

XVI.—UPON THE DETECTION AND ESTIMATION OF NITROUS ACIDS
IN POTABLE WATERS, ACIDS, ETC. — I. WITH METADIAMIDO-
BENZOL ; II. WITH POTASSIUM IODIDE.

By ALBERT R. LEEDS.

I.—WITH METADIAMIDOBENZOL.

This method depends upon the observation, originally made by P. Griess,* that diamidobenzoic acid is an extremely delicate test for nitrous acid, giving in very dilute solutions of this body, an intense yellow color. Later, Griess proposed to employ, instead of this compound, another related compound, *metadiamidobenzol*, which is more readily prepared, and moreover, is twice as sensitive as diamidobenzoic acid. The latter indicates the presence of $\frac{1}{10}$ th mgrm. N_2O_3 in a liter of water; the former, of $\frac{1}{10}$ th mgrm., or 1 part in 10 million.† Since metadiamidobenzol is said to be an article of commerce at present, there is no need, perhaps, to allude to its preparation. But for those who, like ourselves, were unable to purchase it, it may be of service to know that we were able to prepare it more readily by reduction of the dinitrobenzol by means of tin and hydrochloric acid, than by distillation with acetic acid and iron filings.‡ In accordance with the recommendation of Griess, after purifying with animal charcoal, the solution used in testing was acidified with sulphuric acid.

The minutiae essential to employment of the method in quantitative colorimetric determinations, have been elaborated by C. Preusse and F. Tiemann, § who recommend :

I.—A solution of metadiamidobenzol, containing 5 grms. per liter. It is acidified with dilute sulphuric acid.

II.—Dilute sulphuric acid solution (1:3), for acidifying standard and unknown solutions in process of estimations.

III.—A solution of alkaline nitrite, of which 1 cc contains 0.01 mgrm. N_2O_3 . 0.0406 gm. pure, dry silver nitrite is dissolved in hot water and decomposed by potassium or sodium chloride. After cooling, the solution is made up to one liter, the silver chloride

* Ann. Chem. u. Pharm., cliv, 333.

† Ber. der deutsch. chem. Gesell., xi, p. 625.

‡ Aromatic Diamines : Hoffmann, Proc. Royal Soc., xi, 518. Isomeric Diamines : Hoffman, Proc. R. Soc., xii, 639.

§ Ber. der deutsch. chem. Gesell., xi, p. 627.

allowed to settle completely, and 100 cc of the supernatant liquid diluted to 1 liter.

The rest of the operations are quite similar in character to those made use of in Nesslerizing. But instead of using cylinders of colorless glass, as the above-mentioned authors recommend, comparison-tubes and the color-comparator,* may be more conveniently employed. 100 cc of the aqueous solution under examination, is introduced into a comparison-tube, 1 cc of solution (2) and 1 cc of solution (1) added. If the water is not colorless, it should first be decolorized by throwing down the coloring matters through formation of an insoluble carbonate of an alkaline earth, in the water containing them. If, on agitation with a bulb-stirrer, a caramel-like color is developed, the trial is to be repeated with 50, 20, 10 cc of the solution, previously diluted to 100 cc with water (free from nitrous acid). The dilution is sufficient, when a satisfactory reaction is attained in the course of one or two minutes. Various amounts of solution (3) are treated in like manner, until an identical tint is developed, when the amount of N_2O_3 in the unknown solution becomes, of course, known.

Inasmuch as the tints of color developed by the metadiamidobenzol, are so analogous to those exhibited by a dilute caramel solution, that they can be closely copied by the latter, the author uses such a *caramel solution in the glass wedge of the color-comparator for estimations of nitrous acid*. The same wedge, provided with a different scale, answers for the determination of minute amounts of ammonia by the Nessler reagent.

Amounts of Nitrous Acid found in Potable Water.

At the time at which these determinations were made, the water of the Passaic, as drawn from the hydrant in the laboratory, contained 0.12 part N_2O_3 in one million. It is of practical importance to compare this result with the amount of nitric acid contained in the same water. A determination of the sum of nitrates and nitrites (calculated as HNO_3), gave on the same date, May 2d, 1879, 2.37 pts. in a million. If we regard this amount of nitric acid as an index of previous sewage contamination, its amount is strikingly great as compared with the nitrogenous matters present in the water and still capable of undergoing putrefactive decomposition. The amount of "nitrates and nitrites" contained in the Passaic, May 2d, '79 (determined by reduction with pig-iron), did not differ notably from

* Proc. Amer. Chem. Soc., Vol. ii, p. 1.

the amount found Nov. 26th, 1877 (by reduction with the copper-zinc couple), when it was 2.22 parts in a million. The ammonia contained in the Passaic water at latter date, was 0.02 parts; the albuminoid ammonia, 0.215 parts in a million. P. Griess has emphatically insisted upon the importance of determining the nitrous acid in potable waters, and their unfitness for household use, when they contain nitrous acid.* In cases like the one cited, where the "nitrates and nitrites," so called, exceed the amount of the albuminoid ammonia *ten times*, there should be no omission to make a separate examination for, and a separate estimation of, the nitrous acid. The rapidity and ease of Nesslerizing is such, that ammonia and albuminoid ammonia determinations now play the most conspicuous part in reports of water-analyses, especially in this country. To accept or condemn from them alone the character of a drinking-water, we regard as a practice fraught with error. They should be checked by the results afforded by independent determinations of the nitric and nitrous acids. Fortunately, by aid of improved methods, this can be as readily done as the corresponding estimations of ammonia and albuminoid ammonia, and a skillful water-analyst should be able to perform all four within the space of two hours.

We should be very unwilling to say that, by reason of the water of the Passaic containing 0.02 parts of ammonia and 0.215 parts of albuminoid ammonia in a million, it was unfit to drink. But these facts, taken in connection with these two others, that it contains at the same time, 2.14 parts of nitric acid and 0.12 parts of nitrous acid in a million, do, we think, constitute reliable grounds for pronouncing against it. And we regard the two facts last mentioned, of more weight in making up this opinion than the two first. Water flowing from a granitic water-shed and over alluvial country, as the Passaic River does, could not readily obtain this percentage of nitrates from inorganic sources—it has most probably come from the oxidation of nitrogenous animal and vegetable matters. And this opinion is confirmed by finding an amount of nitrous acid, which is *one-half the total amount of the ammonia-yielding bodies present*, and represents how large a portion of these last are still in a state of transition from their evanescent putrescible form, as albuminoid ammonia, to their permanent stage, as nitric acid.

The water of the Passaic has been taken as an illustration, because it happens to be the only potable water which, at the present time, I have occasion to analyze. But having alluded to it, I trust

* Ann. Chem. u. Pharm., cliv, 336.

the importance of the subject will excuse my saying here, that the enforced use of water unquestionably so contaminated as this, is a crime committed against the health and happiness of a quarter of million of people.

II.—WITH POTASSIUM IODIDE.

The well-known method of Trommsdorf is of a colorimetric character.* The potable water to be examined is treated with a solution of zinc iodide, starch and sulphuric acid, which develop, in case nitrous acid is present, a blue color. The amount of nitrous acid corresponding to this color, is found by striking in distilled water containing these reagents, the same tint with a standard nitrous acid solution. Ordinarily, the unknown and known solutions are prepared at the same time and placed side by side, in order that they may be subjected, as nearly as may be, to the same conditions. It is essential, in fact, that they should be equally exposed to the action of the air, and should be acted upon by light of equal intensity and for an equal length of time. To point out the importance and necessity of these precautions, is the object of the present paper. Our attention was drawn to them in the course of preceding studies, upon the rate of change of soluble iodides, in the presence of free acids, and the results of those studies have been given at length (JOUR. AMER. CHEM. SOC., Vol. I, 1879).

Briefly to recapitulate, these results are as follows: *In the dark*, access of air being freely permitted, the amounts of iodine set free, the amount of free acid present being the same in every case, increases with the increase in percentage of dissolved iodide. *In the light*, the iodide liberated, in the case of solutions of equal strength, increases with the amount of exposure to the light and the intensity of the illumination. When air is entirely excluded, no decomposition occurs even at temperatures above the boiling point, and when exposed for days to the direct light of the sun.

These conditions of change having been established, it became of interest to determine in what way the mimetic method of Trommsdorf could be replaced by an absolute mode of volumetric estimation.

