XLIII.—*The Mineral Waters of Askern, in Yorkshire.*

By C. H. BOTHAMLEY.

THE mineral waters of Askern, in the West Riding of Yorkshire, have for a long time been used with success in the treatment of chronic rheumatism and skin diseases, and they constitute a group of sulphuretted waters which, in general character, is unique in this country. The village stands on the edge of an extensive plain, a large part of which is uncultivated and imperfectly drained peat-bog. It is built on strata belonging to the Permian formation, and steep hills of magnesian limestone rise close behind the village on the west. Red Permian marls, containing thin beds of gypsum, also occur in the immediate neighbourhood. To the east of the high road that runs through the village, is a sheet of water about 6 acres in extent, known as "The Pool." It is fed partly by springs and partly by the drains or streams from the common, and is comparatively shallow, except in a few pits or holes, where it reaches a depth of about 25 feet. The sulphuretted springs are situated not far from the edge of the Pool, to the west and south-west.

Askern is mentioned under the name *Askeron* by Dr. Short in his treatise, *A Natural Experimental and Medicinal History of the Mineral Waters of Derbyshire, Lincolnshire, and Yorkshire*, published in 1734, and later the water was examined by Le Gay Brewerton, who published his results, in 1817, in his *Treatise on the Mineral Waters of Askern*. In July, 1821, an imperfect analysis was made by a Mr. Murray, and was published in the *Doncaster Gazette*.

In 1842, Dr. Edwin Lankester published *An Account of Askern and its Mineral Springs, together with a Sketch of the Natural History and a Brief Topography of the Immediate Neighbourhood*. He speaks of six wells, five of which had been opened since the publication of Mr. Brewerton's book. Five wells out of the six were analysed, the experiments seemingly being made in 1840, and Dr. Lankester was assisted in the analytical work by Mr. West, of Leeds.

The dissolved solid constituents in grains per imperial gallon were as follows :—

	Manor Well.	Charity Well.
Sulphate of magnesia	34	18
Chloride of calcium	3	4
Sulphate of lime	110	104
Carbonate of lime	6	12
Carbonate of soda	26	26
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	179	164
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Dr. Lankester states that the solid matter in all the other wells was of similar composition, although differing in each case in total amount, the quantity in the Terrace Well being 144 grains, in the South Parade Well 140 grains, and in the Mather Close Well 100 grains.

The gaseous constituents were hydrogen sulphide, carbonic anhydride, and nitrogen, the volumes of hydrogen sulphide in cubic inches per imperial gallon being: Manor Well 8, Terrace Well $8\frac{1}{4}$, Charity Well $6\frac{1}{2}$, South Parade Well 6, and Mather Close Well 14.

The appearance of sodium carbonate amongst the solid constituents arises from the manner in which Lankester and West combined the acids and bases in calculating their results. As a matter of fact, the water and the residue left on evaporation are not alkaline, and the existence of sodium carbonate in solution with calcium and magnesium sulphates is obviously improbable.

No analyses have been made since those of Lankester and West, 50 years ago, and it seemed that a systematic examination of the Askern waters would form an appropriate continuation of the analyses of the sulphur and other waters of Harrogate, made about 12 years ago (Trans., 1881, 39, 497—516). The investigation extended over a period of about two years, samples of water being collected and the more important constituents estimated at various seasons of the year, the work being done in the Chemical Laboratory of the Yorkshire College, whilst I was Assistant Lecturer on Chemistry.

The Present Wells.

There are now four wells, to each of which is attached a pump-room and a suite of baths, and through the kindness of the proprietors I was afforded every opportunity of collecting samples of the water and making the necessary experiments at the wells.

The *Mather Close Well* supplies the Town End or South Parade Baths, and is situated in lat. $53^{\circ} 36' 41.7''$ N., and long. $1^{\circ} 9' 1.5''$ W. its exact position being shown on the 6-inch Ordnance Survey Map. It is simply a deep tank or shallow well cut in the peat, and has no lining of any kind, but is securely covered in. Immediately above the well is an ordinary pump, with a lead suction pipe that has been in use for many years. The supply of water is abundant, but I am informed that the well has once or twice been pumped dry.

