A STUDY ON THE PHENOLSULFONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

[THIRD PAPER.]

THE CHIEF SOURCES OF ERROR IN THE METHOD.

BY E. M. CHAMOT, D. S. PRATT AND H. W. REDFIELD.

Soon after the method, known also as the Grandval and Lajoux or Sprengel method, became known and quite generally adopted by water analysts, perplexing variations in results and peculiarities in the behavior of the reagents used were reported by many; but it is only within comparatively recent years that a thorough systematic study of the method has been made, the earlier work being abortive because of incomplete knowledge of the composition of the reagent and of the composition of the colored reaction product upon which the entire method depends. The evolution and improvement of the method has already been summarized in the two preceding papers[1] and need not here be again discussed.

For the purposes of study and discussion the chief errors which may affect the results as obtained by the method as now in use may be conveniently grouped under the following heads:

    I. Errors resulting from
        a. The use at different times of sulfonic acids of varying composition.
        b. The use of reagents of different ages and therefore of changing composition.
    II. Errors resulting from the use at different times of varying volumes of reagent.
    III. Errors resulting from variable time of contact between reagent and water residue.
    IV. Errors due to differences in the temperature of the water residue and standard when the reagent is applied or those resulting from a great rise in temperature when the alkali is added.
    V. Errors due to variations in the alkali employed.
    VI. Errors due to the presence of organic matter.
    VII. Errors due to losses through evaporation.
    VIII. Errors due to the presence of carbonates.
    IX. Errors due to the presence of chlorides in the residue.
    X. Errors due to the presence of iron.
    XI. Errors due to the presence of other forms of interfering inorganic compounds not covered above.

The attention of water analysts has been called to most of these sources of error by many previous investigators, nevertheless, it has been thought best to again review all these difficulties and it is the purpose of this paper to discuss in a brief manner these sources of errors and point out the shortcomings of the phenolsulfonic acid method as now practiced and to suggest what appears to be a marked improvement in the process whereby it is possible to eliminate the worst of the troubles.

[1] Chamot and Pratt, THIS JOURNAL, 31, 922; 32, 630.

For convenience the sources of error above listed will be taken up for discussion in the order given.

I. a, b. Errors Due to the Variable Composition of the Reagent.—The fact that the composition and method of preparing the sulfonic acid reagent affected the delicacy of the method and influenced the intensity and shade of the yellow color of the reaction products appears to have been early recognized by analysts, since the literature of this method contains many directions for making reagents in greatly varying proportions of phenol and sulfuric acid and in the subsequent treatment of the mixture.

These reagents fall into four broad classes.

A. Those made by mixing phenol and concentrated sulfuric acid at ordinary temperatures.[1]

B. Those made by mixing phenol and concentrated sulfuric acid to which a little water has been added.[2]

C. Those made by mixing phenol and concentrated sulfuric acid and adding thereto a little concentrated hydrochloric acid.[3]

D. Those made by heating a mixture of phenol and concentrated sulfuric acid.[4]

Until the compound giving the yellow color in the alkaline solution had been isolated and purified, great difficulty was experienced in studying the errors of the method, as no satisfactory and reliable standards could be prepared which would not themselves be subject to part of these same sources of error. The color top, color wheel and tintometer suggested themselves but proved impracticable. As soon, however, as the pure tripotassium nitrophenoldisulfonate was obtained, a means of preparing standards of exactness and permanence became available. It was now possible to weigh out portions of this compound containing known amounts of nitrogen and prepare a series of standards whose color was found to remain unchanged for many months. Moreover, these standards could be diluted with computed volumes of water and still show the correct color tint and intensity in a colorimeter corresponding to the reduced nitric nitrogen content.

The importance of the discovery of this method for the preparation of invariable standards made from the actual color compound will be appreciated by all readers. Directions for preparing tripotassium nitrophenoldisulfonate will be found given in our fourth paper. In order that the results of colorimeter reading should be as free as possible from

[1] Lombard, *Bull. soc. chim.*, [4] **5**, 1092 (1909).

[2] Smith, *Analyst*, **10**, 199 (1885); Girard and Lajoux, *Compt. rend.*, **101**, 62 (1865); Rideal, *Chem. News*, **60**, 261 (1889).

[3] Johnson, *Chem. News*, **61**, 15 (1890); Farcy, *Bull. soc. chim.*, [4] **5**, 1088 (1909).

[4] Gill, *Tech. Quart.*, **7**, 55 (1894); This Journal, **16**, 122 (1894).

the personal equation, in all the work described below, the colors were read in turn by two and usually three observers, absolutely independently and with the key to the strengths of solutions or methods being investigated in the hands of one observer only. It was thus possible to eliminate bias and preformed opinions.

The reagents falling under Class A may vary greatly in composition, depending upon the proportions of phenol and sulfuric acid, upon the way in which the materials are mixed and upon the age of the reagent. In sulfonic acid reagents of this type it is possible to have the orthosulfonic acid remain in the mixture only when no great excess of sulfuric acid is used; otherwise the mixture as first made contains a little ortho, much para and some disulfonic acids. Moreover the amount of the disulfonic acid increases with the age of the reagent. These facts we have been able to prove by analyses of practically all the types of reagents by the methods already described by us in papers I and II. By way of illustration the most recently described reagent, that of Lombard,[1] is made by mixing phenol and concentrated sulfuric acid at room temperature. When freshly prepared this was found to contain large amounts of mono acids. Nitrate-containing water residues treated with this fresh reagent and made alkaline in the usual manner showed in the colorimeter greenish tints, as was to be expected, instead of pure yellows. After ten days the sulfonation had progressed so that nearly all the acid was now phenol-disulfonic acid. Greenish colors in the final product were now obtained only when the residue and reagent were warm. After standing six months little further change could be detected.

It is evident that these variations in the composition of reagents of Class A must introduce decided errors where results of analyses made at one time are to be compared with those obtained at another time, inasmuch as there is both a variation in the final products of the reaction and a variation in the sensitiveness of the reagent. This is especially true if permanent standards are employed. Reagents of Class A type must be allowed to stand some time before use. Since, however, the rate of sulfonation is indefinit and not easily measured, there is no certainty when an equilibrium has been reached. Moreover, it has been shown[2] that the orthosulfonic acid gives greens in the final product in the cold, the intensity of the green being proportional to the amount of ortho acid present, thus giving rise to great variations in the colorimeter readings and rendering comparisons with results obtained with different reagents impossible.

The parasulfonic acid, on the other hand, gives final green colors only when warmed in contact with the nitrate. But it must be remembered

[1] *Bull. soc. chim.*, [4] 5, 1092 (1909).
[2] Paper I, *loc. cit.*

that in this contact, unless special precautions are taken, sufficient heat is generated to nitrify the para acid; moreover, when water is added to dilute the reagent after contact a marked rise in temperature again results, which is further increased when the alkali is added to develop the color. When much para acid is present, green tints must thus invariably result unless the water residue is kept in a freezing mixture during the addition of reagent, water and alkali. The greater the rise in temperature the more intense is the greenish tint. Thus here too a decided error is introduced.

Reagents falling in Class B and Class C have the same faults as those of Class A. It follows, therefore, that any sulfonic acid reagent of greatly varying composition must be regarded as undesirable and that the more stable the reagent is and the smaller the number of component sulfonic acids the better and more reliable will be the results obtained.

Since the final yellow product whose color intensity is measured, in arriving at the amount of nitric nitrogen present in a sample of water, is due to an alkali salt of nitrophenoldisulfonic acid,[1] it follows that reagents of Class D are best and most reliable. This was long ago shown by Gill.[2] Heating the phenol with the concentrated acid accomplishes, in a short time, a degree of sulfonation which only very long standing could bring about.

Gill's reagent having been found to be the best of those proposed and having been adopted by the American Public Health Association, it has been termed the "standard" reagent in the preceding papers and has been selected in the present instance for the study of the sources of error given above. In his paper describing his method for the preparation of the disulfonic acid reagent Gill stated no reasons why the ratio of 3 grams of phenol to 37 grams of sulfuric acid was adopted. It was therefore first necessary to ascertain the proper proportion of phenol and sulfuric acid in reagents which could be prepared by the heating method. With this end in view mixtures were made varying in composition from 1 gram molecule of phenol with 1–16 gram molecules of sulfuric acid. All were heated for six hours at 100° in the usual manner. It was found that the best and clearest yellow colors were obtained when the mixture contained 12 or more gram molecules of sulfuric acid. This proportion is that of Gill's reagent and fully confirms his work. Moreover, it was further found that reagents containing less sulfuric acid would solidify after standing several days in a cool place, owing to crystallization of the sulfonic acid.

The Gill or standard reagent, however, still contains sufficient mono-para acid to yield greenish tints if the reagent is poured upon a warm

[1] Chamot and Pratt, THIS JOURNAL, 32, 630.
[2] *Tech. Quart.*, 7, 55 (1894); THIS JOURNAL, 16, 122, 193 (1894).

nitrate-containing residue, or if there is a marked rise in temperature either upon dilution with water or upon the addition of alkali, thus introducing marked errors at times and of very different degrees. The standard reagent is therefore not a safe or satisfactory one, particularly if permanent standards are employed. The conversion of all of the phenol into the disulfonic acid by the method described later, with the elimination of the small quantity of mono acid still present in the standard reagent, removes at once these sources of difficulty.

II. Errors Due to Variable Volumes of Reagent.—It has been quite generally assumed that providing a volume of the sulfonic acid reagent sufficient to cover the water residue is used it makes little difference whether this volume be much or little within certain narrow limits, although Leffmann[1] appears to have recognized the importance of using exactly equivalent volumes on the known and unknown nitrate residue. This assumption that the color is independent of the volume of reagent used is not warranted, however, the facts being that the final color is actually greatly influenced by the volume of the reagent employed, the intensity increasing with the volume and when more than 4 or 5 cc. of the standard reagent are used, greenish colors appear in the final alkaline liquid. Murky tints almost impossible to match in a colorimeter are also often produced even when no green is discernible. With volumes of reagent in excess of 5 cc. a large amount of inorganic sulfate usually separates, occluding sufficient of the yellow compound to necessitate dilution beyond the capacity of the colorimeter cylinders commonly employed.

The following table shows the average apparent increase of nitrate due to increasing volumes of standard reagent used, the lowest volume being here assumed for purposes of comparison as the correct value.

Cubic centimeters of standard reagent used.	Water residue with N indicated in parts per million.				
	2 parts.	4 parts.	6 parts.	8 parts.	10 parts.
1 cc. taken as............	2	4	6	8	10
2 cc. equivalent to........	2.3	4.4	6.6	8.8	11.1
3 cc. equivalent to........	2.7	5.1	7.7	10.0^3	13.1
4 cc. equivalent to........	3.2	5.6^2	8.2	11.0^3	14.2^3
5 cc. equivalent to........	4	6.4^2	9.8^2	12.9^3	15.5^4

These results clearly show that there is a very decided error unless the standard reagent is very carefully measured and exactly the same volume is employed in treating both the known nitrate-containing residue and that of the sample of water being examined. Practically identical re-

[1] "Examination of Water," page 52.
[2] Murky tints difficult to compare with the 1 cc. color.
[3] Greenish tint.
[4] Very green.

sults as to intensity are obtained when the reagent contains no mono acids, except that in this case neither murky nor green tints develop.

The commonly accepted procedure has been to employ 2 cc. of sulfonic acid. This volume gives satisfactory colors, of sufficient intensity and free from murky or greenish tints and there is therefore no good reason to depart from this volume now used by common consent, but it must be borne in mind that this volume must be carefully measured, if accurate results are required.

Thinking that the very marked increase in color resulting when large volumes of reagent are used might possibly be due in part to ionic concentration and to variation in dissociation, runs were made using a variety of radical combinations, e. g., sodium, potassium, ammonium, magnesium, and calcium nitrates as sources of nitric nitrogen. The concentration of the sulfate ions was also varied by the addition of potassium sulfate. In all cases the final colors were the same both in tint and intensity.

Since the green tints and colors are due to nitrification of monosulfonic acids and since it had already been ascertained that the standard reagent gave green tints only when warmed with nitrates, it appeared probable that the darker colors and changes in tint observed with volumes of reagent greater than 2 cc. resulted from the rise of temperature that naturally followed when stronger acid was neutralized. This heat, curiously enough, seems to account for the changes in color intensity shown in the table.

The color obtained by using 4 cc. of standard reagent is almost exactly matched if to 2 cc. of reagent, 2 cc. of concentrated sulfuric acid is added. Moreover, if 2 cc. of reagent be used, water added and the whole kept boiling while the alkali is added, it is found that the resulting yellow color is darker than that obtained in the usual manner; e. g., with residues containing 10 parts of nitrogen as nitrate per million the following results were obtained:

2 cc. of reagent taken as = 10 parts N.
2 cc. of reagent + 2 cc. of H_2SO_4 = 13.4 parts N.
2 cc. of reagent neutralized hot = 11.3 parts N.