As a preliminary determination, the limits of sensitiveness of the zinc-iodide-starch solution were investigated, and the rapidity with which it would undergo change in presence of acid in diffused day-light. Nine comparison-tubes were placed in the comparator-frame, and in each was introduced 100 cc water, 1 cc H_2SO_4 (free

* Zeitsch. für Analyt. Chemie, viii, 358.

from nitrous acid) and 3 cc zinc-iodide-starch solution. This last solution was prepared by adding to 20 grms. $ZnCl_2$ and 5 grms. starch, 2 grms. ZnI_2 and 1000 cc water. The reagents were prepared in the laboratory and were perfectly pure. To the nine tubes were added 0.2, 0.4, 0.8, 1.00, 1.50, 2.00, 2.50, 3.00 and 5.00 cc of a standard solution of potassium nitrite, containing per 1 cc, 0.01 mgrm. N_2O_3 . In other words—the first tube contained 2 parts; the ninth, 50 parts of N_2O_3 in 100 million. This last changed immediately, the others as follows:

With	3 cc N_2O_3 solution, after 10 minutes.					
"	2.5	"	"	"	15 "	
"	2.0	"	"	"	18 "	
"	1.5	"	"	"	50 "	
"	1.0 and 0.8	"	"	"	1 hour.	
"	0.4	"	0.2	"	"	1 " 50 minutes.

A tenth tube, containing 100 cc H_2O , 1 cc H_2SO_4 and 3 cc ZnI_2 and *no nitrite*, at the end of two hours had acquired a faint blue color; in depth, however, inferior to that given by the .002 mgrm. N_2O_3 in the first tube. It will be seen from this table that the reaction cannot be applied to waters containing as much as 0.05 mgrm. N_2O_3 in 100 cc. Perhaps 0.04 mgrm. N_2O_3 in 100 cc is the superior limit, waters containing larger amounts than this, requiring suitable dilution. And, moreover, since the very dilute solutions did not change at the expiration of intervals increasing progressively with the order of dilution, the determinations in these cases are affected with a corresponding degree of uncertainty. This is still more strikingly the case when ordinary potable waters, which are seldom colorless and contain various substances in solution, are used. For example, we have known the water of the Passaic River, which contained, according to a determination on one sample, by means of metadiamidobenzol, 1.2 pts. N_2O_3 in 10 million, to remain unchanged, on the addition of zinc-iodide-starch and sulphuric acid, at the expiration of eight hours. After the same interval, distilled water, containing the same reagents, but no nitrite, had acquired a well-defined blue tint.

Apparatus for Absolute Volumetric Determination.

The preceding considerations, having demonstrated the importance of comparing the results obtained by the colorimetric method, with those which would be gotten by some mode of absolute volumetric determination, an apparatus for effecting the latter object was

constructed, as follows: Two comparison-tubes were fitted up in a manner similar to wash-bottles, except that the first comparison-tube was made to slip up and down upon its exit-tube. In this way, its exit-tube might be forced down into the bottom of the vessel when desired. The reagents were placed in the first comparison-tube; 100 cc of the liquid to be tested, in the second. After a current of carbonic acid, washed by passage through a potassium iodide solution, had passed through both vessels for an hour, the exit-tube of the first vessel was pushed down, as above described, and the reagents forced over into the liquid under examination. In this way, the air dissolved in the reagents was swept out of them, before they were allowed to come into contact with the unknown solution. A slow current of carbonic acid was maintained for two hours, at the end of which time the liquids were titrated. The reason for allowing so long an interval to elapse before titration, was, that it had been found previously to be necessary, in order to permit so small a quantity of N_2O_3 , as 2 parts in 100 million, to decompose their entire equivalent of potassium iodide. So effectually does the exclusion of air prevent the liberation of iodide under the influence of light alone, that no disturbing influence is exerted upon the results, even when the comparison-tubes are exposed to the direct rays of the sun for two hours or longer.

Example: 100 cc containing 0.05 mgrm. N_2O_3 were introduced in the second comparison-tube, and 6 cc zinc-iodide-starch and 1 cc H_2SO_4 in the first. After complete displacement of the air dissolved in reagents and solution, the reagents were forced over, and the current of carbonic acid gas continued. On titration with sodium hypsulphite, at the end of two hours, the amount required was 0.032 cc = 0.160 mgrm. I. The theoretical amount was 0.0334 cc = 0.167 mgrm. I. = 0.05 mgrm. N_2O_3 .

Effect of Coloring Matters.

These experiments give the key to an explanation of the effect of coloring matters and organic impurities upon the rate of change of acid solutions of the soluble iodides. They suggest, likewise, a method of eliminating the perturbations so arising, from titrations in which iodides are employed.

