

determined by the modified Pemberton method of the A. O. A. C. In no case could any serious discrepancy be observed. About this time, Mr. J. F. Wilkinson, suggested that sulphuric acid was the disturbing substance and that if it were previously removed by means of barium chloride the volumetric method could be applied as usual and accurate results obtained. This proved to be the case. Experiments were conducted with solutions of phosphate rock in hydrochloric acid to which were added respectively sulphuric acid, sodium sulphate and calcium sulphate, in which the P_2O_5 was determined by the volumetric method. The results did not agree with those obtained by the A. O. A. C. gravimetric method when working on the same solutions and varied from 0.2 to 1.00 per cent. P_2O_5 above the gravimetric method. In other words the sulphate ion invariably caused greater or smaller discrepancies. The work shows the necessity of excluding sulphuric acid from the reagents used to dissolve phosphate containing fertilizers for analysis.

The following working method was adopted for fertilizers, particularly acid phosphate, containing sulphates. A long and thorough trial has demonstrated its accuracy and value.

Weigh two grams into a 250 cc. flask, digest by boiling with 30 cc. concentrated nitric acid and 5 cc. concentrated hydrochloric acid, then add 10 cc. water and boil for five minutes. Add 25-30 cc. of 10 per cent. barium chloride solution, cool and make up to volume. Filter through a dry filter, rejecting the first portion of the filtrate and take 25 cc. for the determination. From this point on follow the A. O. A. C. modification of the Pemberton method.

In the presence of sulphates, sulphuric acid or a sulphate was always found by analysis in the yellow precipitate of ammonium phosphomolybdate and it is altogether probable that a complex ammonium sulphomolybdate is formed under the conditions of phosphoric acid precipitation by ammonium molybdate which has the acid nature of ammonium phosphomolybdate and therefore reacts with alkali and phenolphthalein similarly to the latter.

The analytical work mentioned was carried out in large part by Mr. John Jepsen of this laboratory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE
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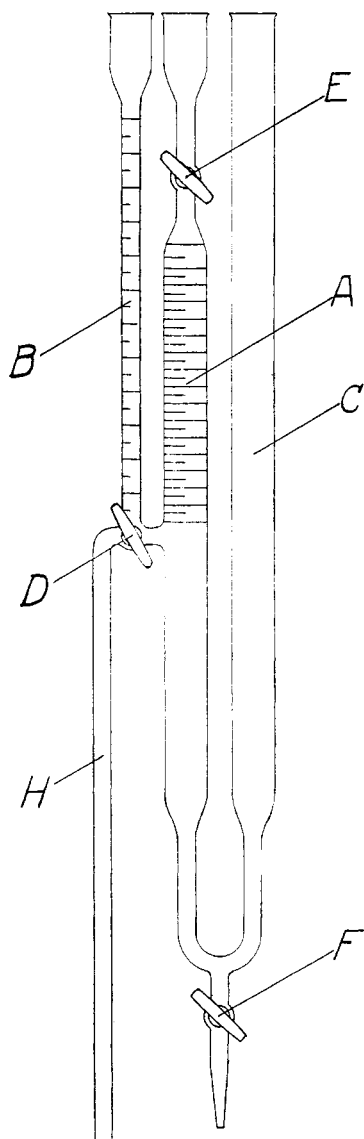
A GASOMETRIC METHOD FOR THE DETERMINATION OF HYDROGEN PEROXIDE.

BY WILLIAM M. DEHN.

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The apparatus depicted in the figure was designed as an ureometer; its construction and the application to this purpose are described in another

contribution¹. It has been found that this instrument can be used also



for rapid and accurate determination of hydrogen peroxide. The reaction involved—

$\text{H}_2\text{O}_2 + \text{NaBrO} = \text{NaBr} + \text{H}_2\text{O} + \text{O}_2$ is immediate² and, as shown below, is sharply quantitative.

Method.—The stopcock E is opened and the stopcocks D and F are

¹ Z. anal. Chem. **45**, 604.