This water comes directly out of the peat, and most nearly of all the four represents the water as it occurs in the peat. It was, therefore, examined somewhat more closely than the other waters.

The *Charity Baths* are near the south-west corner of the Pool, and

are supplied by water from a tank or well, situated some 40 yards away from the Pool and from the pump room. The well is built of brick, with an outer casing of puddled clay, but I was unable to satisfy myself that the top was sufficiently protected from surface drainage.

The *Terrace Bath Well* is on the west side of the Pool, in lat. $53^{\circ} 36' 51''$ N., and long. $1^{\circ} 9' 0''$ W., and is about 40 yards to the south of the pump room. It is dug in the peat, not far from the edge of the Pool, and is constructed of puddled clay with a brick lining, and has been well covered over.

The *Manor Well Baths* stand on the east side of the Pool, and are supplied partly from a well under the buildings and partly from the well at the south-west corner of the Pool, which also supplies the Charity Baths. From the latter the water is brought across the Pool in an iron pipe, and the water from the two sources is allowed to mix in a puddled well.

Collection of Samples.

The waters were collected with the usual precautions. They were all slightly turbid and had a yellowish colour, and none of them, except the Terrace Bath water, on one or two occasions, showed any signs of effervescence. They all smelled strongly of hydrogen sulphide, but the odour was not quite the same as that of hydrogen sulphide prepared by ordinary laboratory methods; it distinctly recalled the odour of some thiocarbon compounds. All the waters were practically neutral to litmus, though now and again a faint indication of acidity was perceptible. When allowed to remain exposed to the air, they very slowly became turbid, in consequence of the precipitation of sulphur.

General Method of Analysis.

The general scheme of analysis adopted was that laid down by Fresenius, such modifications being made as were necessitated by the character of the water.

The residue left on evaporation was dried at 120° , and there was no difficulty in obtaining a constant weight at this temperature. The dried residue was only very slightly hygroscopic. It was found advisable to pass a current of washed carbonic anhydride through the water during evaporation, in order to prevent, or, at any rate, to minimise, separation of sulphur from the hydrogen sulphide, and formation of thiosulphates.

Determinations of all the principal constituents were made on two

distinct series of samples of the waters, an interval of several months elapsing between the collection of the two series. Additional estimations of the hydrogen sulphide and combined sulphuric acid were made at various times of the year.

Sulphur Compounds in the Waters.—Hydrogen sulphide was estimated at the wells, a measured quantity of the freshly-drawn water being run into a measured excess of centinormal iodine solution, and the excess of iodine determined by means of centinormal thiosulphate solution.

It was found that the whole of the hydrogen sulphide could be expelled from the waters by the prolonged passage of a current of purified hydrogen, and it follows that the whole of the hydrogen sulphide is present in the free state.

Neither thiosulphates nor sulphites could be detected in the waters either before or after the passage of the hydrogen.

It is noteworthy that, notwithstanding the absence of sulphides, sulphites, or thiosulphates, the water through which hydrogen had been passed still decolorised a certain quantity of iodine solution. This probably arises from some action of the iodine on the organic matter dissolved in the water. The volume of approximately centinormal iodine solution absorbed in this way by 1000 c.c. of each of the waters was as follows:—

Mather Close.	Charity.	Terrace.	Manor Well.
24·0	34·0	18·0	27·0 c.c.

When calculating the quantity of hydrogen sulphide present, a correction was made on account of this absorption.

Alkalis were weighed both as chloride and as sulphate, the magnesium and sulphuric acid having been removed together by means of barium hydroxide. Iron was estimated colorimetrically by Carnelley's method, with potassium ferrocyanide. I am indebted to Mr. F. Dent, student in the Chemical Laboratory at the Yorkshire College, for his aid in finishing these two estimations.

