collected therein so soon evaporates, especially in hot weather; *vide* " Symon's British Rainfall, 1868 ; " " Rain Gauge Experiments at Strathfield Turgiss, Reading," by the Rev. C. H. Griffith, F.M.S., &c., p. 23, which further establishes my remarks. The absence of outlet for confined air here spoken of, might be remedied, if indeed needed, by drilling small air-holes in the bottom of the receiving cylinder and upright flange, *but not facing each other*. I have two Glaisher's gauges fitted with the inverted flange arrangement, both of which answer remarkably well. I believe the improvement which I have adopted is more effectual against loss by evaporation (during all weathers) than the present (Glaisher's) system.
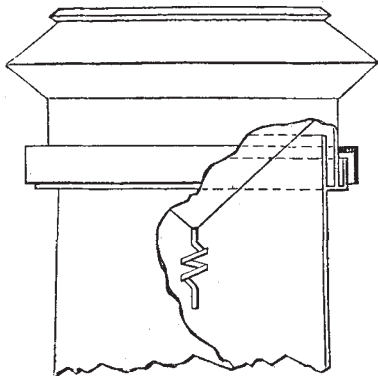
One of my gauges has been further improved at my suggestion by being fitted with a spiral or *helical* pipe in the place of the J-shaped pipe, thereby presenting no direct opening for evaporation, at the same time offering little or no hindrance to the speedy descent of the rain-water ; but this is a matter I hope to enlarge upon in a paper (as yet unpublished) which I hope to communicate to you shortly, " On a Proposed New Form of Rain Gauge (the Atmospileometer)," in which a similar, but more extensive, idea, is shown.

The particulars mentioned in paragraphs 1 and 3 of this letter were long since communicated to and approved by the Secretary of the Rainfall Committee of the British Association (G. J. Symons, Esq., F.M.S., &c.) one of the highest authorities in matters relating to rainfall.

JOHN JAMES HALL

WATER ANALYSIS

I.

IT is now upwards of twenty years since the inhabitants of this country, and especially of the metropolis, were awakened, by a succession of virulent attacks of epidemic cholera, from the profound indifference with which they had regarded all matters connected with the public health for the hundred and eighty years which had succeeded the Great Plague. During that interval builders had been allowed to cover land with hundreds of acres of dwellings built without regard to ventilation, drainage, or water supply. In all the towns and villages of the country the ground was honeycombed with cesspools and wells, the latter deriving their supply of water at least in part from the former, and in all riverside towns the river either received the town sewage at once or after it had passed through the cesspools. Attention once being drawn to the matter, it became the duty of the chemist to detect the various polluting matters introduced by the sewage into the different sources of water-supply, and to discover, if he could, waters that were free from this pollution ; and a still greater field was opened up, for the two first inquiries naturally led to the allied questions—How can sewage be rendered harmless? and Can slightly polluted

water be rendered safely drinkable by the removal from it of the contaminating matter introduced by sewage? We propose in this article to look only at the first of these questions, the one on the successful solution of which depend all the others—Can organic contamination be detected and estimated with accuracy ? As soon as the question was approached it was found to be one of extraordinary difficulty, and in 1856 Hofmann and Blyth drew attention to the inaccuracy of the then existing processes, especially of the one known as " loss on ignition " obtained by igniting the solid residue on the evaporation of the water. This loss, then generally looked on as affording a measure of the organic matter present in the water, they proved to consist of a loss of carbonic anhydride, nitric acid, ammonia, and moisture, &c., and they proposed to render the determination more accurate by the addition of a known weight of sodic carbonate, which, while it drove off the ammonia (usually a very small fraction of the loss), retained the acids and prevented the aqueous magnesic chloride from losing hydrochloric acid. The same chemists pointed out the necessity of determining the amount of nitrogen present, but were unable to recommend any process for its estimation. The methods for estimating the ammonia were also very unsatisfactory, for we find Dr. Dundas Thomson in 1855 distilling as much as fifty gallons of the metropolitan water-supplies in order to estimate the ammonia, which was done by titration with standard acid ; and this when some of the metropolitan supply was taken from the Thames at Vauxhall, and "Fibrin from Fæces" could be distinctly recognised in the Southwark Company's water. Another process, devised by Forchhammer, was also in use for the determination of the organic matter, which consisted in adding a standard solution of potassic permanganate until no further loss of colour occurred. This process had been improved from time to time, and was and is largely used. The only other test was that for hardness, invented by Dr. Clark, and which is still in use, with but slight modification from the original method.[*]