Coloring matters, etc., disturb the identity of conditions, under which the colorimetric titration is made. Such an identity is more especially important in a determination like this, inasmuch as the liquids are undergoing a slow spontaneous alteration by contact with light and air. All coloring matters absorb more or less of the

actinism of solar and other light, and, consequently, the amounts of iodine set free will differ correspondingly in solutions containing them. This absorbing action is especially great in the case of yellow solutions, which, like caramel, cut off the more refrangible rays of the spectrum. If, in addition to being colored, these foreign bodies are decomposable and capable of combining with any of the oxygen of the dissolved air, their disturbing influence is two-fold. In the first place, they alter the rate at which acid solutions of soluble iodides decompose under the action of diffused or direct light, and secondly, they remove a portion of the oxygen which is essential to the progress of this decomposition. The conditions governing the reaction are summed up in the general equation, $4MI + 4HA + O_2 = 4MA + 2H_2O + 2I_2$, where M stands for any monovalent basic radical, and A a monobasic acid radical. (See "Influence of Light upon the Decomposition of Iodides," JOURNAL AMER. CHEM. SOC., Vol. 1, Part 3, by the author.)

Illustration : These suppositions were confirmed by the following experiment : Four comparison-tubes were prepared, each containing 1 cc KI sol. (20 p. c.) + 1 cc H_2SO_4 + 100 cc H_2O + 0.05 mgrm. N_2O_3 . Enough caramel solution was added to each to communicate a strong color. All four were exposed to sun-light for one hour, but through two of them a current of washed carbonic acid was passed, while the remaining two solutions were in direct contact with air. The results were as follows :

Caramel Solutions.

In Air.

I, Required 0.95 cc $Na_2S_2O_3 = 1.4$ mgrm. N_2O_3 .
 II, " 0.90 " " = 1.35 " "

In Carbonic Acid.

III, Required 0.05 cc $Na_2S_2O_3 = 0.099$ mgrm. N_2O_3 .
 IV, " 0.05 " " = 0.099 " "

It will be seen, that even where carbonic acid was employed, the amounts of N_2O_3 which were found, are twice those of the A_2O_3 used. This excess was due to using reagents, out of which the dissolved air had not previously been driven by a current of carbonic acid. When this was done, by means of the apparatus before described, the results agreed with the theoretical. In case of the *solutions exposed to air, the discrepancy is enormous*, being nearly thirty times too great. Similar results were obtained in diffused light, but a greater length of time was required to produce them.

CONCLUSIONS: The following conclusions are to be drawn from the preceding experiments:

I. *When the solutions to be titrated are colorless, and contain no compounds, organic or inorganic, which would affect the percentage of dissolved oxygen, the determination may be made by the colorimetric method.*

II. *When the solutions are colored, or contain organic or other bodies capable of absorbing oxygen, the air must be entirely removed from the liquids in order to obtain good results, and an absolute volumetric determination is essential.*

With regard to the first point, it is to be remembered that, in any case, the colorimetric method less and less approximates to accuracy, as we approach the lower limit of the reaction. This is due to the difficulty of securing equivalent amounts of change in excessively dilute solutions, when these solutions contain iodides in presence of free acid, and are not at the same time absolutely identical in tint and constitution. And, with reference to the second point, inasmuch as the coloring matter cannot always be removed from potable waters, by throwing them down through the formation of an insoluble precipitate, it is of utility to possess a method of determining nitrites in presence of coloring matters, and sometimes of certain classes of organic impurities.

Examination of Hydrochloric Acid for Chlorine, and of Nitric and Sulphuric Acids for Nitrous Acid.

After the preceding statements, it will be easily seen that the ordinary rule given in works on qualitative analysis, for the examination of sulphuric acid (*i. e.*, dilution with 20 pts. water and addition of potassium iodide and starch results), gives erroneous results when employed to detect minute quantities of nitrous acid, and the solution is allowed to stand for some time. But if the trial is made in an atmosphere of carbonic acid, care being used to expel previously all traces of air in reagents and in the dilute acid solution, the test and estimation of percentage may be satisfactorily performed. The same remark applies to the examination of hydrochloric acid for chlorine, by means of a soluble iodide. In the case of nitric acid, however, it is well not to expose the acid when under examination, too long to the action of strong light, owing to the liberation of oxygen from the nitric acid itself under these circumstances. The ease and certainty with which the Griess' reaction for nitrous action is performed, should cause it to replace the former methods in most cases. So delicate is it, that the acids sold as chemically pure, usually give a decided color

when the metadiamidobenzol is added to them, and the general introduction of this reagent into use, will probably raise the standard of so-called purity, at least in this respect.