Constituents present in Small Quantities.—44 litres each of the Mather Close Well and the Terrace Bath waters were evaporated with the usual precautions.

Traces of lithium were found on spectroscopic examination in both waters, and strontium in very minute traces in the Terrace Bath water, but not in the Mather Close water. Special examination was made for barium, but it could not be detected even by the spectroscope.

Iodine was present in distinct, though minute, traces in both waters, but bromine was not present in either. Potassium could not be detected in either water, and cæsium and rubidium were likewise

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TABLE A.—*Dissolved Solid Matter in Parts per 100,000.*

	Rather Close Well.		Terrace Bath.		Charity Bath.		Manor Bath.		The Pool.	
	Sep. 28, 1889.	July 12, 1890.	Sep. 27, 1889.	July 12, 1890.	Sep. 28, 1889.	July 12, 1890.	Sep. 27, 1889.	Sep. 27, 1889.	Sep. 27, 1889.	Sep. 27, 1889.
Specific gravity at 20° . . .	1·0017	—	1·0017	—	1·0021	—	1·0020	—	—	—
Total solid residue at 120° . . .	189·85	201·66	190·84	195·87	229·39	229·52	236·12	217·60	—	—
Sulphuric acid (SO ₄)	70·51	90·78	66·87	76·84	96·40	109·94	94·71	131·5	—	—
Chlorine	2·10	—	3·97	—	7·21	—	7·30	—	—	—
Silicic anhydride (SiO ₂)	1·46	—	1·36	—	2·30	—	2·33	—	—	—
Iodine	trace	—	trace	—	—	—	—	—	—	—
Calcium	49·92	49·64	46·79	50·20	43·25	42·71	43·39	52·62	—	—
Magnesium	7·84	7·98	8·68	6·98	14·53	14·34	13·82	6·25	—	—
Sodium	2·74	—	3·28	—	6·81	—	6·67	—	—	—
Iron	0·24	—	0·50	—	0·14	—	0·20	—	—	—
Lithium	trace	—	trace	—	—	—	—	—	—	—
Strontium	—	—	trace	—	—	—	—	—	—	—
Hydrogen sulphide in volumes per 100,000	5670	5500	4950	5400	3480	2640	3730	None	—	—

absent. Aluminium and phosphoric acid were also looked for, but were not found.

Results.

The quantity of dissolved solid constituents in parts by weight per 100,000 parts by weight of the waters are given in Table A. The quantity of hydrogen sulphide is stated in volumes of gas per 100,000 volumes of the waters.

TABLE B.—*Proximate Composition of the Dissolved Inorganic Matter.*

In grams per litre.

	Mather Close.	Terrace.	Charity.	Manor.
Calcium carbonate	0·8417	0·8232	0·6825	0·6698
Calcium silicate	0·0281	0·0262	0·0443	0·0449
Calcium sulphate	0·5222	0·4434	0·4938	0·5151
Magnesium sulphate.....	0·3874	0·4288	0·7184	0·6834
Sodium chloride	0·0346	0·0989	0·1190	0·1205
Sodium sulphate.....	0·0426	0·0220	0·0659	0·0599
Total.....	1·8566	1·8425	2·1239	2·0936
Hydrogen sulphide (in cubic centimetres)	56·7	49·5	34·8	37·3

In grains per gallon.

	Town End.	Terrace.	Charity.	Manor.
Calcium carbonate.....	58·92	57·62	47·78	46·89
Calcium silicate	1·97	1·83	3·10	3·14
Calcium sulphate	36·55	31·04	34·57	36·06
Magnesium sulphate.....	27·12	30·02	50·29	47·84
Sodium chloride	2·42	6·92	8·33	8·44
Sodium sulphate	2·98	1·54	4·61	4·19
Total.....	129·96	128·97	148·68	146·56
Hydrogen sulphide (in cubic inches)	15·73	13·74	9·66	10·35

It will be observed that the only important solid inorganic constituents are calcium and magnesium sulphates and carbonates. In Table B, the constituents are arranged in the form of compounds, the arrangement being made in the following manner:—All the chlorine was regarded as occurring in the form of sodium chloride, and the remainder of the sodium was calculated to sulphate; all the magne-

sium was calculated to sulphate, and the excess of sulphuric acid and the silica were regarded as being in combination with calcium; the remainder of the calcium was calculated to carbonate.

