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Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. I. Search of the Optimum Analytical Conditions.

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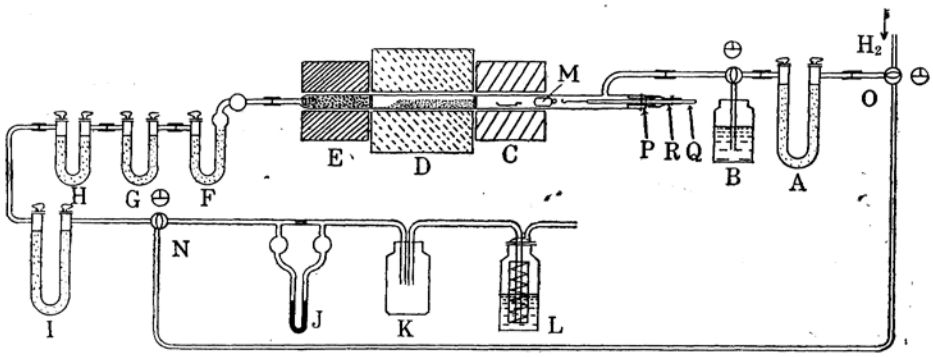
The direct determination of oxygen in the organic compounds by the hydrogenation method according to Meulen[1] was examined in details. Inaba and Abe[2] succeeded in the analysis of saccharose which was considered to be a difficult one. W. R. Kirner,[3] however, could not obtain good results with saccharose and he discussed the problem of application of corrections obtained in the blank experiments. We, therefore, hoped to reexamine and clear up these points by experiments and also by theoretical consideration of this hydrogenation method.

Experimental Details. (1) *The apparatus* used is shown in Fig. 1. It is essentially the same as Russel and Fullton's[4] apparatus.



A: $CaCl_2$ or NaOH granules
B: Conc. H_2SO_4
C: Sample heating furnace
D: Cracking furnace
E: Reduction furnace
F, G, H: $CaCl_2$ or NaOH granules
I: $CaCl_2$ tube
J: Flowmeter
K: Empty bottle
L: Conc. H_2SO_4
M: Quartz plag
N: Three way cock
O: Three way cock
P: Rubber stopper
Q: G'ass tube
R: Rubber tube

Fig. 1. Apparatus.

(1) H. Meulen: *Rec. trav. chim.*, **53** (1934), 118; *Bull. Soc. Chim.*, [5] **2** (1935), 1692.
(2) T. Inaba and R. Abe: *J. Soc. Chem. Ind., Japan*, **39**, 91 B (1936).
(3) W. R. Kirner: *Ind. Eng, Chem., Anal. Ed.*, **9** (1937), 535-539.
(4) W. W. Russel, J. W. Fullton: *Ind. Eng. Chem., Anal. Ed.*, **5** (1933), 384.

(2) *The catalyst*: The cracking (Pt-silica gel) and reducing (Ni-thoria) catalysts were prepared according to Russel's procedure[4]. The latter was reduced with hydrogen at 350°C. for 3 hours and then at 500°C. for 12~15 hours, thereby the water formed by reduction of catalyst would be less than one mg. per hour. After 7–10 analyses the Pt-silica gel catalyst was covered with free carbon deposit and lost its activity and, therefore, it was required to revive it by burning the carbon deposit with streaming air.

(3) *The analytical procedure* was essentially the same as Inaba and Abe's.[2]

(4) *The absorbent*: Calcium chloride was used for typical substances which contained only carbon, hydrogen and oxygen, and caustic soda or soda lime, for nitrogen containing samples, the latter was preliminarily treated with dried ammonia gas.

(5) *The samples* were all Merck's preparations and were dried on phosphorus pentoxide in the Abderhalden vacuum drying apparatus.

