the subsequent development. The sugars increase gradually during the growth of the orange, sucrose and reducing sugar existing in approximately equal quantity.

Storage of the fruit at room temperatures at all stages of its development results in slight loss of acid and of total sugar, a marked increase of reducing sugar, and a corresponding decrease of sucrose. The loss of acid and sugar noted above is to be explained as in the case of apples by the consumption of these substances as a result of the respiration of the fruit. The weight of marc remains practically constant, and the weight of acid appears to decrease slightly on storage during the various stages of the development of the orange.

ON THE ANALYSIS OF LIGNITIC AND SUB-BITUMINOUS COALS[1]

By Alvin J. Cox

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The directions for coal analysis recommended by the Committee appointed by the American Chemical Society,[2] which embody the salient points of the previous work on this subject are satisfactory for coking but not for certain non-coking coals, which were comparatively of insignificant value when the report of the Committee was made. These coals are now of sufficient importance to demand a method which will yield correct results in their analysis. The fact that the use of the directions recommended by the Committee gives uncertain results in the determination of volatile combustible matter in Philippine coals has already been published.[3]

These coals are deposits of the so-called black lignite and belong to the class which are usually spoken of under the name sub-bituminous, adopted by the United States Geological Survey. They are all non-coking. A few show incipient coking.

When the directions of the Committee are followed in the expulsion of volatile matter, their data indicate little if any mechanical loss for non-coking coals; on the contrary my results show a very large mechanical loss. It is not even necessary to have analytical data to prove that this loss is large. One can see the shower of incandescent carbon particles which are driven off during the first one or two minutes' heating.

The publication[4] above referred to in the discussion of certain analyses of Philippine coals says:

"The coal analyses were made according to the directions recommended by the Committee appointed by the American Chemical Society. In the

[1] For the basis of this paper such results as are thought to be of general interest to coal investigators have been selected from an extended investigation of Philippine coals made in the Chemical Laboratory of the Bureau of Science, Manila.

[2] This Journal (1899) 21, 1116; The Coal and Metal Miners' Pocket Book 7th Ed. (1902), Scranton, Pa., 173.

[3] Cox, A. J., Phil. Jour. Science (1906) 1, 890.

[4] Ibid.

determination of volatile combustible matter, it has been found that these give very inaccurate results. The Committee states that the most serious objection brought against their method is that the rapid heating causes mechanical loss in the case of certain non-coking coals; that no evidence has been given as to the amount of such loss, while in the light of certain experimental determinations which are described, they state that the loss can only have been insignificant. It has been observed in this laboratory, that the error from this source on our coals is very large, possibly amounting to a few per cent. in some cases. It has also been found that this could be largely if not entirely eliminated by expelling the moisture and most of the volatile matter at a low heat before subjecting to the full flame of the Bunsen burner for seven minutes. Four to five minutes gentle heating are sufficient to do this. With this exception the official method has been followed in detail."

A paper[1] entitled "Some Experiments on the Determination of Volatile Combustible Matter in Coals and Lignites" indicates that the Fuel Testing Plant of the United States Geological Survey has also found that the official method gives inaccurate results when applied to the analysis of non-coking coals from the western states. The modification described there is very similar to the one we used in this laboratory previous to the beginning of this investigation. Somermeier in referring to the modified process of the Fuel Testing Plant, says, "The difference in results obtained by three, four and five minutes preliminary treatment is small and in all subsequent experimental tests the time of the preliminary heating was four minutes." The author's experiments show that with some Philippine coals a longer period of preliminary treatment is necessary to give very accurate results, as the following data will indicate.

In all of the following experiments platinum crucibles of 20 cc. capacity and with tightly fitting covers were used. The coal was pulverized to pass a sixty-mesh sieve. Mechanical losses are indicated by discrepancies in the percentage of ash for these were always made on the same portion of the coal as the volatile matter.

As an example of the extent of the mechanical losses when the official method is applied to Philippine coals and also to show that a preliminary treatment of four minutes is not sufficient when accurate results are desired the following analysis of an air dried coal from Negros are given.

	By the official method		By four minutes preliminary heating		By the smoking off method	
	per cent. 1	per cent. 2	per cent. 1	per cent. 2	per cent. 1	per cent. 2
Water	18.19	18.29	(18.24)	(18.24)	(18.24)	(18.24)
Volatile combustible matter	38.73	39.13	32.56	32.64	32.03	31.98
Fixed carbon	26.57	25.90	31.39	31.39	31.77	31.74
Ash	16.51	16.68	17.81	17.71	17.96	18.04
	100.00	100.00	100.00	100.00	100.00	100.00

[1] Somermeier, E. E., This Journal (1906) 28, 1002.

The smoking-off method is the one which the author has formulated for use in the analysis of coal when the official method gives mechanical losses. It is as follows: The sample is subjected to a low heat, just enough to keep a visible amount of smoke rising from the crucible but not enough to burn at its edges. The heat is regulated by holding the burner in the hand and slowly moving a small flame back and forth under the crucible. It is important that the crucible should not be allowed to cool after once beginning the operation, as in that case air would be drawn into the coal causing the oxidation of a part of the fixed carbon. The most delicate stage is when the hydrocarbons have been practically all expelled, and only hydrogen is still being liberated. At this point it is very hard to expel the gas slowly enough to prevent its ignition for there is no longer the smoke to serve as a gauge. If the gas ignites, it is coming off fast enough to carry some of the solid carbon particles as will at once be seen by the sparks. With care and practice, however, this can be controlled. Since the eye of the operator is the only gauge, no definite time is prescribed for this preliminary treatment but seven to nine minutes are usually necessary for its completion; in one extreme case sixteen minutes were required. It is not a question however, of an extreme amount of time but of putting the time in the right place. The volatile matter should be smoked off as fast as allowable not to produce sparks but not fast enough for the gases to burn. Without disturbing the crucible the platinum triangle and crucible are quickly placed over the regulation Bunsen flame and gradually lowered until they are finally in position.

It will be noticed by comparing the results obtained above for fixed carbon and ash that the variations between those by four minutes preliminary heating and the smoking off method are directly proportional, that is $31.75/31.39 = 1.01$ and $18.00/17.76 = 1.01$. This signifies that the discrepancy is due entirely to mechanical loss, that there is no difference in the breaking down of the hydrocarbon compounds of the coal.

It has been shown[1] that with coking coals there is a marked difference in the percentage of fixed carbon whether a small flame is at first applied and then the full flame, or the full flame is applied at once, the former giving the higher results. It can be calculated from the above analyses and will be shown later that this difference is much smaller for coals which give mechanical losses with the official method and perhaps it no more prevents the comparison of the results obtained by the smoking off with those obtained by the official method than the possible errors in the latter prevent their comparison one with the other. Even if it were as large, the smoking off would be more accurate than the official method as shown by the following analysis of Negros coal No. 23.

[1] Austin, N. M., This Journal (1899) 21, 1124.

