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### THE MOIST COMBUSTION METHOD OF DETERMINING CARBON IN STEEL.

BY GEORGE AUCHY.

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SOME recent experiences of the writer with the wet method of combustion show that this process may sometimes work faultily in the following particulars: First, the potash bulbs may not absorb all the carbon dioxide; Second, the "prolong" containing calcium chloride may not absorb all the moisture drawn over from the potash bulb; Third, the proportion of moisture so escaping from the prolong is not uniform and unvarying; Fourth, the potash solution may lose something besides moisture; Fifth, some chloro-chromic compound other than that absorbed by Prof. Langley's "pyro" mixture may occasionally form and cause high results.

With regard to the first of these points, it is the almost universal custom to use for the absorption of the carbon dioxide, a single set of weighed potash bulbs as directed by Blair in his description of the wet method. Prof. Langley, however, uses solid potash after the bulbs. Others use soda-lime tubes instead of potash bulbs. The writer in making determinations using the potash bulbs as customary obtained results varying very widely and was very much puzzled by them, believing at that time one set of bulbs to be ample for the complete absorption of the carbon dioxide. It was finally found, however, that a single set of bulbs is not always sufficient to absorb all the carbon dioxide in the wet method of combustion. Following are

the varying results spoken of, using but one set of potash bulbs.

	Per cent.		Per cent.
Steel 59 (Fresh potash).....	1.97	Steel 1.00 standard .....	0.974
“ 59 .....	2.13	“ 1.00 “ .....	0.870
“ 59 .....	2.25	“ 1.00 (Fresh potash) .	0.890
“ 59 .....	2.07	“ 35 .....	0.333
“ 59 (Fresh potash).....	2.01	“ 35 .....	0.288
“ 59 .....	2.277	“ 17 .....	0.636
“ 59 (Fresh potash).....	2.18		

Two sets of potash bulbs were then employed with a calcium chloride prolong to each. After the second set of bulbs and prolong used, a weighed set of potash bulbs with the two anterior bulbs containing strong sulphuric acid was also used, the last bulb empty to avoid all danger of mechanical loss. Following this was the usual calcium chloride guard tube.

	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Steel 59.....	2.267	none	2.267
“ 59.....	2.280	none	2.280
“ 1.00 standard .....	0.88	0.124	1.004
“ 1.00 “ .....	1.005	none	1.005
“ 35 .....	0.261	0.039	0.30
“ 35 .....	0.239	0.073	0.312
“ 17 .....	0.631	0.031	0.662
“ 81 .....	2.257	0.155	2.412
“ 81 .....	2.278	0.042	2.320 <sup>1</sup>
“ 81 .....	2.115	0.285	2.400
“ 80 .....	3.145	0.070	3.215
“ Tool.....	1.009	none	1.009
“ 60 .....	2.30	0.09	2.39
“ a4 .....	0.841	0.041	0.882
“ a5 .....	0.853	0.053	0.906
“ a6 .....	0.823	0.026	0.849
“ 2hh .....	1.014	0.051	1.065
“ 92 .....	0.693	0.302	0.995
“ 93 .....	1.033	0.151	1.184
“ 94 .....	1.010	0.052	1.062
“ 94 .....	0.896	0.176	1.072
“ 95 .....	1.018	8.080	1.098
“ 100 .....	0.206	0.064	0.27
“ 101 .....	0.044	0.021	0.065
“ 20 .....	2.54	0.70	3.24

<sup>1</sup> This result is too low on account of incomplete solution of the steel by the double chloride solution.

The following were obtained by combustion with lead chromate and potassium dichromate :

	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Steel 96.....	0.626	0.348	0.974
“ 97.....	0.732	0.366	1.098

In all the above determinations the potash used was of specific gravity 1.27 as is customary and was frequently changed. In the following the strength of the potash solution was increased to 1.40 specific gravity. This latter strength was found much preferable, not only on account of the solution of that strength possessing greater absorbing power, but also because it can be used much longer in the potash bulbs without change :

Steel.	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Tool, large.....	1.146	0.005	1.151
Tool, small .....	1.128	0.032	1.16
Nov. 13 .....	1.14	none	1.14
Slab .....	1.103	0.015	1.118
E.....	1.042	none	1.042
T.....	1.023	none	1.023
Slab .....	1.09	0.02	1.11
106 .....	1.379	none	1.379
No. 7.....	1.06	none	1.06
Cross cut .....	1.007	none	1.007
106 .....	1.372	none	1.372
20 .....	3.499	0.020	3.519
III R .....	0.858	none	0.858
110.....	1.136	0.010	1.146
113 .....	1.134	none	1.134
114 .....	1.251	0.019	1.27
115 .....	1.104	0.016	1.12
115 .....	1.091	0.050	1.141
116 .....	0.986	0.036	1.012
118 .....	1.02	0.012	1.032
119 .....	0.925	0.031	0.951
Trial .....	2.171	0.273	2.444
120 .....	0.719	0.064	0.783