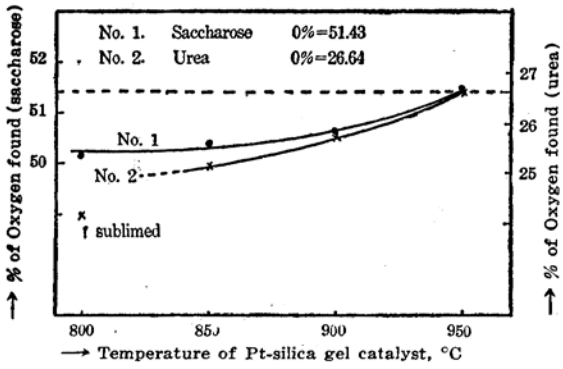
Experimental Results. The optimum analytical conditions were searched with saccharose and the results obtained were given in Fig. 2–5.

(1) *Cracking temperature*: Under 950°C. the analyses gave lower results, indicating the incomplete cracking of organic vapours (Fig. 2).

(2) *Reducing temperature*: The temperature around 350°C. was found to be satisfactory (Fig. 3). Under 300°C. the reducing velocity on Ni-catalyst was too slow and above 400°C. the equilibrium conditions of the following reactions became unsatisfactory for complete conversion of carbon oxides.

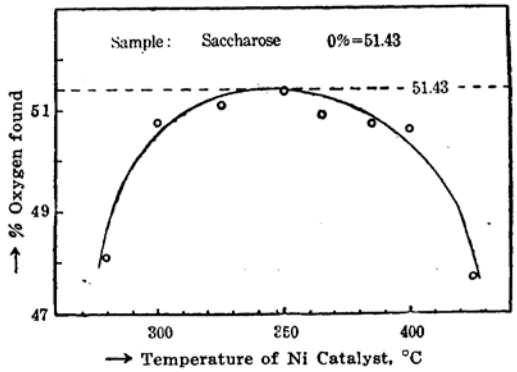
$$CO+3H_2 = CH_4+H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$CO_2+4H_2 = CH_4+2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$



Analytical conditions: Temp. of Ni catalyst 350 C; hydrogen streaming velocity 5 l/hr; analytical time, saccharose 60 min., urea 80 min.

Fig. 2. Influence of Temperature of Pt-silica Gel Catalyst.



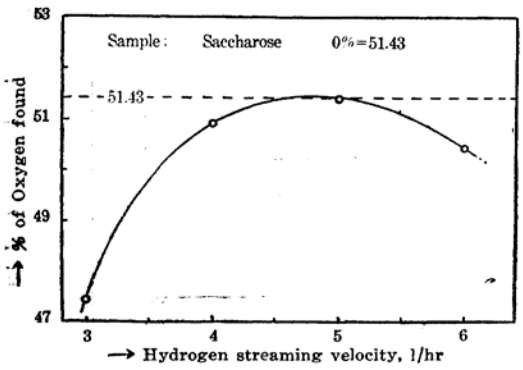
Analytical conditions: Temp. of Pt-silica gel catalyst 950 C; hydrogen streaming velocity 5 l/hr; analytical time 60 min.

Fig. 3. Relation between Reduction Temperatures and % of Oxygen found.

(3) *Streaming velocity of hydrogen*: Around 5 l./hr. was found to be best suited (Fig. 4). When the hydrogen streamed too slowly the

vapour pressure of carbon oxides became too high and, therefore, equilibrium conditions of reaction (1) and (2) became unfavourable for the analytical purpose.

(4) *Amount of sample taken*: The optimum amount of sample to be taken were investigated, and the product of the weight (in gram) and the oxygen content (in percentage) of the sample taken was expressed as K. Only when K was below 12, saccharose and urea gave good results as shown in Fig. 5.



Analytical conditions: Temp. of Pt-silica gel catalyst 950 C: temp. of Ni catalyst 350°C; analytical time 60 min.

Fig. 4. Influence of Hydrogen Streaming Velocity.

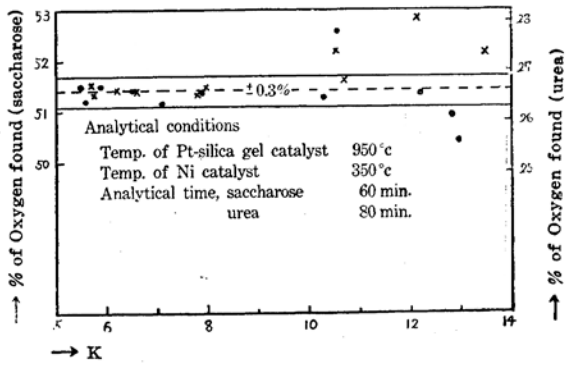


Fig. 5. Influence of weight of sample.

