XXIII.—*Researches on Moorland Waters. I. Acidity.*

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MOORLAND waters are consumed at present by over five and a quarter millions of people in Yorkshire, Lancashire, Westmoreland, and Cumberland. Their well known plumbo-solvent action has been considered of such importance as to warrant a Government investigation, the results of which will be found collated by Mr. W. H. Power, F.R.S., in the Supplement to the Twenty-third Annual Report of the Local Government Board, pp. 332—424, and it is there demonstrated from the work of Mr. and Mrs. Atkinson and Drs. Barry and A. C. Houston that acidity and lead dissolving power run parallel to each other. In common with many analysts, I have long associated plumbo-solvent power with acidity, and in an investigation made for the Halifax Corporation concerning Moorland waters from many gathering grounds, I reported to this effect in 1895. References to the question are made in papers by Messrs. A. H. Allen, C. Rawson, and T. Whitaker (*Journal of the Society of Dyers and Colourists*, 5, 54—71). The question of acidity is undoubtedly of primary importance in considering this class of waters, and the following experiments and observations thereon will, therefore, be of interest.

Method of Estimating Acidity.

The solutions to be dealt with may be under or a little over $\frac{1}{10000}$ th of normal, and as concentration by the usual methods is objectionable, I have adopted the following course of procedure as being both the easiest and quickest, and the least likely to introduce errors.

To 100 c.c. of the water in a beaker, 1 or 2 drops of alcoholic solution of phenolphthalein are added, and N/100 alkali is run in from a burette until a very slight pink tint is obtained; this gives the total acidity. Through a little more than 100 c.c. of water, air, free from carbonic anhydride, is rapidly aspirated for half an hour; titration of 100 c.c. of the water thus treated gives the residual or organic acidity, the difference between the first and second titrations being the volatile acidity, and as this is very largely, if not entirely, due to carbonic acid, it may be termed inorganic acidity. As alcoholic solution of phenolphthalein, when used as an indicator, is sometimes neutralised by the addition of a little alkali, it is well to mention here the precaution that not more than 1 or 2 drops of such a solution should be used in titrating moorland waters, or somewhat discordant results may be obtained; this effect I have traced to the acetate present in the indicator solvent.

Diffusion.

In my earliest observations of waters taken from places contiguous to moorlands, there was gradual decrease of acidity on keeping ; this I was at first at a loss to account for, but it was eventually put down to diffusion ; the Winchester quarts containing the waters were kept in a room where they were freely exposed to sunlight, and they were only opened as required for purposes of analysis. In three of these samples, A, B, and C, the following percentage changes were observed.

Acidity.

Day of testing.	A.	B.	C.	Average.
1st.....	100	100	100	100
8th	86	86	—	86
10th	—	—	76	76
25th	57	63	—	60
36th	—	42	—	42
52nd	—	—	26	26
181st.....	—	29	—	29

A was from a private well not far removed from moorland ; B was from another well of the same kind, and C was from a trench 7 feet deep dug into the side of a moor-capped hill of Millstone Grit.*

It was these results which suggested the advisability of rapid aspiration of air free from carbonic anhydride as a necessary part of any method of estimating acidity. As a preliminary trial, distilled water was charged with carbonic anhydride ; 100 c.c. took 60·1 c.c. of N/100 alkali, but after aspiration for half an hour only 0·3 c.c. of alkali was required for neutralisation, which was the initial acidity of the distilled

* Some other analytical data concerning these samples are as follows.

Parts per 100,000.

	Total solids.	NaCl.	Free NH ₃ .	Albuminoid NH ₃ .	N as nitrates and nitrites.	c.c. of N/100 alkali required per 100 c.c.
A.....	18	.3	nil	0·005	0·56	11
B.....	63	6·4	0·03	0·03	1·2	10
C... ..	10	2·1	nil	nil	—	7·2

It may also be mentioned that all the waters referred to in this paper are of permanent hardness only.

water. A sample of the water C was now sent for and submitted to rapid aspiration for 30 minutes. Its acidity was reduced to 26 per cent. of the original.

Water taken direct from moorland catchwater or stream may exhibit little alteration on aspiration. Thus a water from a clough receiving its supply from the adjacent moorland showed no appreciable alteration by diffusion in 15 days, neither was the effect of aspiration any more marked. Some freshly-collected samples from very peaty gathering grounds gave respectively 14, 11, 5, and 6 per cent. of volatile acidity, calling the total acidity 100. The following figures were obtained with waters from moorland reservoirs.