If the elevation of temperature causes the apparent increase in the nitrate content, the reverse should hold true. This has been confirmed experimentally by treating the cold residue with the standard reagent, diluting with cold water and keeping at 0° by means of cracked ice while the cooled alkali was slowly added. It was found that in all cases the final colors obtained were of less intensity than when the usual practice was followed, the apparent difference being less by 0.2–0.4 of a part per million according to the volumes of reagent used. This discrepancy is here again due to the presence of mono acids, since with reagents containing only the disulfonic acid, equivalent volumes of re-

agent give identical final color intensities irrespective of whether cooled with ice or not.

III. Errors Resulting from Variable Time of Contact between Reagent and Residue being Treated.—In a reaction involving the introduction of nitro groups into a sulfonic acid an appreciable length of time is necessary in order that the final product shall show the full content of nitrogen. In order that the minimum time might be ascertained a number of experiments were performed, all of which showed that the reagent and residue should remain in contact at least two minutes after the complete covering of the residue. By way of illustration it is necessary to cite only one of the series of trials made. In this, residues containing 10 parts per million of nitrogen as nitrate were compared with the pure tripotassium nitrophenoldisulfonate standards.

Time of contact.	Parts N found.
15 seconds	8.8
30 seconds	8.9
1 minute	9.2
2 minutes	10
5 minutes	10
10 minutes	10
19 hours	10

In obtaining contact between reagent and all particles of residue the best practice is to mix the two with a glass rod, crushing all particles that may be found. With waters high in total solids containing little nitrate it is essential that the particles be crushed and that a contact of over two minutes be allowed.

IV. Errors Due to Differences in the Temperature of the Residue when the Reagent is Applied.—Richards and Hollings[1] have pointed out that the final color varied greatly with the temperature at which the reagent acted upon the residue. The usual procedure in America has been to allow the residues obtained by evaporation on the water bath to cool to room temperature before applying the reagent. It has already been shown in the present paper that the final color is greatly intensified by temperature. With reagents containing monosulfonic acids all sorts of variations in intensity and tint are obtained if the reagent be applied to a hot residue and very serious errors result if standard nitrate and water residue are not treated exactly alike as to temperature. Failure to observe this precaution leads to enormous errors. Should the reagent be applied at once to the residue upon its removal from the water bath so much green appears in the final product as to render impossible a comparison with a nitrate standard prepared at room temperature. The greater the proportion of monosulfonic acids present the greater will be the deviation from the yellow color of the nitrate standard.

[1] *Soc. Chem. Ind.*, **22**, 616 (1903).

If a reagent consisting wholly of disulfonic acid be employed, there is no change whatsoever in color intensity caused by heating and no green tints appear. It has been possible to heat reagents of this type for over three hours on the water bath in contact with nitrate residues and still obtain the same brilliant yellow as that of the permanent nitrate standard.

V. Errors Due to Variations in the Alkali Employed.—It has long been recognized that the same alkali must be added to the water residue being tested as that with which the standard has been prepared. But there do not appear in the literature any data showing just what the difference in color intensities may be when using different alkalies nor which alkali gives the darkest color and therefore permits of the recognition of the smallest amount of nitric nitrogen.

In the method as originally described, ammonium hydroxide was employed to render the liquid alkaline and develop the yellow color. Ammonia fumes are decidedly objectionable in a laboratory devoted to water analyses where determinations of free and albuminoid ammonia must be made. Where such conditions obtain a fixed alkali must be substituted in accordance with the suggestion of Hazen and Clark[1] but these investigators give no data upon which to base a decision as to the alkali to be preferred. It was also important that experiments be performed in order to learn the influence if any that an excess of alkali might have on the color.

It had already been ascertained that potassium hydroxide gave yellow colors as intense or slightly more so than the other alkalies,[2] hence the employment of the tripotassium salt of the nitrophenolsulfonic acid as standard.

Experiments were made to ascertain the effect of variable excess of alkali. The following table shows the average results obtained by using varying volumes of 12 normal alkali in excess. In these runs the residues contained 6 parts and 10 parts per million of nitrogen as nitrate respectively.

Comparisons were made with the permanent tripotassium salt standards.

PARTS PER MILLION NITROGEN INDICATED.