Upon the Degree of Concentration at which Soluble Iodides will cease to remain unchanged in presence of Free Acid, even when out of Contact with Air.

The method pursued in examining this question, was to employ solutions of iodides and acid of gradually increasing concentration, until a point was attained at which decomposition ensued, even when all traces of air were rigorously excluded. The reagents were placed in the first, the iodides in the second comparison-tube, of the apparatus before described, and when all the air had been expelled from both, by the long-continued passage of carbonic acid, the reagents were forced over into contact with the iodides. In the first experiment, 1 cc KI (10 p. c.) + 5 cc H₂O and 1 cc H₂SO₄ (chemically equivalent to the 1 cc KI) + 5 cc H₂O, were employed. After expulsion of air, the solutions stood 1 hour in diffused light, and $\frac{1}{2}$ hour in sunlight, a slow current, of carbonic acid flowing. On disconnecting and adding starch, no coloration took place.

In the second experiment similar solutions were used, but instead of being diluted to the $\frac{1}{100}$ th, they were diluted only to the $\frac{1}{20}$ th. They were exposed to diffused and direct sunlight for the same intervals. Before addition of starch, no change of color was perceptible, but afterwards, a *brownish-red*. This compound was entirely unlike in appearance to that formed by the union of free iodine with starch, under ordinary circumstances.

III. The reagent contained 5 cc KI (10 p. c.) + $2\frac{1}{2}$ cc H₂O, in other words, they were now diluted only to one-tenth. After exposure for $1\frac{1}{2}$ hours to *direct sunlight*, they were brought into contact, when the same *brownish-red* precipitate was formed.

IV. No water was employed, but in its place $2\frac{1}{2}$ cc starch-water, with the same amounts of sulphuric acid and potassium iodide. They were exposed, after expulsion of air, to diffused light for 1 hour, and then to sunlight for $1\frac{1}{2}$ hours. No change occurred in either comparison-tube until their contents were mixed, when the *brownish-red* precipitate formed immediately. On the addition of sodium-hyposulphite, the color disappeared, showing that it probably contained either iodine or hydriodic acid. On collecting and washing the precipitate on a filter, it turned blue, and presented the ordinary appearance of iodide of starch.

V. A final experiment was made by dissolving 10 grms. KI in 30 cc starch-water. 20 cc of this solution were placed in the first comparison-tube, 10 cc concentrated H_2SO_4 in the second, and both treated with carbonic acid. The tubes were exposed to direct sunlight. In a few minutes the first comparison-tube exhibited a brown coloration, and after several hours a carmine-red precipitate was formed. After being allowed to stand over night, the red precipitate was still present, but another also, of a darker hue, lay above. On allowing the carbonic acid to flow through both precipitates for 6 hours, in the sun-light, they disappeared, and the original *brown coloration only* was visible. During this part of the experiment, the iodide and starch, it will be noted, were not mixed with the acid. Finally, they were driven over, when immediate decomposition ensued, and a large amount of iodide was set free.

CONCLUSIONS :—1st. In the absence of air and presence of carbonic acid, decomposition of an acid solution of potassium iodide occurs, when the concentration has attained to some point between one-third and one-tenth the weight of the water employed. 2d. During the course of these experiments, a compound of starch has been formed which, from its deportment with reagents, and more especially from its turning blue on absorption of oxygen, may probably be regarded as a *hydriodide of starch*. An attempt would have been made to study it further, had it not been for the difficulty of satisfactorily isolating a body which changed so readily on exposure to air, into ordinary starch iodide.

XVII.—UPON AMMONIUM NITRITE, AND UPON THE BY-PRODUCTS
OBTAINED IN THE OZONISATION OF AIR BY MOIST PHOSPHORUS.

BY ALBERT R. LEEDS.

As long ago as 1848, Dr. T. Sterry Hunt threw out the suggestion, that the nitrogen of the atmosphere is really composed of two equivalents of the element, sustaining towards each other the same relations as the two equivalents in nitrous oxide. He supposed that the group NNO is not a simple oxide, but an anhydrous amide, or nitryl, derived from the ammonium nitrate by the removal of $2H_2O$, and capable, when passed over a mixture of lime and potash at a sufficiently high temperature, of regenerating ammonia and a nitrate.* He insisted upon the parallelism between this case and that of am-

* American Jour. Sci., May, 1848, p. 407.