LXXX.—*Studies in the Composition of Coal. Methods for the Rational Analysis of Coal.*

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IN a previous paper (J., 1928, 2967), the results of rational analyses of coals, as applied to several series of American coals, were given. Each analysis involved the determination of the quantities of free hydrocarbons and resinous compounds (estimated together), organised plant entities, and ulmin compounds of which the coal is composed, together with a measure of the reactivity of its ulmin compounds (*loc. cit.*, p. 2968). We now place on record similar analyses of British bituminous coals and describe in detail the methods of analysis, which are modifications of, and improvements on, those used for the American coals.

The examination of the bright portions, the vitrains and clarains, of British bituminous coals by these methods has presented no difficulty, but the dull portions, the durains, have proved obdurate.

When a durain is treated with an oxidising agent, such as Schultze's solution, to remove the ulmin compounds (by rendering them soluble in alkalis), thus setting free the embedded plant

entities, it is found that more energetic oxidation is required than with the clarain from the same seam of coal. With an oxidising solution of such strength that the plant entities of a clarain remain as transparent reddish-yellow flakes, the residue from the corresponding durain contains many black and opaque particles appearing, under the microscope, to be unaltered coal, save that their edges are ravelled. (In this connexion, see Stopes, *Proc. Roy. Soc.*, 1919, *B*, **90**, 470.)

Durains, therefore, contain material, more resistant towards oxidation than the ulmins and less resistant than the plant entities, that is absent from clarains. The existence of a distinctive resistant material in a durain is emphasised in the original description of it by Stopes (*loc. cit.*) and is deduced, on several grounds, by Kellett (*Trans. Inst. Min. Eng.*, 1928, **75**, 400), Thiessen and Francis (U.S. Bureau of Mines, Tech. Paper No. 446, 1929), and Holroyd and Wheeler (J., 1928, 3197). Its origin is as yet uncertain. There are some reasons for believing that it, or some portion of it, approximates in character to fusain. On the other hand, Holroyd and Wheeler have found that a durain usually exhibits two " active decomposition points," the one identical with that of the corresponding vitrain and the other several degrees higher, both yielding distillation products of the same type ; whilst our earlier work (J., 1925, **127**, 2236) showed that the regenerated ulmins from the durain and the vitrain from the same seam are identical in character. We therefore consider that the distinctive material in a durain (termed by Kellett " residuum," and by Thiessen and Francis " opaque matter ") is for the most part a modified form of ulmin. It may here be remarked, as explaining why in our earlier rational analyses of American coals the difficulty of dealing with durains did not arise, that durain is rarely, if ever, encountered in American bituminous coals (see Thiessen and Francis, *loc. cit.*, pp. 11 and 24).

The general principle underlying the rational analysis of coals is that, as the " coalification " process has proceeded, progressive changes in the molecular arrangement of the ulmins have increased their resistance to oxidation. Oxidation gradually changes the coal ulmins from a form insoluble in alkalis to a soluble form, the rate of formation of soluble ulmins being proportional to the rate of oxidation. The amount of ulmins present in any coal can therefore be deduced from its solubility in alkalis after oxidation, and the degree of " coalification " of the ulmins can be deduced from their reactivity. To complete the rational analysis, it is necessary to determine the amounts of mineral matter, hydrocarbons and resins (soluble in organic solvents), and what we have previously termed " organised plant entities." A better term, per-

haps, for this mixture of many substances is "resistant residue," it being, by comparison with the ulmins, resistant towards oxidising agents. For the most part this resistant residue consists of spore exines and cuticular tissues, substances of similar chemical character, but there are also present, in varying proportion in different coals, black fusainised cellular tissues, such as wood tracheids, which modify its character.

Methods of Rational Analysis of Coal.

Preparation of the Sample for Analysis.—The sample of coal is ground, dried, and sieved through a 60-mesh and on a 120-mesh sieve (I.M.M. standard). A weighed quantity, about 15 g., is boiled over a glycerol-bath during 8 hours with pyridine (15 c.c. per g. of coal) in a round-bottomed flask fitted with a ground-in reflux condenser. After cooling, the mixture is filtered and the residue, the amount of which must be determined, washed with a little pyridine, the filtrate being preserved for later treatment (the determination of the hydrocarbons and resins). Fritted glass filter-discs (type 17 G.3, as supplied by the Jena Glass Works of Messrs. Schott and Gen.) should be used for the filtration.

The extracted coal is transferred to a beaker, boiled for a short time with dilute hydrochloric acid, filtered, washed, and dried in an air-oven at 105°. It is then carefully ground, with frequent and thorough sieving, so as just to pass through a 120-mesh sieve. Any dust passing through a 150-mesh, the formation of which must be avoided, is discarded.

The object of this preliminary treatment of the coals is to remove soluble hydrocarbons and resins, the amounts of which vary from coal to coal, and to obtain the same physical condition, as regards the texture as well as the size of the particles, for all the samples. Pyridine resolves the colloidal aggregates and eliminates any differences in texture that there are between one coal and another (markedly between dull and bright coals).

The Determination of the Resistant Residue.—A 0·5-g. sample of the treated coal is boiled during 7 hours under reflux with the oxidising solution appropriate to its carbon content, as set forth in Table I.

After being cooled, the contents of the flask are filtered through a weighed crucible with fritted glass disc (type 2 G.3). The oxidised coal is washed from the filter into a beaker, the volume made up to 100 c.c., 20 c.c. of N-sodium hydroxide added, and the mixture gently boiled on a hot plate during $1\frac{1}{4}$ hrs.

Before proceeding further, a small sample of the resistant residue at the bottom of the beaker should be removed for examination

TABLE I.

Oxidising Solutions.

Carbon content of coal (on " pure coal " basis *).	Oxidising solution.			
	HNO₃, c.c.			
	N-Acid.	$2N$-Acid.	Water, c.c.	KClO₃, g.
78	37·5	—	12·5	Nil
79	40	—	10	Nil
80	42·5	—	7·5	Nil
81	45	—	5	Nil
82	47·5	—	2·5	Nil
83	50	—	Nil	Nil
84	46 and	4	Nil	Nil
85	—	28	22	0·2
86	—	29	21	0·35
87	—	30	20	0·5
88	—	32·5	17·5	0·625
89	—	35	15	0·75
90	—	40	10	1·0
91	—	50	Nil	1·5

* The estimation of the carbon content of a coal on the " pure coal " basis involves making an allowance for the fact that the " ash " of a coal is not of the same composition or quantity as the original mineral matter (see Tideswell and Wheeler, *Amer. Inst. Min. Met. Tech. Paper*, No. 104, 1928).

under the microscope. If the coal has been correctly oxidised, the particles, other than of fusainised wood tracheids, should be transparent and of a yellow, orange, or red colour. The larger particles will usually be portions of macro-spore exines and may not be quite transparent. The smaller particles will mostly be readily recognisable as micro-spore exines and fragments of epidermal and parenchymatous tissues. If the oxidising solution used has been too weak, the resistant residue will be opaque, whilst too strong an oxidising solution will yield bleached and macerated fragments.

If this examination shows that the oxidising solution has been correctly chosen, the solution is filtered through the crucible previously used, slow suction being applied if necessary. The residue, after having been washed successively with hot water, dilute hydrochloric acid, and hot water (three or four times), is dried and weighed. The weight (P) represents the resistant plant entities together with insoluble ash.

With a durain, because of the presence in it of material intermediate in oxidisability between the ulmins of the corresponding bright coal and the resistant residue, it is necessary to make a series of determinations with oxidising solutions of different strengths. The amounts of residue obtained are then plotted against the volumes of $2N$-nitric acid in the different solutions. When all but the resistant residue has been rendered soluble (as can be confirmed by microscopical examination), a sharp break

occurs on the graph.   The value for the amount of resistant residue
from a durain at this " end-point " is, however, too low in com-
parison with the amount from the corresponding clarain, because

FIG. 1.