Cubic centimeters 12 N alkali in excess.	With KOH.		With NaOH.		With NH₄OH.	
	6 parts.	10 parts.	6 parts.	10 parts.	6 parts.	10 parts.
Just alkaline	6	10.2	5.2	9.2	4.1	7.5
2 cc.	6	10	5.2	8.9	4.8	8.5
5 cc.	6	10	5.3	9.0	4.9	8.8
10 cc.	6	10	5.6	9.2	4.9	9.5
Over 10 cc.	.	10	...	9.2	...	9.5

[1] *J. Anal. Appl. Chem.*, **5**, 301 (1891).
[2] Chamot and Pratt, *loc. cit.*

Other trials with different nitrate content were made with relatively similar results. It appears therefore that potassium hydroxide yields darker colors and that a decided excess of alkali does not appreciably affect the results. In the case of potassium hydroxide, however, it is essential that there be always an excess, since the color just at the neutralization point is slightly reddish and therefore appears darker than when there is a drop or two in excess. For reasons not ascertained ammonium hydroxide has yielded variable results, but since this alkali was otherwise undesirable no further investigations were made.

VI. Error Due to the Presence of Organic Matter in Water.—The residue from a water containing organic matter, when acted upon by the strong sulfuric acid of the reagent, gives rise to brown colors, either before or after the alkali is added, that often completely mask any yellow due to nitrates. This source of error has been so long known and so well recognized that comparatively little time was spent in its study. Many methods have been suggested for removing the organic matter, such as potassium permanganate in acid solution, or in alkaline solution, basic lead acetate, animal charcoal, aluminum cream, etc. Of these methods aluminum cream has proved the most satisfactory and practicable in our hands, when dealing with the usual type of waters used for household and municipal purposes in our section of the United States. In all but very exceptional waters the removal of the coloring matter by this process has been found sufficiently complete and no losses of nitrates have been observed.

VII. Errors Due to Mechanical Losses on Evaporation or during the Addition of the Acid Reagents.—Leeds[1] has stated that nitrates are slightly volatil at 100° and Fox[2] has found nitrates in the distillate from a solution of potassium nitrate. Gill[3] found a slight difference in his results ascribed to loss on evaporation but so small as to be considered within the limits of error of the method.

Until the tripotassium salt standard was adopted in the present investigation it was found practically impossible to properly interpret the results obtained, but with an available standard at hand it was found that the losses on evaporation were negligible, and that the slight variations in colorimeter readings of three different observers were as great as any indicated differences which might be ascribed to evaporation losses.

The method employed in this study consisted in evaporating on the water bath equal volumes of water containing known amounts of nitrogen as nitrate. These residues were treated with standard reagent as usual,

[1] *Am. J. Sci.,* [3] 7, 197 (1874).

[2] *Tech. Quart.,* 1, 54 (1887).

[3] *Loc. cit.*

after various periods of continued heating of the dry residue, and finally were compared with tripotassium nitrophenoldisulfonate standard.

The following are some of the results obtained with 1, 2 and 10 parts per million of nitrogen as nitrate.

Time of heating after residue became dry.	Parts per million of nitrogen found.		
0	1.0	2.0	10.0
30 min.	1.1	1.9	10.0
1 hour	1.0	1.9	10.1
2 hours	1.0	2.0	10.0
4 hours	1.0	2.0	10.2
7 hours	...	...	10.0

The slight differences in the readings are undoubtedly due to the presence of the mono-para acid in the reagent, for runs made with a disulfonic acid reagent free from mono acids gave even better results. Other runs with different quantities of nitrogen were made with similar results. It appeared, therefore, that any losses arising from heating the dry residue in a water bath are not measurable in colorimeters of the types commonly employed. However, it seemed wise to carry the study a trifle farther. After a sample had reached dryness, distilled water free from nitrates was added and evaporated to dryness. This process was continued many times. Finally the residue was treated with the reagent, diluted and made alkaline. No measurable loss of nitrogen could be detected.

The fact that the final colors obtained matched those of the permanent tripotassium salt shows that the thin film of reagent covering the residue is sufficient to hold the nitric acid set free by the strong sulfuric acid of the reagent, and that any losses due to incomplete nitrification are not measurable. Nevertheless, to make assurance doubly sure, samples of water were evaporated in deep crucibles, adding a little at a time so as to have the residue substantially all on the bottom. A rapid application of reagent then gave a much greater thickness of sulfonic acid over the residue. Identical results were thus obtained; in no case was the final color appreciably darker as measured in long Nessler tubes or in a Wolff colorimeter.

The addition of the reagent causes losses in particular cases, however, as for example when carbonates or chlorides are present.