*With fresh potash (sp. gr. 1.40).*

123 .....	0.771	0.006	0.777
121 .....	0.635	0.010	0.646
122 .....	0.279	0.001	0.28
Shear.....	2.547	0.012	2.559

*With new potash (sp. gr. 1.40).*

Steel.	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
G.....	0.730	0.007	0.737
127 .....	1.023	0.013	1.036
129 .....	0.872	none	0.872
130 .....	0.675	none	0.675
128.....	0.98	none	0.98
132 .....	0.554	none	0.554
132 .....	0.571	none	0.571

*With fresh potash (sp. gr. 1.40).*

133 .....	2.452	0.039	2.491
134 .....	2.447	0.044	2.491
135 .....	0.855	none	0.855
1.054 standard .....	1.033	0.030	1.063
136 .....	0.906	0.023	0.929
137 .....	1.301	none	1.301

*With fresh potash (sp. gr. 1.40).*

138 .....	1.298	none	1.298
139 .....	0.98	none	0.98
138 .....	1.27	none	1.27
1 .....	1.167	none	1.167
2 .....	1.122	none	1.122
3 .....	1.101	none	1.101
4 .....	0.957	0.008	0.965
5 .....	1.116	none	1.116

*With fresh potash (sp. gr. 1.40).*

6 .....	0.959	none	0.989
a6 .....	1.127	0.019	1.146
a1 .....	0.984	none	0.994
a5 .....	1.00	0.015	1.015
a3 .....	1.052	none	1.052
Ginsaw.....	0.89	none	0.89

The reason why one set of potash bulbs always suffices to absorb all the carbon dioxide in the dry combustion process,<sup>1</sup> and does not apparently always suffice in the wet combustion method, is doubtless that in the former way the evolution of the carbon dioxide is gradual and the gas largely diluted with oxygen, while in the wet combustion method the carbon dioxide is perhaps given off all at once in the beginning of the process, and hence in a state of greater purity and concentration. Results by the lead chromate method in the preceding table

<sup>1</sup> Dr. Drown, and doubtless many other chemists, by many experiments, has found this to be the case, and with the extensive use made of this method of combustion any tendency to loss in this manner could not have escaped notice.

indicate that when the carbon dioxide is given off almost pure and undiluted, the tendency of the gas to escape complete absorption by the potash bulbs is very great.

But in using potash of specific gravity 1.40, it is seen that the amount of carbon dioxide absorbed by the second set of bulbs is usually very small if any, and this small increase of weight is probably in very many cases not due to carbon dioxide but to moisture, for there is a certain quantity of moisture uniformly escaping absorption by the drying train. The drying train consists in this case of a Liebig bulb with strong sulphuric acid, then a large U-tube filled with calcium chloride followed by potash bulbs with strong sulphuric acid. The unabsorbed moisture is consequently caught, or partly caught, by the absorption apparatus, and constitutes almost, if not quite, the entire "dummy" to be deducted from the result in an ordinary determination. And the amount of the moisture so escaping the drying train, and absorbed, or partly absorbed, by the two sets of potash bulbs and prolongs, although pretty uniform and unvarying in total amount as shown by blank tests, is nevertheless varying as regards the proportion absorbed by each absorption set. Results are shown by the following tests made in blank, with the same amount of reagents, etc., as in a regular test.

	First set of bulbs and pro- long. Equiva- lent to carbon. Per cent.	Second set of bulbs and pro- long. <sup>1</sup> Equiva- lent to carbon. Per cent.	Total moisture equivalent to carbon. Per cent.
One-half hour's aspiration ..	0.015	0.060	0.075
“ “ “ ..	0.051	0.016	0.067
“ “ “ ..	0.060	0.019	0.079
“ “ “ ..	0.056	0.015	0.071
“ “ “ ..	0.076	0.005	0.081
“ “ “ ..	0.055	0.013	0.068
“ “ “ ..	0.061	0.020	0.081
“ “ “ ..	0.055	0.026	0.081
“ “ “ ..	0.030	0.028	0.058
“ “ “ ..	0.041	0.031	0.072
One-fourth hour's aspiration ..	0.041	0.028	0.069
“ “ “ ..	0.049	0.020	0.069
“ “ “ ..	0.019	0.046	0.065
“ “ “ ..	0.024	0.040	0.064
“ “ “ ..	0.036	0.028	0.064
“ “ “ ..	0.035	0.024	0.059

<sup>1</sup> Also weighed strong sulphuric acid bulb to this set.