TABLE I

No.[1]	Source	Index	Official method				Smoking-off method				Total sulphur per cent.	Fuel ratio[2]	
			Water per cent.	Volatile combustible per cent.	Fixed carbon per cent.	Ash per cent.	Volatile combustible per cent.	Fixed carbon per cent.	Ash per cent	Color of ash		Off. M.[3]	S. M.[4]
1	Australia[5]	3	2.53	36.12	48.99	12.36	33.67	51.27	12.53		0.09	1.357	1.530
			2.53	36.07	48.96	12.44	33.47	51.44	12.56				
3	Australia	25	1.26	25.26	63.39	9.88			(9.99)		..	2.474	
			1.25	25.26	63.60	10.10			(9.99)				
4	Batan Island	2	15.41	41.74	39.05	3.80	39.46	41.02	4.11		0.22	0.933	1.040
	Bett's		15.42	41.83	38.97	3.78	39.46	41.00	4.12				
13	Cebu, near Carmen	3	13.51	48.95	32.09	5.45	35.58	44.49	6.42	Yellow	0.23	0.656	1.272
			13.38				34.90	45.13	6.59				
17	Cebu	4	12.29	42.96	41.07	3.68	36.84	47.06	3.81	Brown	0.04	0.956	1.278
			12.31										
18	Japan, Kishima	11	Mechanical method.		loss by	official					..		
20	Mindoro, Bulalacao	7	10.84	44.18	43.54	1.44	39.70	47.84	1.62	Yellowish red	..	0.987	1.215
			10.70				39.41	48.27	1.61				
21	Negros, near Cadiz	1	18.19	38.73	26.57	16.51	32.03	31.74	18.04	White	0.00	0.674	0.989
			18.29	39.13	25.90	16.68	31.98	31.77	17.96				
23	Negros	20	15.81	55.92	18.60	9.67	35.53	34.42	14.24	Dark brown	0.99	0.349	0.969
			15.92	54.08	19.76	10.24	35.50	34.36	14.22				
24	Polillo	6	5.88	42.64	45.49	5.99	39.18	48.90	6.04	Red	..	1.040	1.240
			5.90	42.64	45.48	5.98	39.39	48.75	5.96				
26	Polillo	34	4.36	44.20	47.58	3.86	39.32	52.42	3.90	Red	..	1.073	1.327
			4.51	44.35	47.40	3.74	39.49	52.30	3.70				
28	Philippines[6]	32	16.34	45.30	30.33	8.03	43.87	31.75	8.04	Reddish white	..	0.666	0.724
			16.35	45.64			43.94	31.82	7.89				
32	Samar	31	15.24	46.95	34.97	2.84	45.38	36.36	3.02	Reddish white	..	0.742	0.803
			15.26	46.96	34.70	3.08	45.29	36.40	3.05				
34	Tayabas, Atimonan	10	12.21	46.10	37.96	3.73	44.66	39.43	3.70	Yellow	..	0.824	0.879
			18.33				44.80	39.18	3.69				
36	Wyoming Rock Springs	9	9.84	39.38	49.10	1.68	32.44	55.86	1.86		..	1.257	1.718
			9.74	39.02	49.47	1.77	32.48	55.80	1.96				
37	Zamboanga	5	6.23	43.55	46.43	3.79	39.27	50.72	3.78	Red	0.06	1.067	1.287
			6.47				39.32	50.45	3.76				

[1] Selected analyses. [2] Fixed carbon, Volatile combustible. [3] Calculated from analyses by the official method. [4] Calculated from analyses by the smoking-off method. [5] Coking. [6] Exact source unknown.

	By the official method		By the smoking-off method	
	per cent. 1	per cent. 2	per cent. 1	per cent. 2
Water	15.81	15.92	(15.86)	(15.86)
Volatile combustible matter	55.92	54.08	35.48	35.56
Fixed carbon	18.60	19.76	34.42	34.36
Ash	9.67	10.24	14.24	14.22
	100.00	100.00	100.00	100.00

The percentages of ash as determined by the official method differ widely with each other, but their average compared with that obtained by the smoking-off method corresponds to a mechanical loss in fixed carbon of 10.2 per cent.

Comparative analyses of a number of samples by the official and the smoking-off methods show the variation in the percentages of fixed carbon. The analyses of a few of these are as follows:

Barring mechanical losses, if we arrange the coals of the above table in a series beginning with the greatest variation in the percentage of fixed carbon, we find all of the coals of the class to which the official method of analysis is applicable at the top of the column, and those of the class (the last four) with which the official method gives inaccurate results at the bottom. This is as we should expect. The variation can be due only to the difference in the breaking down of the hydrocarbon compounds and from a knowledge of the coals those at the beginning of the series have the most complex volatile combustible matter.

The analyses of the gases[1] obtained by the destructive distillation of Polillo coal, Australia No. 1, and Zamboanga No. 37, gave 8.1, 6.34 and 6.2 per cent. respectively for the percentage of heavy hydrocarbons (C_nH_{2n}) whereas Batan Island No. 4 and Negros No. 21[2] gave only 2½ to 3 per cent. The series is as follows:

TABLE II.

No.	Source of coal	Difference in per cent.
26	Polillo	4.87
3	Australia	4.57
37	Zamboanga	4.16
24	Polillo	3.34
1	Australia	2.33
4	Batan Island[3]	2.00
32	Samar	1.55
28	Philippines	1.45
34	Tayabas	1.34

[1] Cox, A. J., Phil. J. Sci. (1906) 1, 893-895.

[2] This coal cannot be included in Table II on account of the mechanical loss by the official method.

[3] This sample was taken from the other end of the Island from the Military Reservation. It represents a much poorer grade of coal than that from the government claims.

Another very important factor which demands consideration is the effect of the presence of water upon the analysis of coal. With this in view a series of determinations was made by the smoking-off method with Negros coal No. 21 to which definite amounts of water, as noted below, were added and thoroughly mixed.

TABLE III.