VIII. Errors Due to the Presence of Carbonates in the Water Residue.— The addition of the sulfonic acid reagent to residues containing much carbonate causes more or less violent effervescence due to the liberation of carbon dioxide and a consequent mechanical loss of nitrate, causing in some cases considerable error. This was proved by evaporating waters in round-bottomed flasks, which were then closed with a two-holed stopper carrying a separatory funnel and bent glass tube leading into nitrate-free distilled water. The reagent was added to the residues

through the funnel and the evolved gases swept over into the distilled water by nitrate-free air; this water was then made slightly alkaline and evaporated to dryness. The residue treated in the usual manner showed the presence of nitrates, while blank tests made on carbonates showed none. No uniform loss was found among many samples of waters having similar nitrate and carbonate contents. This was to be expected, as the exact rate of adding the reagent, and the method and the rapidity of its distribution over the residue would naturally materially effect this loss. This loss, however, is insignificant save when the alkalinity of the water is very high or the amount of nitrate present is very low; when these conditions obtain the loss may be easily prevented by adding to the sample before evaporation an amount of 0.02 N sulfuric acid sufficient to nearly but not quite neutralize the alkalinity.

At this stage of the investigation word reached us from Professor Bartow, of the University of Illinois, that he believed that Robert Spurr Weston was at work upon errors due to carbonates. Correspondence with Mr. Weston brought out the fact that he and his assistant, Miss Helen R. Hosmer, had already made sufficient progress on the investigation to demonstrate that carbonates do introduce very appreciable error in the sulfonic acid method.

Weston and Hosmer very kindly placed the results of their investigations in our hand, and it is with great appreciation of their courtesy and kindly interest in our study of the sulfonic acid method that the following results are quoted from their unpublished notes.

"The work was done in March, 1909. We were at a loss to explain the freakishness of the results we were getting with some highly nitrated sewage effluents, and thinking that possibly it might be due to the presence of carbonates, we made a rough experiment as follows:

"Six samples of distilled water, each containing 0.006 mg. of nitrogen in the form of potassium nitrate, were evaporated to dryness, three of them with the equivalent of 2, and three with the equivalent of 5 mg. of calcium carbonate. When treated with phenolsulfonic acid and compared in the ordinary way the approximate readings were as follows:

Milligrams nitrogen taken	Milligrams calcium carbonate, equivalent to sodium carbonate added.	Milligrams nitrogen determined.
0.006	2.0	0.004
0.006	2.0	0.004
0.006	2.0	0.005
0.006	5.0	0.002
0.006	5.0	0.002
0.006	5.0	0.002

"This experiment shows plainly that the presence of carbonates interfered with the formation of color. In order to approximate more nearly

the conditions found in natural waters the experiment was repeated with smaller quantities, as shown in the following table:

Milligrams nitrogen taken.	Milligrams of calcium carbonate added.	Milligrams nitrogen determined		
		A.	B.	C.
0.005	0.00	0.004	0.004	0
0.005	0.05	0.004	0.004	...
0.005	0.1	0.003	0.004	...
0.005	0.25	0.003	0.003	0.004
0.005	0.5	0.002	0.002	0.003
0.01	0.05	0.008	0.008	...
0.01	0.1	0.007	0.007	...
0.01	0.25	0.006	0.006	0.006
0.01	0.5	0.005	0.005	0.005
0.01	0.00	0.010	0.010	...

"It was evident from this experiment that the carbonate prevented the formation of the yellow color to some extent. To confirm our impressions that this was due to the presence of carbon dioxide, evolved when the acid was added to the residue, and not to the presence of the base (potassium, sodium, calcium, etc.), we evaporated samples containing 0.01 mg. of nitrogen in the form of potassium nitrate to dryness, treated them with phenolsulfonic acid, and after diluting them with water, passed carbon dioxide into three of the samples for about 5, 10 and 25 minutes respectively. The results were as follows:

Milligrams nitrogen taken.	Minutes exposure to CO_2.	Milligrams nitrogen determined.
0.01	5	0.008
0.01	10	0.006
0.01	25	0.005

"These experiments proved that the introduction of the gas destroys the color-producing compound.

"Experiments were made to show whether or not the presence of atmospheric carbon dioxide had any effect upon the determination and for this purpose several samples were evaporated in an atmosphere of dioxide without affecting the determination of the nitrogen. Free carbon dioxide has no effect as it is expelled during evaporation, that is, before the phenolsulfonic acid is added.

"The above were only preliminary experiments and are mainly of suggestive value. They were not continued after we heard that you were studying the determination.

"Our suggestion for the overcoming of this difficulty is to add acetic acid to the water before evaporation. No experiments were made along these lines, however, beyond evaporating some of the standard with such amounts of sodium acetate as would be formed were acetic acid so added. This did not prevent the determining of the full amount of nitrogen present.