In support of the view that the magnesium is present as sulphate and that none of it exists in the waters in the form of carbonate, it may be mentioned that the precipitates formed when the waters are boiled, or when the dissolved carbonic anhydride is expelled by the prolonged passage of a current of hydrogen, contain the merest trace of magnesium. Further, I am informed by Dr. J. G. Cassels, of Askern, that the therapeutic action of the waters indicates that they contain magnesium sulphate (see following paper).

General Character of the Waters.

The Askern waters are surface or shallow spring waters, and are chiefly solutions of calcium and magnesium carbonates and sulphates containing a large quantity of dissolved peaty matter, and a considerable volume of free hydrogen sulphide, together with some carbonic anhydride. All the other substances are present in small proportions only.

The absence of bromine is noteworthy, especially in view of the presence of iodine. Still more remarkable is the complete absence of potassium, but this is not difficult to understand in the light of Berthelot and André's observations on the insolubility of potassium humate and the precipitation of potassium from solutions of its salts when brought into contact with humic acid (Abstr., 1891, 1089).

Organic Matter.—The waters are highly charged, even if not quite saturated, with organic matter derived from the peat, and when allowed to remain for some time in closed vessels, a small quantity of a dark-brown, flocculent, humus-like substance separates. The organic matter is unstable and nitrogenous, and when the water is distilled with a small quantity of sodium carbonate, a relatively large quantity of ammonia is given off.

In view of this instability, it seemed that the only satisfactory method of ascertaining the true character of the organic matter would be to concentrate large quantities of the water in a vacuum at the ordinary temperature, but my removal to the south of England prevented me from carrying out this investigation. I believe, however, that results might in this way be obtained which would throw valuable light on the therapeutic action of these and similar waters, and might possibly also help to explain the origin of the hydrogen sulphide.

It seemed of interest to determine the oxygen-absorbing power of the various waters, chiefly in order to ascertain whether there is any

connection between the reducing power of the organic matter as measured in this way, and the quantity of hydrogen sulphide present. The permanganate solution employed was of such strength that each cubic centimetre contained 0·0001 gram of available oxygen, and it was standardised in the usual way against a solution of pure sodium thiosulphate containing 1 gram per litre.

100 c.c. of each of the waters, collected on July 29, 1891, was diluted to 1000 c.c. with distilled water, and 250 c.c. of the diluted water was mixed with 50 c.c. of the permanganate solution, and 30 c.c. of dilute sulphuric acid (1:3), and allowed to remain in closed vessels at the ordinary temperature of the room, 18°, for five hours. The excess of permanganate was then determined in the ordinary manner. The volumes of permanganate reduced in the two series of experiments were as follows:—

	Mather Close.	Charity.	Terrace.	Manor.
I	23·6	18·9	20·2	17·1
II	24·0	19·4	20·3	16·6

After making the necessary corrections for the permanganate reduced by the hydrogen sulphide, the results are as follows:—

<i>Oxygen absorbed per 100,000 parts.</i>				
Mather Close.	Charity.	Terrace.	Manor.	Pool.
5·78	4·92	4·78	4·24	0·015

The degree of organic purity of the Pool water is very remarkable, and is confirmed by the behaviour of the solid residue when heated. The only explanation of this phenomenon seems to be that the organic matter is precipitated by the large quantity of calcium sulphate present.

Origin of the Hydrogen Sulphide.

