

## SELECTION AND TECHNIC OF AN APPROPRIATE METHOD FOR ESTIMATING PHENOL.

BY JOHN W. FORBING.

Text-books, technological treatises, and chemical literature in general have given considerable space in presenting methods and modifications of methods for the estimation of phenol, or carboic acid. Without exception these methods are instructive and ingenious and more or less accurate. A summary, together with brief criticisms, makes interesting reading. There is some use, practical as well as pedagogical, in making a selection from these methods which will prove appropriate to equipment and object in view. The determination of choice rests ultimately on three factors: accuracy, time, and economy. The methods may firstly be divided into two groups: gravimetric and volumetric.

Gravimetric	{	Landolt: production of tribromphenol and weighing per se.
		Riegler: production of an insoluble diazo-acid, $C_6H_4NO_2C_6H_4OH$ with para-diazonitraniline, drying at $100^\circ$ and weighing.
Volumetric	{	U. S. P. (Koppeschaar).
		Koppeschaar, Sutton Modification.
		Koppeschaar, Sutton Modification, with author's modification.
		Iodometric method, Messinger and Nortmann.
		Schwalbe's Diazo method.
		Sodamide Method, S. B. Schryver.

The Landolt method of the volumetric group is not to be considered efficient, in that its operation is tedious and requires too much time with ordinary equipment. From an instructive standpoint, however, it has merit. It teaches that bromine can be made to enter into combination with phenol to form tribromphenol quantitatively. Further, the Landolt method is of historical interest. It formed the basis for the more rapid volumetric methods which followed its introduction.

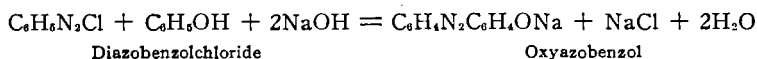
The Riegler gravimetric method (Chem. Centr., 1899, 322) is ingenious but less accurate than that of the Landolt, with no advantages. It is of some value in the dye industry and of special interest to the research worker. It accentuates the fact that the field of research, which is to produce an insoluble phenol derivative for the purpose of gravimetrically estimating carboic acid, is a very barren and unproductive one at the most.

The U. S. P. method has all the essentials of efficiency when a large number of estimations are to be made, or samples to be assayed are to be depended upon to arrive at frequent intervals. For the worker who has occasion rarely to estimate phenol the official method has disadvantages from the viewpoint of economy, and no advantages, even in time. Therefore, for the worker in question, who is by no means in the minority, the U. S. P. method is not to be selected. It requires a preparation of a N/10 bromine V. S., which in turn requires standardization, and sodium bromate, an article rarely carried in stock, necessitating, in consequence, both time and expense.

For the requirements of the workers above described, the Sutton modification as given on p. 393, "Volumetric Analysis," 9th ed., would answer very nicely were it not for the fact that it leaves too many loop-holes for error.

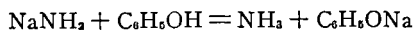
The iodometric method devised by Messinger and Nortmann (Ber., 1891, 2753; J. Soc. Chem. Ind., 1890, 1070) is based on the bromine method; obviates the use of bromine by substitution of iodine. It introduces, while doubtless tending to do otherwise, as much detail as any of the Koppeschaar modifications; does not save time, and is of uncertain accuracy.

Schwalbe's Diazo-Method, applicable for phenol volumetric estimations (Ber. 38, 3072, 1905; Bucherer, Z. Ang. 20, 877, 1907), is used to some extent in the German technical laboratories. It is possibly based on the Riegler method and owes its origin to the facility with which phenols unite with diazo-solutions to form oxyazo dye products. The following is a well-known type of the reaction:



p-Nitrobenzoldiazonium chloride serves best for the titrating solution. N/10 V. S. is produced from p-nitraniline and standardized with resublimed beta-naphthol. This method, interesting to the organic chemist, has a limited technological application, but is of little use to the general and pharmaceutical chemist.

