Summary.

If to a hot ferric chloride solution, strongly acid with hydrochloric acid, diammonium arsenate solution be added to incipient precipitation, and the mixture heated, there forms a white, finely divided precipitate, which analysis showed to be a double arsenate of ammonium and iron of the formula $NH_4H_2AsO_4.FeAsO_4$. Like the corresponding phosphate prepared by the author, the double arsenate readily hydrolyzes when washed with water. It readily dissolves in mineral acids, but is practically insoluble in 50 per cent. acetic acid. Ammonia dissolved it on heating to a deep reddish brown solution, from which 95 per cent. alcohol precipitates a basic double ammonium ferric arsenate. When potassium arsenate was used under the same conditions, a precipitate was obtained which, from the results of a qualitative analysis, appears to be the corresponding double alkali arsenate.

NEW YORK CITY, February, 1910.

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

[SECOND PAPER.]

THE COMPOSITION OF THE YELLOW COMPOUND.

BY E. M. CHAMOT AND D. S. PRATT.

Received February 22, 1910.

In our first paper[1] we discussed the composition of the various sulphonic acid reagents which have been suggested for use in this method[2] and showed that the standard phenolsulphonic acid generally used in the United States (Method Am. Pub. Health Association)[3] made by heating a mixture of 15 grams of phenol and 128 cc. of concentrated sulphuric acid for six hours in a flask immersed in boiling water, consists of phenoldisulphonic acid 1–2–4, with always small but appreciable quantities of phenolmonosulphonic acid (para) and a large excess of sulphuric acid. It was also stated that the yellow color obtained by treating a nitrate-containing water residue with this reagent, diluting and making alkaline, was not due, as had long been taken for granted, to salts of picric acid,[2,3] nor could it be due to salts of mononitro phenols, as believed by Hazen and Clark,[4] nor to salts of dinitro phenols as Montanari supposed.[5]

It had already been shown by Andrews[6] that the mononitro and dinitro

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[1] THIS JOURNAL, 31, 922.

[2] Sprengel, *Pogg. Ann.*, 121, 188 (1863); Grandval and Lajoux, *Compt. rend.*, 62, 101 (1885); Kekulé, *Lehrbuch*, III, 236; Fox, *Tech. Quart.*, 1, 54 (1887); Rideal, *Chem. News*, 60, 261 (1889); Pagnoul, *J. Soc. Chem. Ind.*, 23, 135 (1904); Smith, *Analyst*, 10, 199 (1885).

[3] Gill, THIS JOURNAL, 16, 122 (1894).

[4] Hazen and Clark, *J. Anal. Appl. Chem.*, 5, 301 (1891).

[5] Montanari, *Gazz. chim. Ital.*, 22, I, 87 (1902).

[6] Andrews, THIS JOURNAL, 26, 388 (1904).

phenols are removed from acid solutions by shaking with benzene and that they may be removed from the solvent by shaking with water containing a small amount of alkali, yielding a yellow liquid. Andrews further showed that the nitrophenolmonosulphonic acids are insoluble in benzene and may thus be separated and differentiated from the nitro phenols. Making use of this method, Andrews concluded that mononitro and dinitro phenols and picric acid must be absent from the reaction product of phenolsulphonic acid on nitrates, and therefore assumed that the yellow color must be due to nitrophenolsulphonic acid salts; but as he apparently believed that the reagent consists of monopara acid,[1] one gathers from his paper that he believed the yellow compound to be a salt of the nitromonopara acid. This assumption as to the composition of the reagent and reaction product did not appear to be at all conclusive to the authors, who believed it very necessary to definitely determine the character and structure of the yellow compound by actual isolation and analysis, thus obtaining conclusive proof as to its nature.

As stated in our first paper, it was found early in the investigation that when the cold reagent is poured upon cold residues (the usual method of procedure) no trace of nitro phenols nor of picric acid could be detected in the reaction products when dealing with such amounts of nitrate as are usually met with in water analysis, 0 to 30 parts per million of nitrogen as nitrate. When, however, the amount approaches 50 parts per million, traces, but only traces of picric acid, appear and may be detected by microchemical analysis.