The quantity of dissolved hydrogen sulphide varies in the different wells. It also varies in one and the same well, and there is a distinct general connection between the time of year and the volume of hydrogen sulphide in the waters.

The results of estimates made at intervals extending over nearly two years are given in the following table, in cubic centimetres per litre, together with the quantity of the sulphuric acid radicle (SO_4), in grams per litre, present in each water on the same date.

		Mather Close.	Charity.	Terrace.	Manor.
1889.					
Sept. 27 and 28	{ Hydrogen sulphide .. Sulphuric acid (SO ₄)	56·7 0·7063	34·8 0·9660	49·5 0·6698	37·3 0·9490
1890.					
July 12	{ Hydrogen sulphide .. Sulphuric acid (SO ₄)	55·0 0·9093	26·4 1·1017	54·0 1·7697	— —
Nov. 1	{ Hydrogen sulphide .. Sulphuric acid (SO ₄)	42·3 0·7018	31·7 0·9099	23·6 0·7978	36·1 0·9956
1891.					
Jan. 17	Hydrogen sulphide ..	22·5	—	—	—
April 18	{ Hydrogen sulphide .. Sulphuric acid (SO ₄)	49·6 0·7023	— —	55·3 0·7268	21·9 0·6359
July 29	Hydrogen sulphide ..	52·0	38·4	46·2	34·2

For the reason already stated, special attention was given to the Mather Close Well, and it would seem that in this water, as indeed in all the others, the quantity of hydrogen sulphide varies periodically with the time of year.

July.	November.	January.	April.	July.
55·0	42·3	22·5	49·6	52·0

It is highest in the summer, then gradually decreases until it reaches a minimum in mid-winter, after which it increases as the weather becomes warmer, and again attains its maximum in the summer.

It is important to observe, however, that the quantity of hydrogen sulphide present in the waters during the warmer months of the year, when they are in most frequent use, remains practically the same from year to year, and, moreover, is practically constant for six or seven months in the year.

The origin of the hydrogen sulphide is a question of great interest, but is one on which I am able to offer only indirect evidence. It is well known that sulphates in solution in contact with decomposing vegetable or animal matter are frequently reduced to sulphides, in some cases, at least, in consequence of the action of specific organisms, and there can be little doubt that the hydrogen sulphide in the Askern waters is a product of the reduction of the calcium and magnesium sulphates. Most probably calcium sulphide or magnesium sulphide is the actual product of reduction, and the hydrogen sulphide is liberated by the combined action of the water and the dissolved carbonic anhydride.

The precise mechanism by which the reduction of the sulphates is brought about is still obscure. Confervoid growths, as Dr. Lankester pointed out, are abundant enough in the pipes and wells in which the waters are collected, but similar growths may also be observed at the edges of the Askern Pool, in which there is no hydrogen sulphide.

There are several points that have a more or less important bearing on this problem:—

1. The quantity of hydrogen sulphide present in the waters has no relation to the quantity of sulphates held in solution, and the variations in the hydrogen sulphide have no relation to the variations in the quantity of sulphates.

2. The quantity of hydrogen sulphide in a particular water has no relation to the chemical reducing power of that water, as measured by its action on acidified permanganate solution.

	Mather Close.	Charity.	Terrace.	Manor.
Hydrogen sulphide, per litre. .	52.0	38.4	46.2	34.8 c.c.
Oxygen absorbed, per 100,000 parts	5.78	4.92	4.78	4.24 ,,

3. Sulphuretted water is frequently met with in different parts of the peaty common in which the Askern waters are found, but although the general character of the water is the same over the whole of this area (that is, a solution of calcium and magnesium sulphates highly charged with vegetable organic matter), the distribution of the sulphuretted water is very irregular. I am informed by people living in the district that it is not uncommon for a shallow well cut in the peat to contain water that is free from hydrogen sulphide, whilst a similar well not many yards away may contain sulphuretted water. I was myself able to observe the very irregular distribution of the smaller springs of sulphuretted water in the immediate neighbourhood of Askern.