² Lunge, Ber. **19**, 1886; Tanatar, Ber. **32**, 1013; Forester, J. pr. Chem. **63**, 141.

closed, then the solution of sodium hypobromite¹ is poured in at the top of C until it fills the tubes A and C to some point above the stopcock E. The stopcock E is then closed and the stopcock F is opened so that the hypobromite in C may run down to the constricted portion—the hypobromite in A is then sustained by atmospheric pressure. The stopcock D² is turned from the position shown in the figure and is so controlled that B may first be washed with a little of the hydrogen peroxide and then be filled with the same to a readable height on the scale. Upon turning D so as to admit a regulated volume of the hydrogen peroxide solution, an immediate evolution of oxygen results. After admitting most of the hypobromite held above E, and letting stand for a minute or two so as to drain properly, the columns of hypobromite in A and C are brought to the same level, the volume of oxygen is read, and its weight and that of the corresponding hydrogen peroxide are calculated by the usual formulas.

A sample of hydrogen peroxide, whose specific gravity at 19° was 1.0133, gave by decomposition with a sodium hypobromite solution the following data :

| Experiment | Vol. H ₂ O ₂ | Vol. O ₂ | Temperature | Atmospheric Pressure | Vapor Pressure NaBrO | Weight O ₂ | Per Cent. H ₂ O ₂ |
|--|------------------------------------|---------------------|-------------|----------------------|----------------------|-----------------------|---|
| 1 | 5 cc. | 11.40 | 26.8 | 742.2 | 19.75 | 0.01411 | 2.621 |
| 2 | " | 11.43 | " | " | " | 0.01414 | 2.628 |
| 3 | " | 11.37 | " | " | " | 0.01408 | 2.614 |
| Average | " | 11.40 | " | " | " | 0.01411 | 2.621 |
| The same sample by the iodide titration method = | | | | | | | 2.625 |
| " " " " permanganate " = | | | | | | | 2.641 |

Other samples of hydrogen peroxide gave by this gasometric method results that coincided with the most careful analysis by the iodine titration method.

For most accurate analysis the vapor-pressures of the hypobromite solution used must be taken into account. The usual solution of hypobromite (sp. gr. 1.25) was found to exert the following vapor-pressures :

| Temperature | Vapor-Pressure. | | Difference |
|-------------|-----------------|------------------|------------|
| | NaBrO | H ₂ O | |
| 4 | 1.1 mm. | 6.1 mm. | 5.0 mm. |
| 8 | 1.8 | 8.0 | 6.2 |
| 12 | 3.3 | 10.5 | 7.2 |
| 16 | 5.3 | 13.6 | 8.3 |
| 20 | 8.6 | 17.4 | 8.8 |
| 24 | 12.8 | 22.2 | 9.4 |
| 28 | 18.0 | 28.1 | 10.1 |
| 32 | 24.0 | 35.4 | 11.4 |
| 36 | 29.5 | 44.2 | 14.7 |
| 40 | 36.0 | 55.0 | 19.0 |

¹ The usual method of preparation of this solution is as follows: dissolve 100 g. of caustic soda in 250 cc. of water and to each 100 cc. of this solution add 10 cc. of bromine and finally to the resulting solution add an equal volume of water. The specific gravity of the solution is 1.25. It need not be freshly prepared, nor is its efficiency rapidly impaired by repeated use. However it must be remembered that on diluting its vapor-pressure is increased and, by neglect of the same, errors approaching 1 per cent. may be introduced.

² This stopcock is ground or plugged so as to deliver only in the two directions of a right angle triangle.

Weight in milligrams of H_2O_2 corresponding to one cubic centimeter of moist oxygen.

