Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. IV. Analyses of the Sulphur-Containing Compounds, Coals.

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The method so far developed can not successfully be applied to the sulphur-containing compounds.

Coals contain 0.3–3% of sulphur and give on heating hydrogen sulphide which poisons and reduces the activity of nickel catalyst. We have tried to fix the sulphur as copper sulphide, placing the reduced copper between the Pt-silica gel catalyst and the nickel catalyst in the reaction tube.

Experimental Details. *The apparatus* used and the procedure employed are described in the previous papers.(1)(2)

The desulphuring agent. Copper oxide is easily and completely reduced by hydrogen at moderate temperature, and therefore, the unfavorable reaction of hydrogen sulphide with copper oxide is excluded.

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(1) K. Morikawa, T. Kimoto and R. Abe, this Bulletin, **16** (1941) 1.
(2) K. Morikawa, T. Kimoto and R. Abe, ibid, **16** (1941) 33.

Furthermore copper combines with sulphur very tenaciously and is difficultly reduced by hydrogen under ordinary conditions. These properties of copper were thought to be very suitable for fixing sulphur from the hydrogen stream in this analytical procedure. Kieselguhr is impregnated with copper nitrate solution and the resultant dried mass was ignited.

The 15 g. of copper oxide-kieselguhr mixture thus prepared were inserted between Pt-silica gel catalyst and Ni-thoria catalyst and completely reduced in situ before the analysis.

The time required for analysis. As the amount of kieselguhr was increased the time required for analysis was prolonged to 70 minutes.

Sample:coal. Three kinds of coal of different ranks were used and their analytical data were given in Table 6.

Table 6. Ultimate analyses of sample coals.

Kinds	Ash %	C %	H %	N %	S %	O %	O (pure coal)
Jarahinol.	4.43	67.52	4.54	1.17	0.18	22.16	23.18
Fushun	2.38	76.63	5.30	1.25	0.48	13.96	14.30
Tatong A	2.94	81.99	4.41	0.89	0.37	9.40	9.68
Tatong B	5.18	79.65	4.24	0.78	0.50	9.65	10.18
Tatong C	8.48	76.04	4.78	0.89	0.35	9.46	10.34

Experimental Results. *Examination of Absorbents.* Coals contain nitrogen and, therefore, give ammonia in the process of this analytical method. Inaba and Abe proved that coal which contained 1–2% of nitrogen gave appreciable amount of ammonia, i.e., 2.0 mg. in this procedure. They caught ammonia, by 0.02 N sulphuric acid solution and water by calcium chloride. In the experiments shown in Table 7. We found that copper catalyst not only caught sulphur and extended the life of Ni-catalyst but also decomposed ammonia to its elements and decreased partial pressure of ammonia to the negligible extent; therefore, calcium chloride could be more conveniently used than caustic soda as the absorbent for water.

Table 7. Examination of $CaCl_2$ as the absorbent for water. Analytical condition; Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hyrogen streaming velocity 5 l./hr., time for analysis 70 min., Sample; mixture of saccharose and dimethylglyoxime.

Expt. No.	Sample (g.)	N % in sample	Formed NH_3 (mg.)	O % (Found)	O % (Calculatad)	Error %	absorbent
D-3	0.1510	2.23	0.30	48.78	49.15	−0.37	0.02 N H_2SO_4 + $CaCl_2$
D-6	0.2914	1.51	0.45	49.95	49.90	+0.05	
D-5	0.1907	1.47	0.30	48.94	48.83	+0.11	
D-9	0.1487	3.02	—	48.62	48.41	+0.21	$CaCl_2$
D-7	0.1897	2.12	—	49.05	49.34	−0.29	,,
D-8	0.2134	1.45	—	50.20	49.96	+0.24	,,

Effects of coal ash. We are accustomed to determine the inorganic substances in coal by burning the coal in air and weighing the calcined residue, that is, the ash of coal. It is clear that we deal not with the real inorganic substances as present in coals, but with the oxidized forms. Here on the contrary, in this procedure we are concerned with the reduced forms instead of the real inorganic substances. Considering the nature and composition of inorganic substances which occur in coals, we expect, in general, but not necessarily always, higher values of oxygen by hydrogenation than ordinary oxidation method. The results given in Table 8 may be taken as a good example.

Table 8. Results of direct determination of oxygen in the coals. Analytical condition; Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., analytical period 70 min., absorbent: granules of caustic soda.

Expt. No.	Kind of samples	Heating temp. of the sample	Sample (g.)	Oxygen %	Difference between hydrogenation and oxidation methods.
D–32	Jarahinol	950°C.	0.2125	24.02	+0.84
D–33	,,	800	0.2050	23.62	+0.44
D–28	Fushun	950	0.2177	14.79	+0.49
D–29	,,	950	0.2508	14.86	+0.56
D–35	,,	900	0.2372	14.91	+0.61
D–39	,,	800	0.2287	14.88	+0.58
D–45	Tatong A	950	0.1934	10.22	+0.54
D–43	Tatong B	950	0.2354	10.47	+0.29
D–44	Tatong C	950	0.1999	10.77	+0.43

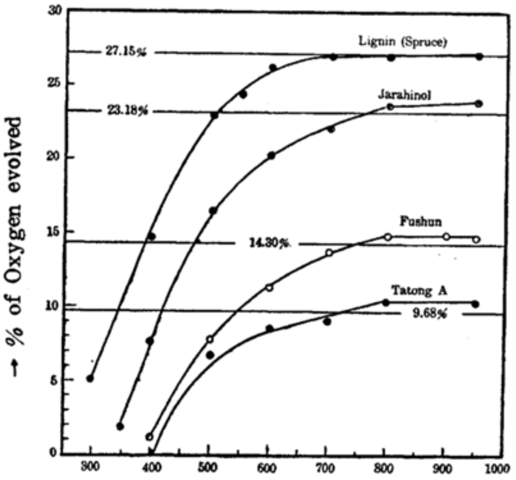

Fig. 15. Relation between the temperature of heating sample and % of oxygen evolved from the various coals.

Effects of coal ranks. The relations between the temperatures of heating samples and the amounts of oxygen caught as water were plotted in Fig. 15.

Degree of polymerisation increases in the order of lignin, Jarahinol, Fushun, and Tatong coals. Extrapolating the curves to the abscissa we know the decomposition temperature of each sample and found that the higher the polymerisation degree the higher the decomposition temperature. Above 800°C. all the three coals gave constant amounts of oxygen which were 0.5% higher than the values obtained by usual combustion method. The presence of copper extended the life of Ni-thoria catalyst and it was actually possible to repeat the analysis 18–20 times with coal samples. Pt-silica gel catalyst was so stable that we could recover the activity by burning the free carbon deposited on the catalyst and found not necessary to replace it during year's experiments.

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