During my visits to the village, I never obtained any evidence of the occurrence of hydrogen sulphide in the water of the pool, though I am informed that occasionally during a very warm summer the gas makes its appearance at one or two of the deeper hollows or pits in the bottom of the pool. Neither, so far as I was able to observe, does hydrogen sulphide occur in the water of a smaller pool lying to the south of the village.

It would seem, therefore, that the reduction of the sulphates is not due merely to contact with unstable organic matter, but is the result of contact with a particular kind of organic matter, probably a *living organism*, which is not uniformly distributed throughout the peat. This view is supported by the fact that the maximum quantity of

hydrogen sulphide corresponds with the season of maximum activity in the growth of all kinds of organisms. The question is, however, one that only a competent biologist can solve. My friend Mr. Harold Wager, Assistant Lecturer on Botany in the Yorkshire College, was good enough to examine some of the water from the Mather Close Well, and some of the sediment that had formed in it, and he reports:—

“Microscopical examination shows that this water contains organic matter such as vegetable hairs and spores, also a quantity of amorphous matter, the exact nature of which could not be made out. Large numbers of minute, rounded, highly refractive spots could also be seen, probably micro-organisms of some kind.”

Askern Waters and Harrogate Waters.

The sulphuretted waters of Askern differ from those of Harrogate in several respects. The Harrogate waters (Trans., 1881, 39, 497) rise from a considerable depth, are almost entirely free from organic matter, and, in addition to hydrogen sulphide, contain a large quantity of dissolved carbonic anhydride. The Askern waters are surface waters, or, at any rate, rise from very slight depths, are highly charged with organic matter, and contain comparatively little free carbonic anhydride. The Harrogate waters contain a very large quantity of dissolved solid matter, amounting, in the case of the Old Sulphur Well, to 1480 parts per 100,000, and in the case of the Montpellier Strong Sulphur Well to 1450 parts per 100,000, whereas the Askern waters contain only about 200 parts of solid matter per 100,000. The difference in the nature of the solid constituents is as striking as the difference in their amount. The Harrogate waters contain chiefly chlorides and carbonates, and are free from sulphates, whilst the Askern waters contain chiefly sulphates and carbonates, and are almost free from chlorides. The quantity of sodium chloride in the Old Sulphur Well amounts to 1262 parts per 100,000, and in the Montpellier Strong Sulphur Well to 1223 parts per 100,000, whilst in none of the Askern waters does the quantity of this constituent exceed 12 parts per 100,000; and this fact is of great importance in connection with the use of these waters in the external treatment of skin diseases.

Therapeutic Action of the Askern Waters.

The value of these waters in the treatment of chronic rheumatism and skin diseases is usually attributed to the hydrogen sulphide that they contain. Barium is absent, and consequently, whatever part it

may play in the case of the Harrogate waters, it is inoperative in the Askern waters. The quantity of iodine present is so minute that it is difficult to regard it as an active constituent.

It is not improbable that the dissolved peaty matter is an important therapeutic agent, especially in the treatment of skin diseases, and this point seems worthy of further investigation. In a curious old work, *A Methodical Synopsis of Mineral Waters, comprehending the most celebrated Medicinal Waters, both Cold and Hot, of Great Britain, Ireland, France, Germany, and Italy, and several other parts of the World*, by John Rutty, M.D. (4to, London, 1757), an account is given of the use of the bog waters of Ireland, and especially of the waters of Lough Neagh, and of Lough Sheighs in the county of Cavan, for the treatment of skin diseases. These waters resemble the Askern waters in containing a large proportion of dissolved peaty matter, but are almost free from calcium and magnesium salts, and contain no hydrogen sulphide.

My best thanks are due to my friend Dr. J. G. Cassels, of Askern, for the assistance that he was always ready to afford me in collecting the waters, making the necessary experiments at the wells, and enquiring into the history of the springs.