"Whether or not an excess of acetic acid added to ordinary waters would cause volatilization of nitrogen from the acid solution during the evaporation of the samples, we cannot say. We feel sure from our experiments that if the alkalinity of the water be not destroyed by so doing, that it may be used with good results."

In view of the above quoted results, it did not appear necessary to spend further time upon the study of the effect of carbonates on the standard reagent, and all further work was confined to reagents containing no monosulfonic acids. In the latter case, the same small mechanical losses were again observed. No appreciable change in final color could be observed even after 12 hours' passing of carbon dioxide through the treated residue, before the addition of the alkali.

IX. Errors Due to the Presence of Chlorides in the Residue.—When a water contains a large amount of chlorine as chlorides, the nitric nitrogen determined by the phenolsulfonic acid method is much too low. This error has been long recognized, but it is not until very recently that it has been shown that even small amounts of chlorides may cause a most serious error. As long ago as 1891 Bartram[1] called attention to the fact that the age of the reagent had an important bearing upon the magnitude of this error; with a freshly prepared reagent there was little apparent loss, but the same reagent after it had aged furnished results lower than before. This variation in behavior we now know to be due to the gradual change of mono acids into the disulfonic acid.

The low results obtained when a water residue contains chlorides are partially due to mechanical loss and in part due to interaction of the hydrochloric and nitric acids liberated. This was proved by proceeding in the manner already described under the losses due to carbonates. While the investigation was in progress, Farcy[2] arrived at similar results by substantially similar methods. Lombard and Laport[3] had already advanced a similar hypothesis without experimental data. Farcy has also shown[4] that bromides and iodides introduce a similar error. Determinations were made by this author and by Perrier and Farcy of the losses in nitric nitrogen when more than six parts per million of chlorine as chloride were present. The data published show a striking regularity in the proportion of loss to halogen present. The proportional increase in loss with the increase in halogen is such that a correction for error would be possible. But Stewart and Greaves[5] obtained no such proportional regularities. We had already arrived at a similar result. The loss in nitrogen increases with the amount of chlorides present but the

¹ *J. Frank. Inst.*, **131**, 385 (1891).
² *Bull. soc. chim.*, [4] **5**, 1091 (1909).
³ *Ibid.*, [4] **5**, 321 (1909).
⁴ *Ibid.*, [4] **5**, 178, 563 (1909).
⁵ THIS JOURNAL, **32**, 756 (1910).

per cent. of loss is so very irregular that it was not possible to adopt any numerical correction.   The more mono acid the reagent contained the greater the variation in the nature of the loss.   Even when a reagent containing no mono acids is employed the amount of loss is too irregular with below 10 parts per million of chlorine to permit of correction, but with over 10 parts of chlorine the loss approximates 30 per cent. of the nitric nitrogen.   Space forbids the incorporation here of more than one series of experiments by way of illustration.   In the table given each water residue contained 10 parts per million of nitrogen as nitrate and the amount of chlorine as chloride indicated.   In each case the limits given are from the results of at least five different water residues and in several instances many more.   Comparisons were made with a pure tripotassium nitrophenolsulfonate standard.

Parts per million of chlorine present.	Parts per million of N found.	
	Minimum.	Maximum.
0	10	10
0.5	9.35	9.75
1	9.25	9.85
2	8.50	8.75
3	8.30	8.75
4	7.80	8.45
5	7.65	7.80
10	7.20	7.45
15	7.20	7.30
20	7.05	7.35

It appears therefore that the method of procedure for the prevention of error, consisting in the addition of a like quantity of chlorides to the standard as has been determined in the sample, is not always safe and is applicable only when over 10 parts per million of chlorine are present.

When accurate results are required, the halogens must be removed by means of silver sulfate.

Silver compounds have long been employed for the removal of chlorine and prevention of loss.   Shaking the sample with silver sulfate is at the present time the method in general use.   Shaking with silver oxide has also been suggested,[1] but neither process is satisfactory.   Marcille[2] advocates using an ammoniacal solution of known strength, evaporating to dryness, adding the sulfonic acid, diluting as usual and adding ammonium hydroxide to develop the color and dissolve the silver chloride formed.   This method has given in our hands perfectly satisfactory results, but is objectionable in a water analysis laboratory because of the ammonia fumes evolved.   The procedure which has given us the best results and eliminates ammonia consists in determining the chlorine present in the sample, then adding to the volume of the sample to be

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[1] Tatlock and Thompson, *Chem. Ind.*, **23**, 428 (1904).