*Fresh sulphuric acid in drying train.*

	First set of bulbs and pro- long. Equiva- lent to carbon. Per cent.	Second set of bulbs and pro- long. <sup>1</sup> Equiva- lent to carbon. Per cent.	Total moisture equivalent to carbon. Per cent.
One-fourth hour's aspiration.	0.047	—0.006	0.041
“ “ “ ..	0.052	0.016	0.062
“ “ “ ..	0.048	0.019	0.067
“ “ “ ..	0.039	0.021	0.060
“ “ “ ..	0.000	0.057	0.057

That these gains in weight are due mainly if not quite to moisture that the drying train failed to absorb, is shown by the following tests in which purified air was simply aspirated through the apparatus for about the same length of time, and as nearly as possible at the same rate of speed as the gas is evolved and air aspirated in an ordinary test.

	First set.	Second set.	Total moisture.
One-half hour's aspiration .....	0.058	0.000	0.058
One-fourth “ “ .....	0.038	0.026	0.064
“ “ “ .....	0.032	0.044	0.076
Five minutes' aspiration .....	0.012	0.033	0.045

It is seen that there may be, in different determinations, considerable variation in the proportion of moisture absorbed by each set of bulbs, although the total amount is usually 0.065 per cent. in terms of carbon, or quite close to it. So in deducting “dummies” from each set of bulbs, this variation may cause an absorption of carbon dioxide to be indicated by the second set of bulbs, when in reality the gain in weight of this set of bulbs may be due merely to a variation in moisture from the “dummy” subtracted. The results with use of potash of 1.40 specific gravity therefore do not prove, when the amount of carbon is not unusually large, and the potash solution not too long in use, that one set of bulbs, using potash of that strength, is insufficient. These results, and the dummy results following, indicate very plainly, however, the necessity for using more than one drying apparatus after and with the potash bulbs. Mr. David H. Browne, in his admirable “Hints to Beginners” in *Journal of Anal. and Appl. Chem.*, speaks of this in connection with the wet method, although the necessity of it is perhaps not generally recognized. But there is some little difference of opinion among chemists who use the other (dry) method of combustion;

<sup>1</sup> Also weighed strong sulphuric acid bulb to this set.

Dr. Drown, for instance, has found a single prolong filled with calcium chloride sufficient to catch all the moisture from the potash bulbs. On the other hand Mr. Andrew A. Blair has noticed a loss of moisture from the prolong; and Dr. Dudley also hints at the same thing, and thinks it probable that "some of the difficulty in getting absolute blanks may be accounted for in this way." It is not strange that in the dry method with a careful performance of the operation there should be, with some manipulators, a complete absorption of the moisture by the prolong. But in the wet method where the evolution of gas is more abundant and longer continued, it is the writer's experience, at least, that the prolong filled with freshly dried calcium chloride usually falls very short of absorbing all the moisture from the potash bulbs, the moisture thus lost amounting sometimes to as high as 0.14 per cent. in terms of carbon with one-half hour's aspiration.

But the escape of moisture from the prolong would be of no serious consequence (if dummy tests were carefully made) provided the moisture so escaping was invariably uniform in amount. The following tests, however, show a very great lack of uniformity in this respect and illustrate the necessity, in the wet method, of having more than the usual drying agencies after the potash bulbs to insure a uniform though probably still not complete absorption of the moisture from the potash bulbs. In these tests the moisture lost from the prolong was determined by absorbing it in a weighed potash bulb following and connected with the prolong, and having the two anterior bulbs filled with strong sulphuric acid. The results are consecutive, and are expressed in terms of carbon per cent:

One-fourth hour's aspiration—equivalent to carbon, per cent.: minus 0.005 per cent.; plus 0.004 per cent.; 0.004 per cent.; 0.004 per cent.; 0.002 per cent.; 0.015 per cent.; 0.008 per cent.; 0.010 per cent.; 0.019 per cent.; 0.017 per cent.; 0.013 per cent.; 0.023 per cent.; 0.021 per cent.; 0.026 per cent.; 0.021 per cent.; 0.048 per cent.; 0.062 per cent.; 0.060 per cent.; 0.062 per cent.; 0.058 per cent.; 0.060 per cent.; 0.052 per cent.