| $t^{\circ}\text{mm.}$ | 728 | 732 | 736 | 740 | 744 | 748 | 752 | 756 | 760 | 764 | 768 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 4° | 1.2664 | 1.2734 | 1.2802 | 1.2872 | 1.2942 | 1.3011 | 1.3081 | 1.3151 | 1.3222 | 1.3290 | 1.3359 |
| 8 | 1.2463 | 1.2531 | 1.2600 | 1.2669 | 1.2736 | 1.2805 | 1.2876 | 1.2944 | 1.3014 | 1.3081 | 1.3150 |
| 12 | 1.2251 | 1.2317 | 1.2387 | 1.2454 | 1.2522 | 1.2589 | 1.2657 | 1.2726 | 1.2823 | 1.2860 | 1.2928 |
| 16 | 1.2044 | 1.2111 | 1.2178 | 1.2245 | 1.2311 | 1.2378 | 1.2444 | 1.2512 | 1.2578 | 1.2646 | 1.2713 |
| 20 | 1.1817 | 1.1884 | 1.1948 | 1.2015 | 1.2080 | 1.2145 | 1.2213 | 1.2279 | 1.2345 | 1.2410 | 1.2475 |
| 24 | 1.1583 | 1.1649 | 1.1719 | 1.1777 | 1.1843 | 1.1907 | 1.1972 | 1.2036 | 1.2100 | 1.2169 | 1.2230 |
| 28 | 1.1345 | 1.1411 | 1.1476 | 1.1538 | 1.1603 | 1.1665 | 1.1731 | 1.1796 | 1.1857 | 1.1922 | 1.1986 |
| 32 | 1.1085 | 1.1149 | 1.1213 | 1.1275 | 1.1338 | 1.1401 | 1.1465 | 1.1528 | 1.1589 | 1.1652 | 1.1715 |
| 36 | 1.0843 | 1.0905 | 1.0967 | 1.1030 | 1.1093 | 1.1155 | 1.1214 | 1.1279 | 1.1341 | 1.1402 | 1.1465 |
| 40 | 1.0605 | 1.0666 | 1.0725 | 1.0786 | 1.0849 | 1.0909 | 1.0971 | 1.1033 | 1.1094 | 1.1155 | 1.1216 |

Here the vapor-pressures of the hypobromite solution are seen to be considerably less than the pressures of pure water. The effect of *different concentrations* of hypobromite may be seen in the following table :

| NaBr Solution | H ₂ O added | Specific Gravity | Vapor Pressure | Difference H ₂ O |
|---------------|------------------------|------------------|----------------|-----------------------------|
| I | 0 | 1.253 | 10.70 | 9.56 |
| I | 1 | 1.131 | 12.77 | 7.49 |
| I | 3 | 1.052 | 15.73 | 4.53 |
| I | 7 | 1.033 | 17.50 | 2.76 |
| I | ∞ | 1.000 | 20.26 | 0.00 |

In the preceding table, (p. 1318) cubic centimeters of oxygen under various conditions of temperature and pressure are calculated to milligrams of hydrogen peroxide, corrections for the aqueous pressure of the hypobromite (sp. gr. 1.25) and the effect of temperature on the barometric column are included.

By the use of this new gasometer, this hypobromite method and the table for calculating, the determination of hydrogen peroxide is made not only rapid and accurate but the necessity of preparing and correcting standard solutions is avoided and the presence of the usual preservatives in the peroxide solution can be neglected.

URBANA, ILL.
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THE ACTION OF PHOSPHORUS OXYCHLORIDE ON 1,8-NAPHTHYLAMINE SULPHONIC ACID.

BY FREDERIC DANNERTH.

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As early as the year 1887 Schultz made short mention of an inner-anhydrid of 1,8-naphthol-sulphonic acid which he had prepared for the first time by heating this latter compound with concentrated sulphuric acid. The pure product appears as colorless difficultly soluble prisms having a melting point of 154°. Because of its similarity to the lactones he named the new substance Naphtsultone. Our knowledge of the lactone of hydroxy-benzoic acid and the lactam of amino-benzoic acid suggests at once the possibility of an amino derivative similar to this naphtsultone. Dressel and Kothe in their researches on the sulphonation of naphthalene derivatives succeeded in preparing compounds of this type.

On treating 1,8-naphthylaminesulphonic acid with concentrated sulphuric acid and heating, they obtained a body which according to the analysis and its chemical behavior seemed to be a sulphonic acid of an inner-anhydrid, which they then called naphtsultam. Unfortunately this anhydrid formation was always accompanied by sulphonation in the nucleus so that it at that time appeared impossible to obtain the pure mother-substance. Bearing this in mind an attempt was made to remove the molecule of water with a reagent which would leave the nucleus in-