Volume of 2N-nitric acid in oxidising solution, c.c.
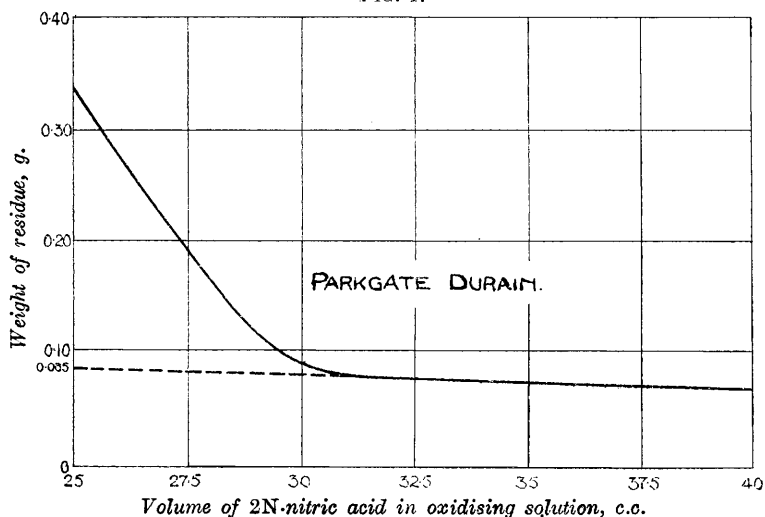
the stronger oxidising solution used destroys some of the residue.
A correction can be applied by producing backwards the flat portion
of the graph (see Figs. 1 and 2) to cut the value for the correct

FIG. 2.

Volume of 2N-nitric acid in oxidising solution, c.c.
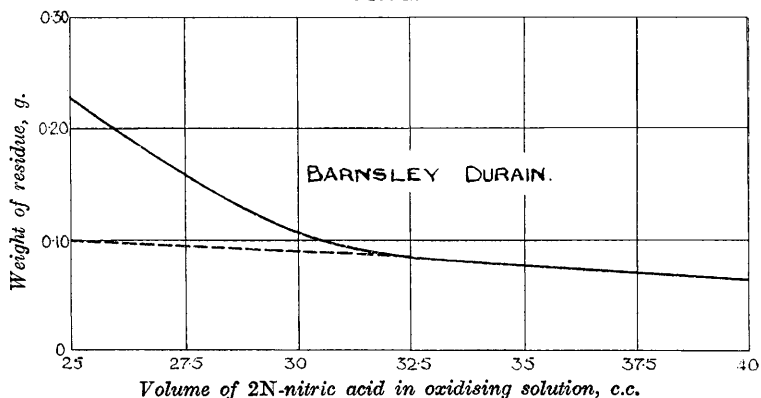
oxidising solution for the corresponding clarain, which must be
previously determined.

The validity of this correction has been checked in many deter-

minations. Microscopical examination of the residues obtained on treating durains with a series of oxidising solutions shows that, at any point on the steeply sloping portion of a graph such as those in Figs. 1 and 2, they are for the most part black and opaque. When the break in the graph is nearly reached, most of the particles are translucent, and when the break has been passed they are all transparent and bleached. The weight of residue obtained when the larger particles begin to lose their opacity corresponds closely with the " corrected " weight obtained from the graph. Examples are given in Table II of the examination of two durains, Parkgate and Barnsley " hards," in this manner.

TABLE II.

The Determination of the Resistant Residue in Durains.

Volume of 2N-nitric acid in oxidising solution, c.c.	Weights of residues, g.	
	Parkgate hards.	Barnsley hards.
25 *	0·333	0·227
28	0·162	0·154
30	0·090	0·109
32·5	0·074 †	0·083 †
37·5	—	0·062
40	0·064	0·063

* Correct oxidising solution for corresponding clarain.

† All residue transparent or translucent.

These figures are used for the construction of the graphs in Figs. 1 and 2, from which the " corrected " weights of the resistant residues are taken to be 0·085 and 0·10 g. respectively.

The Determination of the Hydrocarbons and Resins.—The pyridine extract originally obtained from about 15 g. of the coal is distilled to remove as much of the pyridine as possible, and excess of dilute hydrochloric acid is added to the residue. The mixture is boiled during about ¼ hour and filtered through coarse filter-paper when cool. The residue is washed copiously with water, dried, and completely extracted with ethyl ether in a Soxhlet apparatus. From the weight of extract a sufficiently accurate estimation of the amount of hydrocarbons and resins (together) in the coal is made.