With fresh calcium chloride in prolong: 0.015 per cent.; 0.003 per cent.; 0.018 per cent.; 0.012 per cent.; 0.015 per cent.; 0.000 per cent.; 0.018 per cent.; 0.015 per cent.; 0.010 per cent.; 0.009 per cent.

With fresh calcium chloride, and one-half hour's aspiration: minus 0.006 per cent.; 0.005 per cent.; 0.015 per cent.; 0.023 per cent.; 0.018 per cent.; 0.018 per cent.; 0.012 per cent.; 0.018 per cent.; 0.027 per cent.; 0.032 per cent.; 0.010 per cent.; 0.006 per cent.; 0.016 per cent.; 0.012 per cent.

cent.; 0.020 per cent.; 0.025 per cent.; 0.022 per cent.; 0.016 per cent.; 0.022 per cent.; 0.028 per cent.; 0.044 per cent.; 0.049 per cent.; 0.076 per cent.; 0.077 per cent.; 0.071 per cent.; 0.055 per cent.; 0.046 per cent.; 0.053 per cent.; 0.119 per cent.; 0.138 per cent.; 0.074 per cent.; 0.081 per cent.; 0.065 per cent.; 0.053 per cent. Then with one-fourth hour's aspiration 0.043 per cent.; 0.052 per cent.; 0.050 per cent.; 0.042 per cent.; 0.081 per cent.; 0.050 per cent.; 0.043 per cent.; 0.043 per cent.; 0.046 per cent.; 0.029 per cent.

The sulphuric acid bulbs in their turn doubtless let some moisture through; but that by their use in connection with the prolong uniformity is obtained, is shown by the dummy results already given.

It is not supposed that the prolong and the sulphuric acid bulbs together absorb absolutely all the moisture from the potash bulbs for the reason that the drying train before the potash bulbs, consisting of two sulphuric acid bulbs, and one large calcium chloride tube, allows moisture equivalent to 0.065 per cent. carbon to escape in the course of a determination and therefore the drying apparatus after the potash bulbs doubtless also allows moisture to escape.

The writer is inclined to think that no apparatus now used in the absorption of moisture in the carbon process will absorb the moisture completely when the flow of gas is brisk and continued as in the wet method. Mr. A. A. Blair considers anhydrous copper sulphate an excellent absorbent of moisture. In fact it dries the gas too thoroughly; so that, as Mr. Blair says, "the gas leaves the prolong with more moisture than when it entered the absorbing apparatus." He therefore places a plug of moist cotton wool after the copper sulphate in the drying train and before the calcium chloride tube of the drying train in order to secure a uniformity of conditions in this particular. The loss of moisture from the prolong is thus equalized by a gain of moisture from the calcium chloride tube of the drying train. In this connection it is interesting to note a difference of opinion between Mr. Blair and Dr. Drown and others. Dr. Drown says that he finds no advantage in the use of the plug of moist cotton wool. Mr. Shimer, Dr. Dudley, and others seem to find no occasion for its use. As the only difference between the apparatus of Messrs. Drown, Dudley, and Shimer on the one hand, and Mr. Blair on the other (excepting the preheating furnace), is that the



former contains ferrous sulphate solution in the train immediately preceding the copper sulphate tube, it would seem a plausible inference that in the former case a plug of moist cotton wool, before the calcium chloride train is not needed because the moisture from the ferrous sulphate solution supplies the amount necessary to counterbalance that lost from the prolong—the anhydrous copper sulphate intervening in Messrs. Drown and Shimer's apparatus being in that case not so good a drying agent after all.

However easy and tempting this deduction may be, it is nevertheless inadmissible from the simple fact that Dr. Drown finds that no moisture at all escapes from the prolong in his use of it. Hence the only explanation left us for the fact that Mr. Blair finds the use of moist cotton wool necessary or advisable and Messrs. Drown, Dudley, and Shimer do not, is of course the simple one that in the one case the passage of gas and the aspiration of air is allowed to proceed more gently than in the other, so that in this case moisture is neither drawn from the drying train on the one hand, nor lost from the prolong on the other. This is of course a perfectly reasonable supposition, but if a difference in manipulation merely (and probably a slight difference) is responsible for this difference in behavior, then it would seem best for the ordinary operator to be on the safe side by assuming that moisture does escape from the prolong, and to proceed accordingly.