If these processes are considered but shortly, the defects they possess are at once apparent. Take, for instance, Hofmann and Blyth's improved solid residue process. On ignition there was great danger of decrepitation and consequent loss, notwithstanding the high temperature ($120°$ to $130°$ C.) to which the residue had been exposed. Frankland and Armstrong have shown that portions of the nitrogenous matter were liable to remain fixed in the ignited residue as cyanogen compounds. Again, in the case of some artificial residues prepared by treating dilute solutions of urea as in the above process, from 44 to 59 per cent. of the urea used was found to have been lost during the preliminary evaporation, the sodic carbonate having expelled it as ammonic carbonate. And on the treatment of similar residues by ignition, from 58 to 85 per cent. of the organic matter was left in the residue. It was usual also to restore the lost carbonic anhydride to the ignited residue by evaporating a solution of that gas on it and weighing until a fresh treatment did not increase the weight ; but to still further increase the difficulty of this unhappy process, it was shown that some residues seemed to have the power of taking up such quantities of carbonic anhydride, that they weighed more after this treatment than they did before ignition. The estimation of ammonia by titration with acid needs no argument against it ; the enormous quantities of water necessary for the determination sufficiently condemn it ; and it has been long superseded by the admirable quantitative form of the Nessler process invented by the late Mr. Hadow, of King's College. The permanganate process, however, being an easy one to perform, still survives in the laboratories of many analysts. Indeed, not content with giving the results of this determination as " oxygen required to oxidise the organic matter present," the lively imagination of some led them to the remarkable conclu-

sion that every grain of oxygen oxidised eight grains of " organic matter."

Whether this test is to be trusted may be judged from the following facts. Potassic permanganate is deoxidised by ferrous salts, nitrites, sulphites, &c., much more rapidly than by organic substances, so that a water absolutely free from any organic matter, but containing one of these compounds, would be set down as requiring so much " oxygen to oxidise organic matter." Secondly, in the case of water to which known weights of various organic compounds were added, Frankland and Armstrong found that in no instance was the oxidation complete, even after the lapse of six hours. In fact, even after that time the amount of oxygen actually absorbed was in every case a mere fraction of the quantity actually required to completely oxidise the organic substance. The test, though thus shown to be valueless as quantitative, is of some value qualitatively, as it can be easily and quickly applied; and it may be said that, though it might induce a person to abandon a good water, it would not often lead him to use a bad one.

All the above processes were in use up to 1868, when Messrs. Chapman, Wanklyn, and Smith proposed to determine the organic matter in water from the amount of ammonia evolved when the water was treated with a strongly alkaline solution of potassic permanganate and then distilled, the ammonia being determined in the distillate by Hadow's modification of the Nessler test.

That albumin is decomposed and the nitrogen thus evolved, they had shown in a paper presented to the Chemical Society in the preceding year. The way in which this process was applied to the water may be briefly stated as follows :—A measured quantity of the water was rendered alkaline with freshly-ignited sodic carbonate, and the ammonia distilled off and estimated by Hadow's modified Nessler process. As soon as all the ammonia thus obtainable had been expelled, the alkaline permanganate solution (50 cubic centimetres of a solution containing 200 grammes of potassic hydrate and 8 grammes potassic permanganate per litre) was run in. The distillation was then resumed, and the ammonia estimated as before. This last was set down as " albuminoid ammonia," and as the average evolution of ammonia from the following substances, gelatine, caseine, dry albumin, uric acid, creatine, theine, dried fish flesh, amounted to 10 per cent., it was suggested the albuminoid ammonia multiplied by 10 gave a fair estimation of amount of organic matter.