(5) Typical results with several compounds containing only carbon, hydrogen, and oxygen are shown in Table 1.

(6) Typical results with several compounds containing only carbon, hydrogen, oxygen, and nitrogen are indicated in Table 2.

Table 1. Analyses of CHO compounds.

Analytical conditions: Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., time required for these runs 60 min.

Expt. No.	Sample		Water obtained g.	Blank value mg.	Oxygen found %	Error %
	Kinds	Wt. g.				
58		0.1070	0.0642	2.2	51.50	+0.07
57	Saccharose	0.1121	0.0670	2.2	51.34	−0.09
25		0.1152	0.0688	2.0	51.50	+0.07
56	(0% = 51.43)	0.1282	0.0772	3.0	51.40	−0.03
24		0.1537	0.0912	2.2	51.42	−0.01
				mean	51.43	+0
78	Benzoic	0.0869	0.0265	0.8	26.26	+0.04
94	Acid	0.1000	0.0315	1.7	26.46	+0.24
76	(0% = 26.22)	0.1144	0.0346	0.8	26.32	+0.10
92		0.1153	0.0354	1.7	25.96	−0.26
				mean	26.25	+0.03

Table 1.—(*Concluded*)

Expt. No.	Sample Kinds	Sample Wt. g.	Water obtained g.	Blank value mg.	Oxygen found %	Error %
67	α-Naphthalic Acid (0% = 18.60)	0.1002	0.0237	3.5	18.52	−0.08
97	β-Naphthalic	0.0752	0.0174	1.7	18.54	−0.06
105	Acid	0.1027	0.0237	2.2	18.59	−0.01
104	(0% = 18.60)	0.1113	0.0259	2.5	18.67	+0.07
106		0.1148	0.0262	2.2	18.56	−0.04
				mean	18.58	−0.02
63	Anthraquinone	0.0642	0.0129	1.8	15.36	+0.02
64	(0% = 15.38)	0.0799	0.0163	2.2	15.56	+0.18
65		0.0993	0.0196	2.2	15.56	+0.18
62		0.1163	0.0222	2.0	15.43	+0.05
				mean	15.48	+0.10
C- 9	Cellulose	0.1932	0.1069	3.1	49.88	−0.29
C-10	(indirect method)	0.2441	0.1403	2.1	50.28	+0.11
	(0% = 50.17)			mean	50.08	−0.09

Table 2. Analyses of CHON compounds.

Analytical condition: Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., time required for these runs 80~90 min.

Expt. No.	Sample Kinds	Sample Wt. g.	Water obtained g.	Blank value mg.	Oxygen found %	Error %	Absorbent
116	Urea (0% = 26.64)	0.1147	0.0355	2.0	26.71	+0.07	Granules of caustic soda
119		0.1325	0.0416	2.0	26.54	−0.10	,,
118		0.1329	0.0422	2.0	26.84	+0.22	,,
117		0.1478	0.0434	2.0	26.68	+0.04	,,
135		0.2252	0.0688	1.3	26.62	−0.02	Soda lime
136		0.2446	0.0750	1.3	26.79	+0.15	,,
				mean	26.70	+0.06	
121	Dimethyl-glyoxime	0.0809	0.0258	2.0	27.77	+0.20	Granules of caustic soda
140	(0% = 27.57)	0.1170	0.0383	2.0	27.88	+0.31	Soda lime
139		0.1198	0.0396	2.0	27.55	−0.02	,,
				mean	27.73	+0.16	
L-3	Beech-Lignin (indirect method) (0% = 30.66)	0.1234	0.0423	0.1	30.47	−0.19	Granules of caustic soda
L-6		0.1432	0.0500	0.9	30.51	−0.15	,,
				mean	30.49	−0.17	

Discussion of Results. (1) *Analysis of saccharose*: W. R. Kirner[3] was inclined to believe that saccharose left much carbon residues which retained some oxygen very tenaciously and thus gave lower values than the calculated ones. Russel, Fullton[4] and Inaba, Abe[2] and the authors all employed Pt-silica gel catalyst for the cracking purpose and they all obtained good results with saccharose. As made clear above there is an optimum range in every analytical condition and, therefore, one mistake in selecting these ranges would bring unsatisfactory results.