Grams water added per gram of coal	Total volatile matter 1	2
0.00	50.22%	50.26%
0.05	50.08	....
0.10	50.22	50.27
0.15	50.10	....
0.20	50.34	50.17
0.30	50.22	50.27

Still another sample was dried at 107° for one hour and the total volatile matter determined as 50.22%.

These results show that with this method the amount of water does not affect the percentage of volatile combustible matter, but the tendency of the fine particles to fly off in sparks was perceptibly lessened.

The addition of a small amount of water almost eliminated the loss when the official method was used, as shown by the following results:

TABLE IV[1]

When the mixing was done with a wire.

Grams water added per gram of coal	Total volatile matter	Ash	Average Total volatile matter	Ash
0.00	56.92%	16.51%	57.68%	16.32%
	57.42	16.68		
	58.69	15.77		
0.05	52.25	17.63	52.30	17.66
	52.34	17.68		
0.1	52.59	17.76	52.64	17.82
	52.50	17.65		
	52.85	18.06		
0.2	53.71	17.98	53.80	17.98
	53.90			
0.3	52.85	17.80	52.85 (?)	17.80

When the mixing is done with a spatula.

Series 1,	Series 2.			
0.1	51.03		51.39	17.71
	52.42	17.71		
50.72				
0.2	52.74	17.78	51.64	17.78
50.54				
0.3	52.55	17.94	52.01	17.94
51.47				

The cause of variation in these averages when the amount of water is

[1] It was thought that there might be a difference in the results if a spatula were used instead of a wire, as with the former the water could be more perfectly introduced into the interstices of the coal.

changed is the resultant of two opposing factors. First, the water serves to dampen and hold together the solid particles, thereby preventing mechanical loss. Second, the water exerts an influence on the decomposition of the coal tending to increase the percentage of volatile matter.[1]

In order to show the extent of the action of water alone experiments were made with two coals, namely, Polillo No. 24 and Australia No. 1, as follows :

TABLE V[2].

Grams water added per gram of coal	Total volatile matter	Ash	Averages Total volatile matter	Ash
		Polillo coal No. 24.		
0.00	48.52%	5.99%	48.53%	5.98%
	48.54	5.98		
0.1	49.77	5.90	49.69	5.85
	49.61	5.80		
0.2	50.19		50.26	
	50.34			
0.3	50.32	5.89	50.32	5.89
		Australia coal, No. 1 (coking).		
0.0	38.60	12.44	38.62	12.40
	38.65	12.36		
0.05	40.09		40.09	
0.1	40.24	12.38	40.24	12.38
0.2	40.70		40.70	
0.3	41.20		40.99	
	40.77			
0.4	41.60	12.33	41.60	12.33

The results shown in Tables III, IV and V give the following figure when expressed as curves :

In the figure the difference x represents the sum of two factors, the change in the percentage of volatile matter due to the different heat treatments of the two methods and the deviation due to the presence of loosely held water ; y and z represent only one factor, the deviation due to the presence of water. Notwithstanding this, y and z are each greater than x.

The results in Table V show that the greatest increase in the percentage of volatile matter is produced by the presence of the first 5% of water. The results in Table II and V show that this is roughly the same as the increase in the percentage obtained by the use of the smoking-off method over that by the official method. In other words, the variation produced by the different heat treatments of the official and

[1] The percentage of ash increases until about 20% of water has been added, when the value is very close to that obtained by the smoking-off method. Before this point is reached the first factor predominates; after this the second factor is made evident.

[2] The duplication in the percentages of ash by the two methods, as given in Table I, show that the official method of analysis is accurate, and none of the variations noted below are mechanical losses.

smoking-off methods in the breaking down of the hydrocarbon compounds of the coal, is approximately the same and in the same direction as that produced by the variation of the water content of a single coal

