chemically pure, may be taken into the measuring tube of the apparatus whenever desired.

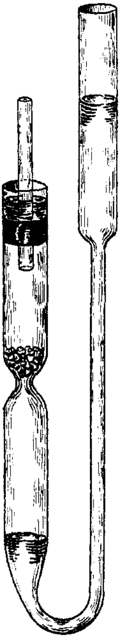

Fig. 2.

The analysis is carried out as follows: In the case of illuminating gas the carbon dioxide is absorbed in potassium hydroxide of sp. gr. 1.27, the illuminants in fuming sulphuric acid followed by the caustic potash, and the oxygen in an alkaline solution of pyrogallol. The residue is then left over the pyrogallol, the side bottle is raised till all gas is expelled from the capillary tube of the apparatus, and then about eighty-five cc. of air are taken in and accurately measured. In all measurements three minutes were allowed for the water to run down the walls of the burette. The burette was kept at a constant temperature by running water through the jacket surrounding it, as the temperature of the room where we worked was quite variable. To facilitate accurate reading, a scale corresponding to the scale of the burette, was made on the edge of the case of the apparatus. By means of such a scale it is very easy to bring the water in the side bottle to the level of the water in the measuring tube and also to bring the eye to the exact level required. After measuring the air, gas is admitted from the residue over the pyrogallol. The amount to be taken will vary, of course, with its character. It should be taken in such amount as to require nine to ten cc.

of oxygen for its complete combustion. If too much is taken, there may be danger of burning nitrogen, and also there will not be enough oxygen left for the second explosion with hydrogen. With a gas of unknown composition six to eight cc. may usually be taken at first and, if the mixture will not explode, hydrogen may be added, one cc. at a time, till an explosion can be secured. From the data thus secured the amount of the gas which should be used can be determined. Before attempting an explosion the gas should be passed into an explosion pipette and back to the measuring burette at least twice, and better three times, to secure thorough mixing. After the explosion the contraction is determined and then the carbon dioxide. Then about twenty cc. of hydrogen are added, and after mixture as before, and explosion, the contraction is determined. One-third of this contraction will give the amount of oxygen remaining after the first explosion. If this amount of oxygen be subtracted from the amount in the air originally taken, the difference will be the amount of oxygen used in the first explosion. Air is assumed to contain 20.9 per cent. of oxygen in these calculations.

The calculation of the results is based on the following equations, in which the symbols are used to represent volumes of gas:

1. $CH_4 + CO + H + N =$ Gas taken.
2. $2CH_4 + \frac{1}{2}CO + \frac{3}{2}H =$ Contraction.
3. $2CH_4 + \frac{1}{2}CO + \frac{1}{2}H =$ Oxygen consumed.
4. $CH_4 + CO = CO_2$ formed.

Hence

$H =$ Contraction less oxygen consumed.
$CO = \frac{2}{3}(2CO_2 + \frac{1}{2}H - O$ consumed).
$CH_4 = CO_2 - CO$.
$N =$ Total gas $- (H + CO + CH_4)$.

The following is an illustration of the record of an analysis:

	Reading.	Volume.
Air	12.96	87.04
Gas	0.58	12.38
Contraction	15.4	14.82
CO_2	23.39	7.99
H	1.24	22.15
Contraction	24.35	23.11
Oxygen originally present	....	18.19
" of second explosion	....	7.71
" of first explosion	....	10.48

Hence

		Per cent.
Hydrogen	= 4.34	= 35.06
Carbon monoxide	= 5.12	= 41.38
Methane	= 2.87	= 23.19
	12.33	99.63

To determine the accuracy of the method, a mixture of known composition was prepared. Hydrogen was first admitted into the measuring tube of the burette, from the generator described, and then methane, generated from sodium acetate and soda-lime, was introduced. After thorough mixture, three determinations of the proportion between the methane and hydrogen were made in the usual manner by explosion. The results agreed quite closely with the composition of the gas as determined by measurement, indicating that the methane was practically pure.[1] The results were :

	Calculated.	Found.			Average.
Methane	38.5	39.9	39.3	39.2	39.5
Hydrogen	61.5	60.0	60.0	60.7	60.2
	100.00	99.9	99.3	99.7	99.7

	Calculated.	Found.			Average.
Methane	37.6	38.2	38.0	38.5	38.2
Hydrogen	62.4	60.9	61.3	60.2	60.8
	100.00	99.1	99.3	98.7	99.0

There seems to be some tendency to high results for methane, but the close approximation to 100 for the total indicates that there was probably some loss of hydrogen by diffusion or absorption. If the gases are thoroughly mixed before explosion, there would seem to be no occasion for such gross errors in the determination of hydrogen as were observed by Gill and Hunt.[2] Gases mix by diffusion very much less quickly than is commonly supposed.