The Determination of the Reactivity of the Ulmins.—A sample of the prepared coal is heated under pressure with an oxidising agent under standard conditions, and the quantity of alkali-soluble ulmins thus formed is determined. The determination is conveniently carried out on 0·5 g. of the coal which, with 0·9 g. of potassium chlorate and 50 c.c. of N-hydrochloric acid, is placed in a 300-c.c. pressure-bottle. The bottle is weighted and immersed in a water-

bath which is quickly brought to its b. p. Boiling is continued during 7 hrs., the bottle allowed to cool over-night, and its contents filtered through a crucible with fritted glass disc (type 1 G.3). The residue is washed and rinsed with water into a beaker, the volume made up to 100 c.c., and 20 c.c. of N-potassium hydroxide solution, accurately measured, are added. A clock-glass is placed over the beaker, and its contents are boiled gently on a hot plate during $1\frac{1}{4}$ hrs. The solution is then filtered through the crucible previously used, the residue washed successively with hot water, dilute hydrochloric acid and, several times, with hot water, slight suction being applied only if unavoidable. The filtration and wash-ing should occupy about $\frac{1}{2}$ hr. The weight (R) of the residue is obtained after drying it in an air-oven at 105°, and its ash content (A_1) determined.

The ash content of the original sample having been determined, the reactivity index of the ulmins can now be calculated from the following data :

A = Weight of ash in 0·5 g. of the coal after extraction with pyridine.

A_1 = Weight of insoluble ash, i.e., ash in residue R.

P = Weight of resistant plant entities together with insoluble ash.

R = Weight of residue after pressure oxidation and extraction with potassium hydroxide solution.

Reactivity index $= \dfrac{(0\cdot5 - A) - (R - A_1)}{(0\cdot5 - A) - (P - A_1)} \times 100$

When carrying out this determination, special care should be taken that the samples of extracted coal used are well mixed, sieved, and dried. Leakage of oxidising agent from the pressure-bottles must be prevented. For routine work, screw-stoppered or spring-controlled pressure bottles, or reaction-bottles closed with ground-glass discs, can be used, but for research purposes it is better to employ flasks the necks of which are sealed with the blow-pipe. When opening such flasks, care must be taken to avoid an explosion of the chlorine dioxide within. The crucibles with fritted glass discs used should be tested beforehand as regards their speed of filtration, by recording the times taken for them to become empty of water, no suction being applied. The most suitable crucibles drain almost completely in from 4 to 10 minutes.

It should be noted that the reactivity index as thus determined has a different value from that obtained by the method described in J., 1928, 2967, because an oxidising solution of greater strength is used. Parallel determinations made by the two methods on the

American coals previously used, show that the relationship, New Value $= 0.8$ Old Value $+ 18$, holds sufficiently closely to enable comparison to be made between the results recorded for the American coals and those for the British coals here given.

These methods of analysis are used for the routine examination of coals, in connexion with various researches, in the Fuel Technology Laboratories of Sheffield University. The least satisfactory determination is that of the " resistant residue." The results obtained are always too low by an indeterminate amount, for the plant entities in coal are not wholly resistant to oxidation and all are not equally resistant. Typical rational analyses of British coals are recorded in Table III.

TABLE III.

Rational Analyses of British Coals.

Rational analysis, %.

Description of coal.	Hydro-carbons and resins.	Resis-tant residue.	Ulmins.	Reac-tivity index of ulmins.	Carbon, % on ash-free dry coal.
Seven Foot (Warwickshire) ...	2·9	2·8	94·3	81	78·2
Hamstead, durain (Stafford-shire)	3·5	21·4	75·1	77	80·9
Yard (Lancashire)	3·7	6·9	89·9	76	81·4
Waterloo (Derbyshire)	3·2	4·7	92·1	68	82·1
Barnsley, brights (Yorkshire)	3·4	10·8	85·8	62	85·5
Deep Hard (Derbyshire)	2·7	4·8	92·5	61	83·3
Barnsley, hards (Yorkshire) ...	2·9	18·2	78·9	58	84·5
Silkstone (Yorkshire)	4·0	3·4	92·4	58	83·6
Wigan Six Foot (Lancashire) ...	3·0	4·1	92·9	57	82·5
Parkgate, brights (Yorkshire)	3·4	11·3	85·3	56	85·6
Swallowood, brights (Yorkshire)	3·4	10·8	85·8	56	84·6
Swallowood, hards (Yorkshire)	3·1	15·7	81·1	55	84·2
Hutton (Durham)	2·6	23·8	72·6	54	86·3
Parkgate, hards (Yorkshire) ...	3·0	13·2	83·8	52	84·7
Busty (Durham)	2·6	18·4	79·0	47	85·6
Chislet (Kent)	4·8	13·8	81·4	44	88·6

" Hards " and " brights " are terms used locally to describe parts of the seams mined separately, the " hards " being mainly durains with vitrain bands and the " brights " mainly clarains.