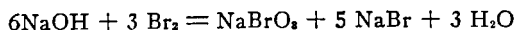
The sodamide process, originated by S. B. Schryver (J. Soc. Chem. Ind., 1899, 553), takes advantage of the reaction between hydrocarbons containing hydroxyl groups, and  $\text{NaNH}_2$ , liberating  $\text{NH}_3$ , which is collected and titrated with acid. A type of the reaction is the following:



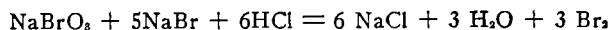
The method is decidedly applicable and especially praiseworthy for the estimation of phenol in the presence of hydrocarbons which are attacked by bromine. It has its specialized application, but it is not to be thought of for a simple phenol assay.

For phenol assays the author proposes that a stock solution of C. P. NaOH, 40 percent, be kept on hand. This solution is an inexpensive one, and may serve many purposes; preparation of 5 percent reagent, for making volumetric solutions, Kjeldahl estimations, etc. Due to its concentration, the carbonate formed unavoidably is rendered less soluble than in more diluted solutions; is precipitated, and thus by decantation a solution of comparatively pure NaOH may at any time be easily obtained. From this solution 100 Cc. of N/1 NaOH is prepared. 10 Cc. of the 40 percent solution is run from a burette into a 100 Cc. graduated flask and water added to mark. This solution, which approximates a N/10 NaOH V. S., is titrated with N/10  $\text{H}_2\text{SO}_4$ . A series of titrations are made, using as indicator methyl-orange, and the mean taken. Thus, for example, if 10.7 Cc. of the soda dilution is required to neutralize 10 Cc. N/10  $\text{H}_2\text{SO}_4$ , then 10.7 Cc. of the 40 percent stock solution of C. P. NaOH diluted to 100 Cc. will produce 100 Cc. of N/1 solution. The N/2 NaOH, thus produced, enables us to measure off positively known quantities of pure NaOH.

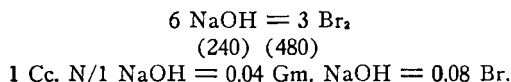
A solution of NaOH, when treated in the cold with bromine, unites according to the following equation:



If  $\text{NaBrO}_3$  and  $\text{NaBr}$  be treated, according to the molecular proportions represented in the above equation, with  $\text{HC}_1$ , the entire equivalent of bromine is liberated.

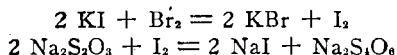


Thus:

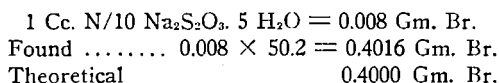


As we depend on nascent bromine derived from this source to act on the phenol to be estimated, the reaction was checked as follows:

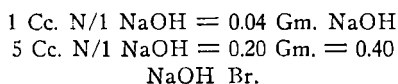
5 Cc. N/1 NaOH was run from a burette into a 50 Cc. conical beaker with lip, and pure bromine added by means of a pipette. This was agitated and sufficient bromine added to produce a solution having a decided brownish color. The excess of Br was then driven off by boiling until the solution was perfectly colorless. This solution was washed into a 100 Cc. glass-stoppered flask containing 5 Gms. KBr (KBr being added to increase the solubility of bromine liberated later). The washings complete should make a solution measuring approximately 75 Cc. 5 Cc. HCl was added and care taken to replace stopper immediately. The flask was shaken and 5 Cc. of a solution (1 in 20) KI added, stopper replaced, flask shaken, and the iodine, liberated as represented in the following equation, was titrated with N/10  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .



The mean of a series of titrations was 50.2 Cc., N/10  $\text{Na}_2\text{S}_2\text{O}_3$ , using starch solution as indicator.



Calculation for theoretical:



This preliminary work gives assurance that the N/1 NaOH will carry and liberate the theoretical amount of Br within limits of negligible error.