(2) *Blank experiments*: The reduction of Ni-thoria catalyst prepared by the ignition of mixed nitrates requires 3 days at 400°C. and 12–15 hours at 500°C. after which the reduction water would be less than 1 mg.. Even though the catalyst tube was left overnight under hydrogen pressure, a little above the atmospheric pressure, 7–16 mg. of water were always caught in the first blank run of the next morning, and, therefore, it was necessary to reduce the catalyst half an hour at 450~500°C. and to make one blank run at 350°C. every morning. When the catalyst was sufficiently reduced for use, and if we streamed hydrogen through catalyst tube without opening the end of the tube for 1 hour at

Table 3. Effects of Blank Value.

Analytical condition : Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., time required for these runs 60 min.

Expt. No.	Analytical order	Sample		Water obtained g.	Blank value mg.	Oxygen found %	Error %	Note
		Kinds	Wt. g.					
(1) Case in which the Ni-catalyst was not yet completely reduced								
55	1	Saccharose	0.1089	0.0659	3 5	51.19	−0.24	
56	2	(0% = 51.43)	0.1282	0.0772	3.0	51.40	−0.03	
57	3		0.1121	0.0670	2.2	51.34	−0.09	
58	4		0.1072	0.0642	2.2	51.50	+0.07	
104	1	β-Naphthalic	0.1113	0.0259	2.5	18.67	+0.07	
105	2	Acid	0.1027	0.0237	2.2	18.59	−0.01	
106	3	(0% = 18.60)	0.1148	0.0262	2.2	18.56	−0.04	
(2) Cases in which the Ni-catalyst was almost completely reduced								
75	1	Benzoic	0.0913	0.0259	0.6	24.61	−1.61	too low
76	2	Acid	0.1144	0.0346	0.6	26.39	+0.17	
77	3	(0% = 26.22)	0.0869	0.0264	0.6	26.35	+0.12	
86	1	Saccharose	0.1042	0.0610	1.7	50.55	−0.88	too low
87	2	(0% = 51.43)	0.2007	0.1176	1.7	51.29	−0.14	
88	3		0.2510	0.1442	1.7	50.42	−1.01	sample excess (K = 12.9)
89	1	Saccharose	0.2147	0.1241	1.6	50.67	−0.76	too low
90	2	(0% = 5143)	0.2449	0.1450	1.6	50.96	−0.47	sample excess (K = 12.8)
91	3		0.2211	0.1295	1.6	51.37	−0.06	

the rate of 5 l./hr., we would obtain about 1 mg./hr. of water. If, however, we followed the procedure just as in the actual analysis, that is, opening the end of the tube and streaming out the air in the reverse direction for 10 minutes, we always obtained about 2–3 mg./hr. of water. Strictly speaking we should apply these values to the analysis as corrections of the blank experiments, and so we have adopted this way of correction throughout this paper and obtained satisfactory results.

When the Ni-catalyst was reduced completely, the blank water value would be 0.6~1.7 mg./hr. and in these cases the first run used to give somewhat low results as clearly shown in Table 3. This means that the over-dried catalyst surface retained very tenaciously some water produced during the analysis and therefore, did not recover the original surface conditions within the limited experimental period. Thus we should make three successive runs of which the first might be looked upon as preliminary and the last as the check.

(3) In this hydrogenation analysis the sample should be very slowly vaporized or cracked so as not to cause a rapid decomposition of the sample, accordingly not to raise too high the partial pressure of carbon monoxide or carbon dioxide; otherwise the reduction equilibrium of reaction (1) or (2) becomes unfavourable for the complete reduction of carbon oxides and would give the analyses low results. From these standpoints we should make the preliminary run and should find the suitable heating rate for unknown sample to be analysed. These points will be discussed in details in the next paper.

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