THE DETERMINATION OF PHENOL.

BY S. J. LLOYD.

Received October 27, 1904.

NUMEROUS attempts have been made to devise a satisfactory method for the quantitative estimation of phenol.

Beckurts[1] mixed the phenol with its own volume of petroleum spirit, shook with a strong solution of caustic soda in a graduated tube, and noted the change in volume; Bader[2] titrated against a decinormal solution of sodium hydroxide with symmetrical trinitrobenzene as indicator;[3] Messinger and Vortmann[4] precipitated the triiodo derivative with an alkaline solution of iodine; Carré[5] treated the phenol with nitric acid and determined the resulting picric acid colorimetrically; Schaedler[6] used sulphuric acid, and determined the phenolsulphonic acid indirectly with barium; Riegler[7] weighed the precipitate with *p*-diazonitraniline; Toscher[8] oxidized with volumetric permanganate in boiling alkaline solution; while the reaction with sodamide has been applied by Schryver[9] to the determination of the "hydroxyl value" of phenol.

Of these methods, the first evidently makes no pretense to accuracy, and indeed, like the sulphonic acid process, is intended for use with crude phenol only. Titration with soda is not possible with solutions containing less than 2 per cent. of phenol,[10] and in any case the end-point is not sharp. Precipitation with iodine requires careful manipulation and exact regulation of the temperature in order to obtain accurate results;[11] the colorimetric method is unsuited to the determination of phenol in other than very small quantities, the reaction with the diazo compound leads to a tedious gravimetric process, and the sodamide method requires special apparatus, and can be used only with perfectly dry phenol.

The reaction of phenol, however, which is best suited for the

---

[1] *J. Soc. Chem. Ind.*, **5**, 546 (1886) (from *Arch. Pharm.*, **24**, 567 (1886)).

[2] *Ztschr. anal. Chem.*, **31**, 58 (1892).

[3] For the behavior of phenol with other indicators, see Imbert and Astruc: *Compt. Rend.*, **130**, 35 (1900).

[4] *Pharm. Ztg.*, **29**, 759.

[5] *Compt. Rend.*, **113**, 139 (1891).

[6] *Centrbl.*, 1872, p. 506 (from *Pharm. Centrbl.*, **13**, 225).

[7] *Centrbl.*, 1899, II, p. 322 (from *Buletinul din Bucuresci*).

[8] Meyer's *Jahrbuch, d. Chemie*, 1901, p. 253 (from *Pharm. J.*, 1901, No. 1602).

[9] *J. Soc. Chem. Ind.*, **18**, 553 (1899).

[10] Frerichs: *Centrbl.*, 1896, II, p. 2141 (from *Apoth. Ztg.*, 11, 415).

[11] Frerichs: *Loc. cit.*

purposes of quantitative determination, is that with bromine,

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$$

Landolt,[1] who was the first to suggest its use, precipitated the tribromphenol with bromine water, dried in a desiccator and weighed; Chabrie[2] extracted with ether and dried in a special apparatus. Koppeschaar[3] shortened the process by using a measured quantity of bromine water, and titrating back the excess with potassium iodide and sodium thiosulphate; he also found it advisable to replace the unstable and disagreeable bromine water by a mixture of potassium bromide and bromate, from which the bromine was liberated at the proper time by acid. Degener,[4] who was apparently unacquainted with Koppeschaar's work, also used bromine water, but determined the end-point by the disappearance of the yellow color of the solution, or by potassium-iodide-starch paper. Chandelon[5] found the time required for an analysis by the Koppeschaar method too long, and in order to shorten it and avoid loss of bromine as vapor and as a mechanical enclosure in the precipitate, he substituted for the bromide-bromate mixture a hypobromite solution which contained sufficient alkali to hold the tribromphenol in solution. The disappearance of the yellow color of the solution, or the failure to discolor potassium-iodide-starch paper, marked the end of the reaction. Telle[6] used volumetric sodium hypochlorite, which he added to the solution of phenol containing excess of potassium bromide, and determined the end-point by the color of the solution. Waller's[7] method differed from that of Degener only in the addition of a saturated solution of alum to make the precipitate more dense. Seubert[8] followed Koppeschaar in liberating the bromine from a bromide-bromate mixture, and added the phenol solution from a burette until the filtrate gave no further color with potassium-iodide-starch paper while Beckurts[9] used an excess of the bromide-bromate mixture, and titrated back with iodide and thiosulphate. The last-named chemist recognized the presence of tribromphenolbromide

---

[1] *Ber. d. chem. