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.

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

[FOURTH PAPER.]

## A MODIFIED PHENOLSULFONIC ACID METHOD.

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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]

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

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

After studying many methods of preparation the following is suggested for trial by water analysts.

*Preparation of Phenoldisulfonic Acid Reagent.*—Dissolve 25 grams of pure white phenol in 150 cc. of pure concentrated sulfuric acid, add 75 cc. of fuming sulfuric acid (13 per cent. $SO_3$), stir well, and heat for two hours at about 100°.

The reagent thus prepared contains no mono acids, and no tri acids so far as we have been able to ascertain, and may be heated in contact with water residues for many hours without suffering any development of interfering colors, and is far less sensitive to the interfering action of the substances causing errors than when the old standard reagent is used.

Complete sulfonation usually takes place in from thirty minutes to one hour, but the time of heating suggested is to absolutely insure the absence of even a trace of mono acid. The proportion of acids given is such that the viscosity of the final product is sufficiently low to permit measuring the reagent from a 2 cc. pipet and also prevent the solidification of the reagent should the temperature of the laboratory fall to a little below 15°.

It has been tested during the past year in our student laboratories in large classes and appears to be a great improvement over the reagent commonly employed.

Theoretically 2 cc. of this new reagent should be capable of taking up 297 parts per million of nitrogen as nitrate. But on trial it has been found that the results are not always reliable when over 50 parts per million are treated and serious discrepancies arise should the nitrate content be over 80 parts per million. The old reagent is in this respect much worse.

*Determination of Nitrates in Water.*—First determin the alkalinity, the chlorine and nitrite content and the color of the sample. Should the color be high decolorize with "aluminium cream."

Measure into an evaporator 100 cc. of the sample, or if the nitrates are very high, such a volume as will contain about 10 parts per million of nitric nitrogen, fairly low colorimeter readings having been found most reliable. Add sufficient 0.04 $N$ or 0.02 $N$ sulfuric acid to not quite neutralize all the alkalinity, then a volume of standard solution of silver sulfate free from nitrate (4.3969 grams per liter, 1 cc. = 1 cc. of standard silver nitrate solution = 1 mg. Cl per cc.), which will precipitate all but about 0.5 mg. of the chlorine. Heat to boiling, add a little "aluminium cream," filter and wash with small amounts of hot water. Evaporate the filtrates to dryness, add 2 cc. of the disulfonic acid reagent, rubbing with a glass rod to insure intimate contact Should the residue be compact or vitreous in appearance from much magnesium or much iron present, place the evaporator on the water bath for a few minutes. Dilute with distilled water and add slowly a strong solution of potassium hydroxide (10–12 normal) until the maximum color is developed. Transfer to a colorimeter cylinder, filtering, if necessary, and compare with a potassium nitrate or tripotassium nitrophenoldisulfonate standard.

Should nitrites be present in excess of 1 part per million of nitrogen a slight error will be introduced. They should therefore be removed by heating the sample a few moments with a few drops of hydrogen peroxide[1] (free from nitrates) repeatedly added or dilute potassium permanganate may be added in the cold until a trace of pink appears, and a correction applied to the final nitrate nitrogen reading due to the conversion of the nitrites to nitrates.

*Permanent Standards.*—Permanent standards made according to the method ot the American Public Health Association[2] using the reagent suggested above, or a series of standards using tripotassium nitrophenoldisulfonate may be employed.

The use of permanent standards with the reagent suggested, containing as it does no mono acids, introduces no errors, since the reagent does not change its composition with age, the color of the final product is not influenced by heat, nor by moderate variation in volume of reagent or volume of alkali used. Nor does dilution change the relative value of the standards.

*Preparation of Tripotassium Nitrophenoldisulfonate*, $C_6H_2OK(SO_3K)_2NO_2$. —The pure salt isolated in the progress of the investigation of the nature of the compound producing the yellow color proved so valuable as a standard for the study of sources of error that much time was spent in an attempt to discover a convenient method for its preparation. None of the methods given in the literature of the nitrophenolsulfonic acids proved successful. As a warning to future investigators it should be recorded that every attempt to sulfonate *o*-nitrophenol with fuming sulfuric acid at 100° resulted in violent explosions. Treatment with fuming acid in the cold for twenty-four hours causes the splitting off of the nitro group and an impure phenoldisulfonic acid results.

The only method that has proved practicable thus far in our hands consists in adding, in the cold, to the disulfonic acid reagent, described above, the theoretical amount of dry finely powdered potassium nitrate in very small pinches at a time (for every cubic centimeter of reagent 0.1076 gram of potassium nitrate), stirring thoroughly after each addition. The product is then diluted, treated with dry barium carbonate until a deep yellow color results, filtered, and the precipitate washed with boiling water to dissolve the barium nitrophenoldisulfonate which is but sparingly soluble in cold water. Much of the product sought is lost unless the

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

[2] *J. Infect. Dis.*, 1905, May Sup., 41. Jackson, *Tech. Quart.*, 13, 320 (1900).

extraction with boiling water is thorough. Filtrates and washings are united, the barium removed by adding potassium carbonate until alkaline, the solution filtered and the filtrate concentrated to crystallization. The yield obtained is about 60 per cent. of the theoretical. The salt may be easily purified by recrystallization from water. This method is suggested provisionally until a better one has been devised.

To prepare the standards, the recrystallized salt thus obtained is dissolved in distilled water and the solution compared in a colorimeter with a known weight of potassium nitrate treated with the reagent in the usual manner. From the value obtained the proper dilutions for a series of standards are calculated.

Carrying the purification of the tripotassium salt to a point where the theoretical amounts might be weighed out for a set of standards is not recommended, since the products must be dried in a current of carbon dioxide.[1]

Standards prepared as above described were checked repeatedly, both with the C. P. salts and with potassium nitrate standards, during many months and have as yet shown no tendency to change. During most of this period they have stood in clear glass bottles in diffused daylight. The authors therefore believe that such standards may be recommended as convenient, reliable, and as doing away with the very strongly alkaline standards formerly employed.

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## NOTE.

*A Simple Hydrogen Sulfide Generator.*—Many generators have been devised for hydrogen sulfide and I offer no apology for adding one to the number. Chemists have suffered so much at the hands of this bad-smelling gas that they will be ready to welcome anything which promises to alleviate their discomfort. The simple apparatus which I here submit will be of great service in small laboratories and to chemists who want moderate quantities of the gas from time to time at a moment's notice.

There are two principles involved in the various forms of hydrogen sulfide generators. In the one the acid in bulk is applied to the sulfide repeatedly, thus becoming weaker and weaker, and must finally be removed before it is fully exhausted. This is the principle of the long used and popular Kipp generator. In the other form a small quantity of acid is applied to a large quantity of the sulfide and when spent flows away automatically. This is the principle of the generators of Parsons, Dudley and others and is the one used in the apparatus here described.

The sulfide is placed in the body (*a*) of the apparatus. The acid, best

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[1] THIS JOURNAL, 32, 635 (1910).