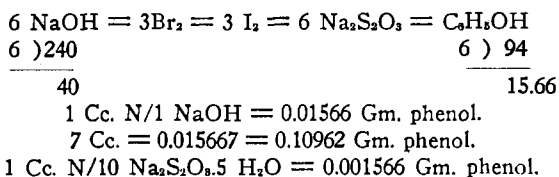
The next step is the preparation of a phenol solution 10 Cc. of which will contain supposedly 0.1 Gm. phenol. In our laboratories we keep on hand a 90 per cent stock solution of carbolic acid which is used for the determination of the phenol coefficients of disinfectants. This solution was used for assay. 1.11 Gm. diluted to 100 Cc. produces 100 Cc. of solution, 10 Cc. of which equals 0.1 Gm. phenol. The ordinary liquid phenol of the Pharmacopœia, any phenol solution, or crystals may, of course, be made into such a solution. 10 Cc. of this solution is placed in a 200 Cc. glass-stoppered flask. 7 Cc. of the N/1 NaOH is run from a burette into a 50 Cc. conical beaker, treated with bromine as described, boiled and washed into the flask containing the phenol. 5 Gm. KBr is added, dissolved, and contents cooled by affusion of cold water. 5 Cc. HCl is added quickly and the flask stoppered at once and shaken at intervals for 15 minutes. The bromine liberated according to the equation previously given unites with phenol to form insoluble yellow-colored 2-4-6 tribromphenol.



5 Cc. of a solution of KI (1 in 20) is then added. The bromine not taken up by the phenol liberates its equivalent of iodine, the flask with washings and addi-

tions contains about 150 Cc. of fluid. N/10 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O is run in until but faint color of iodine remains, starch solution added and titration completed.

Calculation:



6.04 Cc. (the means of a series of titrations) were required for excess of iodine, or excess of bromine in terms of phenol would be  $6.04 \times 0.001566 = 0.00946$  Gm. phenol, which subtracted from the total amount equivalent to 7 Cc. N/1 NaOH, or 0.10962, is 0.10016 Gm., or amount of phenol present in 10 Cc. of the phenol dilution. 10 Cc. of the phenol solution is equal to  $1.11 \times 10 = 0.111$  Gm. sample used for assay.

$$\begin{array}{l}
 0.1002 : 0.111 : : \times : 100 \\
 \times = 90.28 \text{ percent}
 \end{array}$$

This analysis was checked by that given in "Essentials of Volumetric Analysis," Schimpf, 2d ed., which is essentially the same as U. S. P. A series of analyses by the U. S. P. method (Schimpf) gave 90.8 percent phenol.

RÉSUMÉ.

Author's Koppeschaar Modified Method, Phenol..... 90.28 percent  
 U. S. P. .... 90.80 percent

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PRESENCE OF OXYGEN IN RANCID FATS.

It is well known that many fats, such as butter, lard, olive oil, and oil of sweet almonds, when exposed to the air, and becoming rancid, absorb oxygen. This is not, as has been stated, due to the presence of an oxidase in the fats. The author finds that after having been heated to a temperature of 120° C. they absorb oxygen as readily, on exposure to the air, as they do previous to being so heated. If, however, they are heated to 200° C. the property of absorbing oxygen is lost. Rancid fats are found to give the characteristic blue color with tincture of guaiacum and blood or hæmoglobin solution, similar to that given by hydrogen peroxide, or oxidized oil of turpentine. In the presence of a peroxidase, therefore, the oxygen, combined by the rancid fats, is liberated. The test may be used to determine the freedom of fats from rancidity. About 10 Gms. of the material, if butter or lard, previously melted, is treated with 4 or 5 drops of an aqueous dilution of blood, or of 3:100 aqueous solution of hæmoglobin, 10 drops of 5:100 solution of guaiacum resin in alcohol 70 percent, and 10 mls of distilled water. After thorough shaking together for one minute the vessel is corked and set aside. Fresh fats or oils free from rancidity will show no color. With those that are rancid the emulsion will show a more or less pronounced blue tint proportional to the degree of rancidity. When the change in the fat is only slight, a sharper and more delicate reaction is obtained by adding to the emulsion an equal volume of alcohol 95 percent. The acidity of rancid fats does not interfere with this reaction, and its removal does not lessen it. Fresh oils exposed to the air will give the blue color in twenty-four to forty-eight hours. Lard and butter require longer, not showing any reaction until after four or five days' exposure, by which time the rancid odor will be very perceptible.—J. Vintilecco and A. Popesco (*J. Pharm. Chim.*, 1915, 12, 318).