The writer nevertheless ventures to question whether there is any real need of introducing the moist cotton wool into the apparatus—whether, in fact, it is not distinctly inadvisable so to do. For, the less moisture carried into the weighed absorbing apparatus, the less variable will obviously be the amount of moisture escaping from it and the less, therefore, “the difficulty of obtaining absolute blanks,” and the more concordant the results. If more moisture escapes absorption by the prolong than is gained from the drying train, and the dummy is therefore a minus quantity, so much the better, showing, as it does, that the drying train is a good one and allows but little moisture through it. And it is just as easy to apply a plus correction to the result in a regular determination as a minus one; that is, if our dummy is minus we add instead of subtracting it from our results. The important matter is, of course, to get an absolute

dummy—one that does not vary, and the writer therefore thinks it better still to use a weighed sulphuric acid bulb or some other additional drying apparatus after the prolong to secure this uniformity until convinced by many such trials that (in the operator's manner of procedure) no moisture escapes absorption by the prolong. For the writer, moisture does escape from the prolong, in the dry as well as in the wet method of combustion, varying in the dry method from 0.000 per cent. to 0.08 per cent. in terms of carbon, according to the freshness of the calcium chloride, its state of division, and the speed of aspiration. In using calcium chloride Dr. Dudley directs that it be freshly dried before use. This is such a necessary precaution as to bear much iteration.

A calcium chloride tube filled directly from a half-emptied bottle and therefore without previous drying lost by aspirating dry air through for two hours, equivalent to carbon: 0.047 per cent.; repeated, lost 0.14 per cent.; again, gained 0.02 per cent.; again, lost 0.19 per cent.; again, lost 0.48 per cent.

A wash-bottle with water was followed by this calcium chloride, and that in its turn by a weighed sulphuric acid bulb. The bulb gained in weight 0.32 per cent. and 0.29 per cent., so that the drying of the calcium chloride previous to use is an absolutely necessary precaution.

It seems to be necessary with some potash solutions to aspirate air through before using. Several blank tests made without doing this showed a loss of weight, in the one case equal to 0.048 per cent. carbon and in the other 0.019 per cent. carbon.

In the writer's experience a most serious difficulty with the wet method of combustion is, that occasionally results are obtained from 0.05 to 0.07 per cent. above the truth, due apparently to some chloro-chromic compound other than that absorbable by Prof. Langley's "pyro" mixture. At least the writer can offer no other explanation, the purifying train including: water kept cold for hydrochloric acid according to Porter Shimer; ferrous sulphate for chlorine according to Dr. Dudley; "pyro" mixture for chlorine, oxides of chlorine, and chloro-chromic anhydride according to Prof. Langley; and silver sulphate in strong sulphuric acid for hydrochloric acid.

It is known that the wet method is unsuited for graphite de-

terminations owing to a portion of the graphite being oxidized merely to carbon monoxide.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 30.]

## COMPARISON OF THE STANDARD METHODS FOR THE ESTIMATION OF STARCH.<sup>1</sup>

BY H. W. WILEY AND W. H. KRUG.

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THE study of the nature of the carbohydrate bodies which exist in foods has been vigorously prosecuted by chemists in different parts of the world during the past few years. The result of these studies has been to arouse new interest in the standard methods of starch determination. The numbers which are secured by different workers for starches vary so greatly as to lead to the belief that the estimation of starch is not such an easy matter as is generally supposed; in fact, long experience has convinced us that there are few operations in agricultural analytical chemistry which require greater skill, or are attended with greater difficulties than the estimation of starch in the presence of the other carbohydrate bodies.

At a recent meeting of chemists in England, it was stated in one of the papers that the methods of starch determination are now so easy of application and so accurate that there is no longer any excuse for being ignorant of the exact content of starch in any body. Stone, in Bulletin No. 34 of the Office of Experiment Stations, described a method which was easily seen to be erroneous, yielding only about half as much starch as was really contained in the samples examined. A cursory glance at the methods of analysis employed by him convinced us that the fault was insufficient saccharification, due to the weakness of the acid and the shortness of the time of heating.

In a subsequent article<sup>2</sup> Stone called attention to the error of his previous statements, and proposed a modification of his first published method, which, as is seen below, gives very much better results. Having to estimate, annually, the starches in many hundreds of substances, we were led to make a compara-

<sup>1</sup> Read before the American Chemical Society and Section C of the American Association for the Advancement of Science, at Detroit, August 12, 1897.

<sup>2</sup> This Journal, 19, 347.