When either the reagent or the water residue is hot, or when the residue is heated after adding the reagent to it, different results are met with and under these conditions even 5 parts of nitrogen as nitrate may then give slight traces of picric acid, the amount increasing according to the heat treatment, but never reaching more than appreciable traces. The monoparasulphonic acid present is also nitrated by this heat treatment. The presence of these exceedingly small amounts of picric acid was proved by extracting with benzene a large number of water residues after treatment with phenolsulphonic acid, evaporating the solvent and subjecting the extracted material to microchemical tests. Picric acid could not, however, be detected unless a large number of water residues were extracted and hence this compound cannot legitimately be regarded as a product of the reaction as the method is carried out in practice.

In order to obtain the compound yielding the yellow color in alkaline

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[1] Since the preparation of this article, Lombard (*Bull. soc. chim.*, 6, 1092 (1909)) advances the theory based upon the work of Obermiller on phenolsulphonic acids, that the reagent consists chiefly of orthophenolsulphonic acid and paraphenolsulphonic acid and that the yellow compound consists of about 2 parts of alkali salts of orthonitro phenol and 3 parts of orthonitrophenolsulphonic acid. No details are given, however, to substantiate this conjecture, which is erroneous

solution, it was decided to isolate it from actual natural water residues containing nitrogen as nitrate. This source of material was adopted in order that there could be no question as to the reactions in the standard method, the authors believing that the pouring of the reagent on pure nitrate residues and the subsequent isolation therefrom of a yellow-colored salt might possibly be regarded as no proof of the products of the reactions obtained in practice.

Several thousand residues were obtained by evaporating to dryness, on a water bath, 100 cc. portions of a natural water containing about 10 parts per million of nitrogen as nitrates. These residues were then separately treated in the cold with 2 cc. each of the standard phenolsulphonic acid and the resulting products united. From this acid liquid no color-giving material could be extracted by benzene.

Experiments on a small scale demonstrated that it was possible to separate the yellow-colored salt from the other products present in the alkaline solution by fractional crystallization, and that the potassium salts were best suited for this procedure. Potassium was chosen as the base for several reasons. The reagent always contains a large excess of sulphuric acid and it is evident that the major portion of the products formed must be inorganic sulphates. It is therefore advantageous to have this of a low solubility and as easily crystallizable as possible, hence, potassium is more to be desired than either sodium or ammonium, any one of these three being used in the method. Moreover, potassium is better adapted to quantitative determination.

For the above reasons the acid liquid resulting from the combined residues was carefully neutralized with just sufficient potassium hydroxide solution to develop the maximum color, care being taken to avoid, as far as possible, a marked rise in temperature. The resulting solution was alkaline to litmus. This yellow alkaline liquid was then subjected to fractional crystallization in the usual manner, by evaporation, pouring off mother-liquors and combining similar fractions. In another portion of the alkaline liquid fractional precipitation by means of alcohol was resorted to. In both cases potassium sulphate first separated, always, however, stained yellow. The yellow compound, being far more soluble, accumulated in the end fractions. It was soon evident that the compound under investigation was much more soluble in hot than in cold water. After the isolation and purification of the yellow salt, solubility determinations showed that 100 parts of water dissolve 28.8 parts at 40°, 100 parts of water dissolve 19.4 parts at 20° C. The solubility of potassium sulphate, on the contrary, is but slightly increased by a rise of temperature.[1] The fractionations were therefore carried on in warm

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[1] Andreae, *J. prakt. Chem.*, 29, 471.
100 parts water at 20° C. dissolve 11.11 parts K_2SO_4
100 parts water at 40° C. dissolve 14.76 parts K_2SO_4

solutions, making use for this purpose of a large incubator regulated for 40° in our bacteriological laboratory. No attempt was made to ascertain the most suitable temperature for fractioning, since 40° proved remarkably efficient and satisfactory, and this incubator temperature was available.