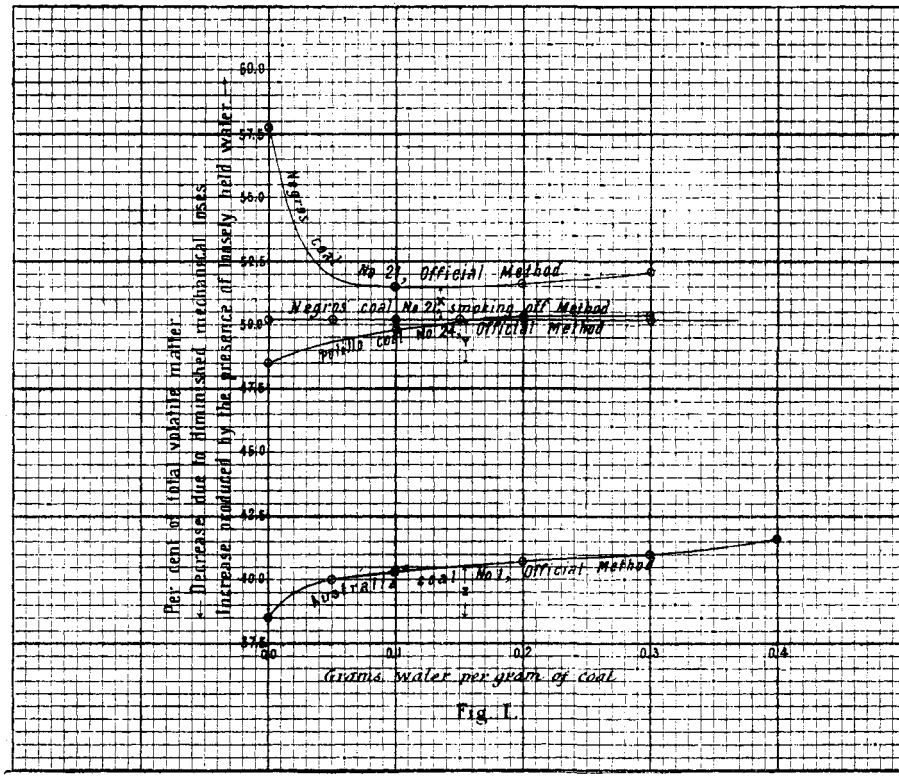

Fig. 1.

when analyzed by the official method. Hence, only one-half of x in the above figure is due to the different heat treatments. It is evident then that the variation due to the varied heat treatment is smallest in the case of coals which can be analyzed only inaccurately by the official method. If the smoking-off method be used only in the analysis of such coals, there will be an error not so large as that produced by varying the amount of moisture to a very slight extent in a coal analyzed by the official method. Such variation often happens in shipping the sample from the mine to the laboratory[1]. For the present, at least, this difference can be neglected in commercial analyses, and the results considered as directly comparable with those obtained by the official method.

Portions of the same coal, Australia, No. 1, were subjected to the regulation flame for varying lengths of time in order to demonstrate how

[1] Somermeier, E. E., This Journal (1906) **28**, 1630.

many minutes are necessary to expel all of the volatile matter in the analysis of coals by the official method :

Time over the full flame in minutes	Total volatile matter
3	38.65
4	38.65
7	38.65

To determine the number of minutes required over the full flame in the smoking off method the following experiment was made on Negros coal No. 21. The samples were carefully smoked off and then treated as above :

Time over the full flame in minutes	Total volatile matter	
1	48.53	
3	49.46	
4	50.27	Constant
5	50.24	Constant
6	50.21	Constant
7	50.24[1]	Constant

The above results show that with either the official or the smoking off method the gases are all expelled after four minutes heating over the full flame of a Bunsen burner. They also show that no loss is entailed when the heating is continued for three minutes longer ; since no loss ensues by the seven minutes treatment prescribed by the Committee, it is well to maintain uniformity.

The official method is assumed to approach the conditions existing in a coke oven. However in actual practice the coal is charged in large quantities and the distillation for the most part begins slowly as in the smoking off method. The latter method is universally applicable and is therefore recommended for general adoption. A qualitative experiment will show in a few minutes whether or not a coal suffers mechanical loss by the official method. For the present we shall continue to use the official method in this laboratory wherever applicable, in order to facilitate direct comparison with coals from other sources, but in those cases where it entails large losses we shall employ the smoking off method followed by seven minutes over the full flame.

It is hoped that the Committee on Coal Analysis will recognize the demand and modify their method to include the non-coking coals which are causing so much difficulty. More data and a more complete treatment of this subject will appear in the Philippine Journal of Science under the title of "The Proximate Analysis of Philippine Coals."

MANILLA, P. I., January 1907.

NOTES

The Determination of Sulphurous Acid in Gelatine: A Manufacturer's Position with Regard to the Food and Drugs Act.—In the deter-

[1] The average of four results the greatest variation of which is 0.06 per cent.