The remainder of the mixture of methane and hydrogen was then carefully measured and a mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with concen-

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[1] This accords with the statement of Freyer and Meyer, *Zeit. phys. Chem.*, 11, 28, but not with that of Gill and Hunt in this Journal, 17, 988.

[2] This Journal, 17, 992.

trated sulphuric acid was added. After removal of the carbon dioxide, the gas was again measured, and, on the basis of the result, combined with the results of the analysis of methane and hydrogen, the composition of the total gas was calculated. A series of analyses of the mixture was then made.

FIRST SERIES.

	Calculated.	Found.					Average
Methane	23.08	23.6	23.0	22.8	23.3	23.3	23.21
Carbon monoxide	41.52	39.6	40.6	40.9	41.2	40.5	40.55
Hydrogen	35.23	35.0	35.6	35.4	35.0	34.5	35.09
	99.83	98.2	99.2	99.1	99.5	98.3	98.85

SECOND SERIES.

	Calculated.	Found.						Average
Methane	22.37	22.7	23.1	22.6	22.7	22.7	22.4	22.68
Carbon monoxide	41.48	40.4	40.0	40.5	40.2	39.8	40.0	40.15
Hydrogen	35.80	35.3	35.4	35.6	35.9	35.7	35.9	35.64
	99.65	98.4	98.5	98.7	98.8	98.2	98.3	98.47

The objection that the error is multiplied because of the small amount of gas which must be taken for the explosion, applies to this method as it does to the usual explosion method for methane and hydrogen, of course. It is to be noticed, however, that the determination of methane, the most valuable constituent as a fuel, depends on the combined measurements of the carbon dioxide, the contraction, and the oxygen consumed, instead of depending on the carbon dioxide alone, as is the case with the older method. By the method in common use any carbon monoxide which has failed of absorption is counted as methane after the explosion. Another advantage is that the errors are of a compensating nature, so that when methane is found too high, carbon monoxide and hydrogen will usually be found low, and in such ratio that the total fuel value will be nearly constant.

We have used with the Orsat apparatus a stop-cock lubricant described by Professor Ramsay at the Toronto meeting of the British Association, though he said it was not original with him. Equal parts of black rubber, vaseline, and paraffin are heated to gentle boiling for a quarter of an hour in a beaker. The lubricant is sufficiently viscous to hold against an atmosphere of pressure, if necessary, gives no hydrocarbon vapor to a vacuum, and the stop-cocks in which it is used do not become set even after long standing. The last property makes it especially valuable for the Orsat apparatus.

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PROTEIDS OF THE PEA.[1]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

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IN a paper on the "Proteids of the Pea and Vetch"[2] the legumin obtained from these seeds was described and some account was also given of other accompanying proteids. Further study has furnished much additional information concerning these substances and made necessary a review of our former work on the pea and vetch.

On investigating the proteid constituents of the horse bean and lentil we found that by repeated fractional precipitations, the globulin from these seeds was separated into fractions, on the one hand wholly free from coagulable matter and on the other consisting of substance which was substantially all coagulable. The former we found to be legumin, in all respects like that described by us from the vetch, and the latter to be a new proteid of different composition and properties, to which we have given the name *vicilin* since we first recognized its presence in the horse bean (*vicia faba*).

This discovery led us to reinvestigate the proteids of the pea and we thus found that the legumin of that seed, as formerly described by us, was contaminated with more or less vicilin and that when the latter is completely separated the differences noted in our former paper between the legumin of the pea and that of the vetch disappear and preparations from these two seeds are identical in composition and reactions.

Leguminous seeds contain about one and two-tenths per cent. of alkali and one per cent. of phosphoric acid, while in the seeds of the cereals but five-tenths and seven-tenths per cent. of these substances respectively are present.

Liebig and Rochleder as well as Ritthausen attributed the

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[1] Reprinted from advance sheets of the report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

[2] This Journal, 18, 583; Report of the Connecticut Agricultural Experiment Station for 1895.