solutions. These features make it very convenient, especially if a number of determinations are to be made at points some distance apart.

If a table or bench is at hand, the box is placed in the position shown in Fig. 2, when the 6-inch porcelain dish can be set conveniently under the glass-stoppered acid burette. When using a 100 cc. tube or the large flask in which dissolved oxygen is titrated, the box is brought forward so that the burettes project over the edge of the table. The outfit can be used, however, under almost any conditions which one is liable to encounter in field work.

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SPRENGEL'S METHOD FOR COLORIMETRIC DETERMINATION OF NITRATES.

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THE colorimetric determination of small amounts of nitrates which is based on the use of phenol and concentrated sulphuric acid, appears to have been first devised and used by Sprengel.[1] It is probably the method now most frequently used for the determination of nitrates in water analysis and is the best of the rapid methods. Sprengel states that the yellow color obtained in the process is due to the formation of picric acid, a statement which has been repeated in text-book after text-book for forty years, seemingly without criticism or examination, until recently Montenari[2] has sought to show that not picric acid, but dinitrophenol is produced in this reaction.

Previous to the publication of Montenari, I had been impressed with the inherent improbability of the formation of trinitrophenol under the conditions of the experiment, that is, with the phenol in great excess as regards the nitric acid, and had also observed that the yellow coloring-matter formed does not give the characteristic reactions of picric acid. Since the conclusions of Montenari also appeared extremely improbable, I thought it worth

[1] Pogg. *Ann.*, **121**, 188 in 1863.
[2] *Gazz. chim. ital.*, **32**-I, 87 (1902).

while to submit the question to renewed examination, with results which it is the object of the present paper to present.

As is well known, the reagent employed in this test is prepared by heating phenol with an excess of concentrated sulphuric acid for several hours to 100°.[1] It consists, therefore, of a solution of phenol parasulphonic acid in sulphuric acid.[2] Hence, it was *a priori* most likely that the primary product of the action on it of relatively small amounts of nitrates would be orthonitrophenolparasulphonic acid, with the possibility that the sulphonic group might split off, forming orthonitrophenol. The latter in turn might be further nitrated to di- or trinitrophenol. It was consequently necessary, in the first place, to ascertain by what reactions small quantities of these possible products can be readily distinguished from one another and, if requisite, separated. All the compounds in question dissolve in water with a yellow color. This color is discharged, in case of paranitrophenol and of its sulphonic acid, by acidification with a minimum excess of a highly dissociated acid, as hydrochloric or sulphuric, while, on the contrary, dinitrophenol and trinitrophenol exhibit their characteristic yellow tint in acidified solutions also. Further, if an acidified solution of either of the nitrophenols is shaken with benzene, the nitro-bodies pass into the benzene layer and the latter, after separation, imparts a yellow color to potassium hydroxide solution when shaken with it. Ortho- or paranitrophenolsulphonic acid solution, on the other hand, when acidified with dilute hydrochloric or sulphuric acid and shaken with benzene, does not dissolve in the latter, and the separated benzene does not impart the faintest yellow color to alkali solutions. These reactions were established by experiments in dilute solutions of the pure compounds and were found to be extremely delicate. They furnish the means of distinguishing, with certainty, between the ortho- or paranitrophenol, and its sulphonic acid on the one hand and between both these substances and the more highly nitrated compounds on the other.

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[1] Johnson: *Chem. News*, **61**, 15 (1890); Gill: This Journal, **16**, 122, etc., etc. (1894).

[2] According to Gill (*l. c. supra*) phenoldisulphonic acid is present in this mixture, while Beilstein (1st ed., 1065) following Kekulé (*Ztschr. Chem.*, 1867, 199) states that only paraphenolsulphonic acid is formed under these conditions. In view of Gill's observations it is, however, probable that *both* the *p*- mono- and the *o-p*-disulphonic acids are produced.

About 50 mg. of finely pulverized potassium nitrate were now gradually added to 10 cc. of the reagent[1] in a porcelain mortar and rubbing the mixture thoroughly with the pestle. After standing for half an hour, the liquid was diluted with 100 cc. of water. The resulting solution was not yellow, but became so on making it alkaline; hence the polynitro derivatives alluded to above can not, and either mononitrophenol or nitrophenolsulphonic acid must, be present. Half the acid solution was then shaken in a separatory funnel with 50 cc. of the purest benzene. The latter, after washing with water, imparted no yellow color to potassium hydroxide solution; hence non-sulphonated nitrophenols must be absent, and some nitrophenolsulphonic acid present. As a control of the sensitiveness of the test, 3 mg. of paranitrophenol, corresponding to about one-tenth the nitrogen present, was added to the acid solution left from the last experiment, which was again shaken with benzene. The latter then gave a very strong reaction with potassium hydroxide. A far smaller amount could have been detected. Incidentally, a quantitative colorimetric comparison was made between a solution prepared by the action of the phenolsulphonic acid reagent on a weighed amount of potassium nitrate with one made from a known amount of paranitrophenol. Both solutions were so made up as to contain the same amount of nitrogen per cubic centimeter. Practically perfect agreement was attained, the solution prepared from the nitrate showing a tint corresponding to only 1 per cent. less nitric acid than that from the nitrophenol. It appears, therefore, that a given amount of nitrogen in solution as paranitrophenol[2] (potassium salt) has, within the errors of the experiment, the same depth of color as the same amount of nitrogen in solution as the potassium salt of orthonitrophenolparasulphonic acid. This fact can be taken advantage of in the preparation of a standard type solution for comparison in nitrate determinations. A solution of 0.993 gram of paranitrophenol in a liter of water contains 0.1 mg. of nitrogen per cubic centimeter. For use, a measured volume can readily be made alkaline and diluted to match the color obtained in the usual manner.

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[1] Prepared by heating a mixture of 75 grams of pure phenol, containing enough water to liquefy it, with one-half liter of sulphuric acid to 100° for eight hours.

[2] Previous experiments had shown that equal weights of *o*- and of *p*-nitrophenol give the same depth of color in highly dilute alkaline solution.

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THE DISSOCIATION OF LEAD NITRATE.[1]

BY LEO BAEKELAND.

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IT IS generally accepted that all nitrates of heavy metals, under the action of heat, decompose, producing NO_2, oxygen and a metallic oxide. Whenever the oxides of the metal are not stable at high temperatures, further decomposition may set in, thus producing oxygen and metal.

The final reaction can be summarized as follows:

$$M''(NO_3)_2 = M''O + O + 2NO_2.$$

In the case of lead nitrate, the decomposition begins at a temperature between 205° and 223°. Even at these temperatures the decomposition proceeds very slowly and it is only when temperatures as high as 357° are reached that the reaction becomes more energetic.

However, if the experiment be carried on *in vacuo* nitrous gases develop more abundantly, even at temperatures as low as 205° to 223°.

It is interesting to note that ordinary lead nitrate, as sold in the trade under the name of chemically pure, gives off acid vapors at much lower temperatures; in some cases simple heating at 100° may produce this result. This is due to the presence of very small amounts of moisture. In the experiments I am about to describe I used a specially prepared lead nitrate, very

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[1] Read at the December meeting of the New York Section.