Inasmuch as the reagent consists of phenoldisulphonic acid 1–2–4, together with a small amount of phenolparasulphonic acid, the possible products of the reaction are the normal and acid salts of the two nitrosulphonic acids, the unnitrated sulphonates, mononitro phenols, dinitro phenols, picric acid and dinitro phenolmonosulphonates. Of these compounds the unnitrated sulphonates are colorless, but the nitro compounds are all more or less yellow in alkaline solution.

Both Andrews, by his solubility method, and the authors, by microchemical analysis, have shown that mononitro phenols, dinitro phenols and picric acid are not products of the reaction. The authors have further shown[1] that under the usual method of procedure no nitro group is introduced into the parasulphonic acid. This leaves as the possible compounds formed, the alkali salts of nitrophenoldisulphonic acid and dinitrophenolmonosulphonic acid, the latter resulting from the replacement of one sulphonic acid group by a nitro group—such a reaction, in the cold and with such small amounts of nitric acids as are met with in water analysis, is, however, very improbable, theoretically. Moreover, no evidence of such a compound could be obtained by the authors in any of the material studied. By elimination there remains only the alkali salt of nitrophenoldisulphonic acid.

Nevertheless, as the fractionation proceeded, there separated what appeared to be two nitro compounds. Eventually this was found to be erroneous, one of these being a salt of phenoldisulphonic acid which in crystallizing always occludes relatively large amounts of the nitrosulphonate, thus acquiring shades of yellow, from which it can be completely freed only with great difficulty. Instead, however, of being the tripotassium salt as we assumed at first, because of the presence of a slight excess of potassium hydroxide, it proved, upon isolation and analysis, to be the dipotassium salt of this acid, $C_6H_3OH(SO_3K)_2.H_2O$. This salt is colorless when pure, crystallizing in highly refractive orthorhombic prisms, exhibiting exceptionally strong double refraction (Fig. 1). It cannot therefore be confused in microchemical examinations with the salt of the nitro acid.

The other yellow salt separating was fractioned to free it from potassium sulphate, until its solution failed to yield a turbidity with barium chloride. It was then recrystallized from water at room temperature.

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[1] Chamot and Pratt, *Loc. cit.*

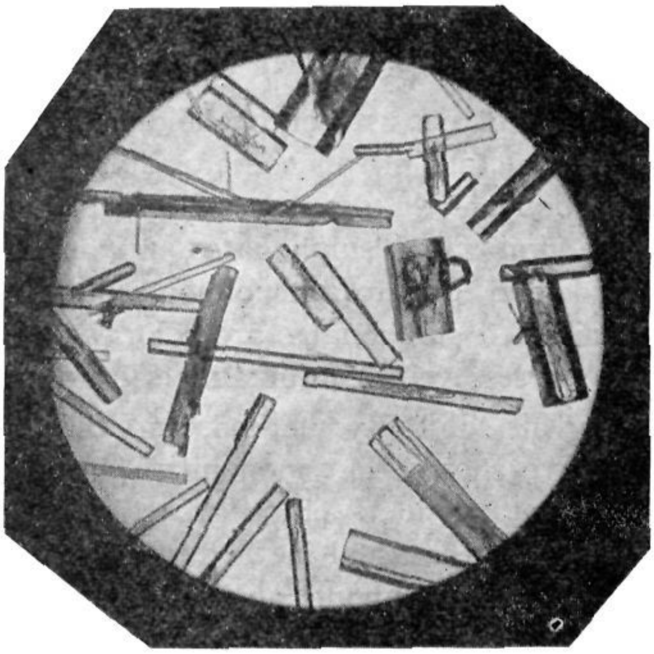


Fig. 1.—Dipotassium phenoldisulphonate × 15.