It had at first been stated that albumin gave up the whole of its nitrogen when treated with alkaline permanganate, but the statement was subsequently modified to "It appears to be two-thirds, being at any rate a constant quantity." Now this process would indeed be a valuable one if the 10 per cent. average could be depended on, or if the albumin evolved a certain quantity, and the above substances were alone found in water. Unfortunately, none of these suppositions are true. With regard to the last, the authors themselves recognised the difficulty, and accordingly examined a number of other nitrogenous organic bodies ; which examination led to the publication of two lists of bodies that evolve the whole of their nitrogen as ammonia, and bodies that yield various fractions. Frankland and Armstrong also made some experiments on this subject. With regard to the list of bodies yielding half their ammonia, the numbers given by the authors vary from 44 per cent. in the case of papaverine to 58 per cent. in the case of sulphate of cinchonine ; and whilst narcotine appears in Wanklyn, Chapman, and Smith's list as evolving all its nitrogen, Frankland and Armstrong give it as evolving about 46 per cent. Strychnine, given by the former authors in their list as evolving 53 per cent., is given by the latter as evolving 31½ per cent., and sulphate of quinine also in the list with 50 per cent., appears again with Frankland to have evolved nearly 57 per cent.

No other examples will be necessary to show the extreme uncertainty of the process. If the authors had enabled us to ascertain the absolute error on the quantity taken instead of the per-centage error, by giving us the quantities from which the results were taken, it would no doubt be much more apparent ; the results given above in the case of those from Frankland and Armstrong's paper are absolute errors.

But it may be urged in defence of the method that none of these bodies are found, or are likely to be found, in natural waters. Let this be granted, and the process must be defended on the albumin and other bodies mentioned, and on the list of bodies giving up all their ammonia. The average from this is 11·82 per cent. ; from the albumin list, 9·92 ; or, taking the two, 10·87. So far the lists hold good. But it must be borne in mind that we have three different statements about the ammonia evolved from albumin—first, that all is evolved ; secondly, " two-thirds, or, at any rate, a constant quantity ;" thirdly,[*] that 100 parts of albumin give 10 parts of ammonia.[†] The inconsistency of these statements needs but this comment, that they can only be caused by the extreme uncertainty of the process ; in fact, the amount of nitrogen converted into ammonia will be influenced by the nature of its previous combination, the degree of concentration of the solution, and the amount of heat applied to the retort, and consequent rate of distillation and time to which the solution is exposed to the action of the alkaline permanganate. That this is the case is proved by the fact that water which has been distilled from alkaline permanganate, and gives no trace of reaction with Nessler's test, will evolve ammonia if again boiled with the permanganate. Lastly, let any one take a water which has been largely contaminated with sewage and then filtered, such as the effluent water from a sewage farm. Such water, as a rule, contains much nitric and nitrous acid, and comparatively small quantities of organic nitrogen. A water of this character continues to evolve albuminoid ammonia till boiled nearly to dryness, and not unfrequently the retort requires to be filled up with pure water, and the operation carried on. The process is thus not only rendered tedious, but the necessity of repeatedly taking samples of the distillate and estimating the ammonia in them introduces an amount of experimental error which becomes serious when calculated out in milligrams per litre, though its actual amount on each cylinder of distillate may be very small.

When it is added that Mr. E. T. Chapman has included in the second edition of Wanklyn's " Water Analysis " a process for the estimation of volatile organic matter, founded on the fact that water largely contaminated with sewage evolves volatile bases when boiled with potassic hydrate, the question is still further complicated ; for it cannot be doubted that some portion of these bases would be driven off by the action of the alkaline permanganate before it had time to act on and destroy them.[‡] Whether this is the case ought at once to be determined by those who use the process.

In a second article we shall consider Frankland and Armstrong's process for the analysis of potable water, and also those determinations, such as nitrous and nitric acids and chlorine, which are of great value as enabling us to trace back the history of a water, and to tell from whence it is derived and what it has received in the way of animal contamination before it came into our hands.

* " Water Analysis," 2nd edition, p. 66.
† If Lieberkühn's formula for albumin H Na $C_{72}H_{110}N_{18}SO_{22}$, H_2O be taken as the true one, 10 parts of ammonia (N H_3) from 100 parts of albumin will be equal to 8·23 parts, or little more than half the total nitrogen, which is for that formula 15·25 per cent. If the sodium in the above formula be replaced by hydrogen, the discrepancy is still greater.
‡ An action of this nature apparently occurs when sewage is treated with alkaline permanganate, as nearly the whole of the ammonia comes off in the first 100 cub. cent. of the distillate, and after that the evolution soon stops. Waters that evolve small quantities of albuminoid ammonia seem almos always to require a long time for its liberation. Is this because the organic bases are so diluted that they cannot be driven out, and so slowly decompose