[2] *Ann. chim. anal.*, **14**, 303 (1909).

used for the determination of nitrates such a volume of a solution of silver sulfate as will remove all but about 0.5 of a part per million of chlorine, heating to boiling, adding a little "aluminum cream" to aid in clarifying and to remove color, filtering and evaporating to dryness on the water bath, the residue is then treated with sulfonic acid as usual. As thus practiced the method becomes very little longer than without the removal of chlorides and requires substantially no more time than that of Marcille.

X. Errors Due to the Presence of Iron.[1]—When dealing with ferruginous waters very high in iron a residue is obtained which is penetrated only with great difficulty by the sulfonic acid reagent. The results obtained therefore show great variations. These variations are not however in proportion to the iron present. With the standard or Gill reagent the losses in nitrogen are sometimes very great, but it was found that when the reagent is of such composition as to permit heating in contact with the residue for a few minutes no such discrepancies can be detected. Should the composition of the reagent preclude heating with the residue, the iron must be removed.

The effect of the presence of iron was tried on many samples of water, containing up to 5 parts per million of Fe.

When much iron is present and the alkali used for the development of the color is added very slowly a red or brown solution is obtained whose color is destroyed by the addition of a slight excess of alkali with the formation of a precipitate of iron hydroxide and the usual yellow color of the nitrophenoldisulfonate. The red coloration may thus serve as an indication of the presence of much iron and as a warning that losses of nitrogen may be expected unless the contact of reagent and residue has been unusually intimate.

XI. Errors Due to Other Interfering Inorganic Substances.—Both nitrites and magnesium compounds have been stated at various times to introduce errors of sufficient magnitude to necessitate special treatment of the water.

To test the influence of nitrites, nitrate-free silver nitrite was prepared, decomposed by pure sodium chloride and the resulting sodium nitrite employed.

A large number of water residues containing known added amounts of pure sodium nitrite but no nitrates were treated with the sulfonic acid reagent as usual. It was found that nitrites in amount less than 0.2 parts per million of nitrogen gave no yellow color and therefore had no influence upon the determination, but if present in excess of this value

[1] Drown and Hazen, "Purification of Water and Sewage," Special Report, Massachusetts State Board of Health, 1870, 712.

the amount of nitric nitrogen is found too high, apparently due to a higher oxidation of part of the nitrogen in the nitrite.

According to Pouget[1] this oxidation takes place in accordance with the equation

$$3HNO_2 = 2NO + HNO_3 + H_2O$$
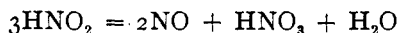
and is quantitative for amounts of nitrite from 0.1 to 0.3 mg. In the case of nitrites present in water residues, however, we have obtained yields of nitric nitrogen always much below that indicated by this equation, and it is not until the nitrogen reached 1 part per million that the final yellow color was of sufficient intensity to appreciably affect colorimeter readings.

Waters very high in magnesium compounds yield residues whose particles, as in the case of iron compounds, are penetrated only with great difficulty by the sulfonic acid reagent, and it appears that the difficulty lies in failure to obtain intimate contact between reagent and nitrate. Very thorough rubbing with a glass rod is essential. The chief error when dealing with waters high in magnesium chloride is due to the effect of the chlorine and not of the base.

Summary.

1. Sulfonic acid reagents containing mono acids are subject to change with age and yield results greatly affected by temperature, concentration, variation in character of alkali, etc. They cannot be satisfactorily employed with permanent standards.

2. In order that accurate results may be obtained chlorides, carbonates, and organic matter must be removed.

3. Nitrites present in small amount do not appreciably effect the final results, but when exceptionally high must be destroyed or corrected for.

4. A sulfonic acid reagent of definit composition should be used. Such a reagent is described in our fourth paper.

LABORATORY OF SANITARY CHEMISTRY,
    CORNELL UNIVERSITY.

A STUDY OF THE PHENOLSULFONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

[FOURTH PAPER.]

A MODIFIED PHENOLSULFONIC ACID METHOD.

BY E. M. CHAMOT. D. S. PRATT AND H. W. REDFIELD.

In order that reliable results may be obtained and comparisons with permanent standards shall be possible we have shown that the phenolsulfonic acid reagent must contain no monosulfonic acid.[2]

[1] *Bull. soc. chim.*, **7**, 449 (1910).

[2] THIS JOURNAL, **32**, 630 and preceding paper.