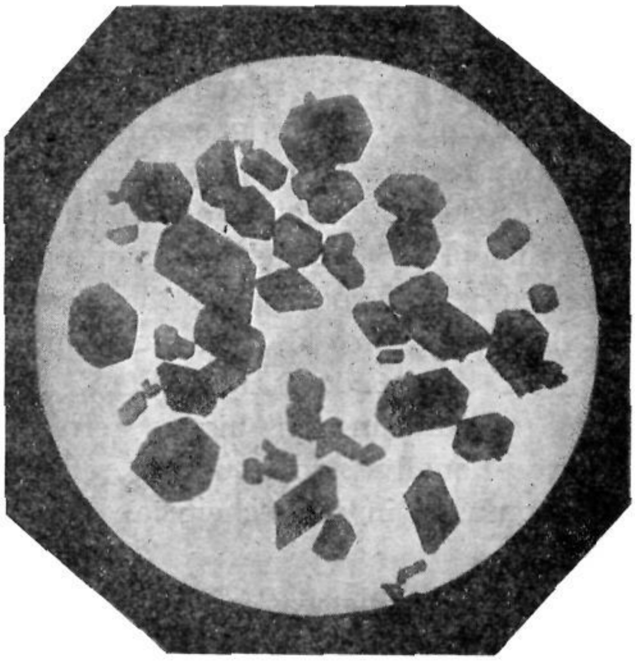


Fig. 2.—Tripotassium nitrophenoldisulphonate × 15.

There was thus obtained between one and two grams of a beautifully crystalline, very brilliant, highly refractive orange-yellow salt.

Dry air passed over these crystals caused a loss of water of crystallization, as did heating to 100°. In attempting to dry to constant weight in air it was found that a gradual increase of weight took place, probably due to oxidation. To avoid this, a small electric resistance furnace was designed in which the heating could be done in an atmosphere of carbon dioxide under reduced pressure. This apparatus consisted of a short piece of Jena glass combustion tube wound with nickel wire and surrounded with asbestos-magnesia pipe covering. The temperature could be easily and accurately regulated by a resistance lamp-board and the material contained in platinum boats was readily accessible. The tube was partially exhausted by means of a Chapman filter pump and pure dry carbon dioxide was passed through to remove the moisture liberated. A temperature of 200° was found to be most convenient for removing the water of crystallization. Above 240° the compound turns brown and decomposes without melting. A determination of the melting point of the compound is therefore impossible.

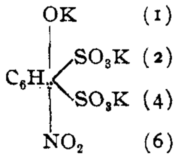
The air-dried, orange-yellow salt gave, upon heating as above described, a loss of weight corresponding to one and one-half molecules of water o crystallization.

Found: 6.16; 5.97; 6.45; 6.47; 6.09; average 6.22 per cent.
Theory for $C_6H_2OK.(SO_3K)_2.NO_2.1\frac{1}{2}H_2O$, 6.13 per cent.

The analysis of the anhydrous salt gave the following results:

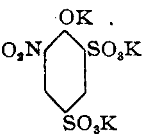
	Per cent. found.			Theory for $C_6H_2OK.(SO_3K)_2.NO_2$.
K	28.46	28.35	28.43	28.37
N	3.43	3.45	.....	3.37
SO_4	46.25	46.21	.....	46.47

The salt therefore has the following formula:



$$C_6H_2\begin{cases}OK & (1)\\ SO_3K & (2)\\ SO_3K & (4)\\ NO_2 & (6)\end{cases}$$

$1\frac{1}{2}$ H_2O or



Potassium was determined as the chloroplatinate in the usual manner on the salt direct.

Nitrogen was determined by the Kjeldahl method after first reducing by boiling with zinc dust in a slightly acidulated solution.

For the determination of the sulphonic acid radical the material was first oxidized by several treatments with fuming nitric acid (sp. gr. 1.52) and subsequent precipitation with barium chloride.

This tripotassium nitrophenoldisulphonate crystallizes from aqueous solutions in beautiful orange-yellow, triclinic, many-sided prisms of high refractive index (Fig. 2).

Through the kindness of Professor A. C. Gill, of the Department of Mineralogy and Petrography, the following crystallographic note is given:

"The yellow salt occurs in stout prisms or tabular triclinic crystals. Most of the crystals were too small to measure, but one of the tabular ones, about 0.5 mm. in length, gave fairly good reflections on the goniometer. The plane angle of the large face was a little less than 70°. Each of the edges of the plate is formed by a pair of long, narrow faces. The angles from the top plate to the bottom over one pair are 70° 40′, 64° 25′, and 44° 55′, while over the other pair the angles are 52° 49′, 64° 47′, and 62° 24′. The prismatic habitus as shown in the photograph is much more common than the tubular habitus of the crystal measured.