Acidity.

c.c. of N/100 alkali required per 100 c.c.

Sample.		Total.	Organic.	Inorganic.
D.	Centre of large peaty reservoir	5.3	4.1	1.2 = 22 per cent.
E.	Small reservoir.....	1.3	0.8	0.5 = 38 „ „
F.	„ „	2.9	2.0	0.9 = 31 „ „

Configuration of Gathering Grounds.

Some of my observations appear to throw a new light on the somewhat old problem, why one gathering ground should yield waters which acted much more quickly on lead, or, in other words, were so much more acid, than others. This has been a fruitful subject of discussion and of municipal inquiry, in the course of which expressions have been evolved, and have come into use as synonymous with bad and good waters as, for instance, “high” and “low-level” supplies, the former being regarded as productive of epidemics of plumbism. I have found that mere altitude of gathering grounds is not sufficient to account for some of the striking differences observed in these waters. Certainly, one of the worst waters with which I have had to deal is a high-level one, the reservoir being 1300 feet above sea-level, and better waters have been had from reservoirs 860 to 1020 feet high; on investigation, however, it appeared that some of the latter have gathering grounds rising to a higher level than in the former case. The “high” and “low-level” distinction has, therefore, seemed to me of little or no value, and I have come to the conclusion that, other things being equal, it is rather a question of the average gradient of a gathering ground. The reasons for this conclusion are that the acidity is due to the peat through which the water passes, and that there will be less time for solution or the taking up of the acid where

the gradient is a high one than where it is a low one. I have submitted this hypothesis to the test in a comparison of four gathering grounds on like geological strata—the Millstone Grit—with the following results.

Gathering ground.

Reservoir or clough.	Height above sea level.	Gradient.	Total acidity.
G.....	1330 to 1450 feet	1 in 44	5·3
H.....	980 „ 1100 „	1 in 23 to 1 in 28	2·2
I.....	985 „ 1430 „	1 in 12	1·4
J.....	1075 „ 1344 „	1 in 12	1·0

Correlation of Acidity and Absorbed Oxygen Numbers.

Another fruitful source of speculation has been the nature of the acidity of moorland waters. The earliest idea attributed it to mineral acids; now it is put down to peaty acids or, to be more precise, to humic acid. It appeared not unlikely that moist combustion combined with organic acidity determinations might throw further light on the subject, as, for example, some direct relation between the absorbed oxygen numbers and those for organic acidity, on the assumption that the organic acidity represents the presence of a carbon compound of definite composition. Forschammer's permanganate process was employed, the length of the time allowed being 4 hours. The following observations are for waters from widely different moorland sources.

Sample.		Parts per 100,000.		
		Organic acidity.	Absorbed oxygen.	Calculated organic carbon.
K.....	From a large service reservoir of public supply.....	0·6	0·021	0·050
L.....	Another supply of inferior quality....	1·1	0·045	0·108
M.....	From the feeder to a reservoir of compensation water; running.....	5·1	0·77	1·848
N.....	From the same source as M; feeder stagnant.....	5·9	0·94	2·256
O.....	Mountain stream.....	1·4	{ By interpolation Found	{ 0·125 0·15

The absorbed oxygen is here converted into organic carbon by using Sir E. Frankland's factor 2.4. This step was checked by referring back to his analysis of a moorland water, made for official purposes, and of which I had a duplicate sample, O. The organic acidity was 1.4; this gives 0.125 part of organic carbon per 100,000 by interpolation, as against 0.15 part returned in the analysis.

The direct relation looked for only appears in the first two observations. Afterwards, as the acidity increases and the yellow colour deepens, the carbon appears to increase abnormally, as shown in curve I. in the diagram.

The general assumption that the acidity is due to humic acid is somewhat wanting in precision, seeing that some half-dozen humic acids have been found of late years. The basicity of two have been ascertained, namely, Detmer's octobasic acid, $C_{60}H_{54}O_{27}$ (*Watts' Dictionary*, 7, 648), and Berthelot and André's tribasic acid, $C_{18}H_{16}O_7$ (*Abstr.*, 1891, 1089). The curve for the carbon of the latter approaches nearest to my observations for moorland waters (curve II, diagram); yet it is so far away from it that one is warranted in concluding that the organic acidity of moorland waters is due to an acid or acids of lower equivalent than that of the humic acids whose basicity has been ascertained up to now.

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