"The crystals show pleochroism from orange- to sulphur-yellow, are strongly double refracting, and have marked dispersion both of the optic axes and axes of elasticity."

The anhydrous salt is quite a little darker orange in color than the hydrated, and when hot is a cherry-red, retaining its orange color upon cooling. In dilute solutions it is clear yellow but tends towards red as the concentration is increased. With ferric chloride solution it gives a violet-red. Acids added to its solution do not decolorize it, but simply weaken the tint, accounting for the yellow color always obtained in acid solution when a residue high in nitrates is treated with standard sulphonic acid.

A small amount of the dipotassium phenolsulphonate present in the fractions usually greatly modifies the crystal form of the tripotassium nitrophenoldisulphonate, and there may then appear, on rapid crystallization, blade-like crystals pointed at each end or sheaves or clusters of these crystals. It is these modified crystals which confused us for some time, as stated above.

The last fractions of a series always contain as an impurity the very soluble potassium salt of the monoparasulphonic acid, a small amount of this acid being always present in the standard reagent. This salt crystallizes in exceedingly slender and delicate hair-like tufts.

To determine whether the same product is always obtained when the amount of nitrogen as nitrate ranges between the usual limits present in water a special series of water residues was examined. These differed by increments of about two parts of nitrogen per million between the limits of 2 and 30. Each residue was treated with 2 cc. of the standard reagent, diluted and made alkaline with potassium hydroxide. In every case, by microchemical analysis, the yellow color was found to be due to tripotassium nitrophenoldisulphonate. A residue containing 60 parts nitrogen per million gave similar results.

In a third paper the authors will discuss the phenolsulphonic acid method as applied in practice with special reference to sources of error.

Summary.

The yellow color of alkaline solutions of nitrate containing water residues treated with standard phenolsulphonic acid reagent is due to the tripotassium salt of nitrophenoldisulphonic acid, this salt having been isolated and its properties studied.

No other compound giving a yellow color with alkalies could be isolated or detected in appreciable amount, in treated water residues containing from less than 1 to 60 parts per million of nitrogen as nitrate.

In water residues containing over 50 parts per million nitrogen as nitrates traces of picric acid detectable by microchemical methods may be formed in the cold, but traces only.

Water residues heated in contact with phenoldisulphonic acid yield traces of picric acid, but only traces, unless the heating is long continued and the quantity of nitrate high, when appreciable amounts of picric acid may be formed.

Alkali salts of phenoldisulphonic acid occlude sufficiently large amounts of the alkali salts of nitrophenoldisulphonic acid to so color them and so modify their crystal form as to simulate in appearance and behavior another nitro compound.

CORNELL UNIVERSITY CHEMICAL LABORATORY.

[CONTRIBUTION FROM THE LABORATORY OF DR. HERBERT M. HILL, BUFFALO, N. Y.]

THE MERCURY CATHODE IN RAPID ELECTROANALYSIS.

BY W. S. KIMLEY.

Received October 8, 1909.

Mercury is superior to platinum for a cathode in several electroanalytical determinations; in some others there is no decided choice, and in several others there is no substitute for the platinum cathode. Some metals can be determined by using a mercury cathode, in an electrolyte that would not give a quantitative deposit on platinum in that the metal seems to be withdrawn from the solvent action of the electrolyte to a certain extent, *e. g.*, copper may be deposited from a solution containing 10 per cent. of nitric acid to within 0.05 per cent. by use of a mercury cathode, while with platinum it would be difficult to recover over 98–99 per cent. With some other metals mercury is superior because it will amalgamate with metals that would not always adhere well to platinum.

The method of H. Filippo,[1] in which the method of Kollock and Smith

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[1] Leiden Univ., *Chem. Weekblad*, **6**, 2269.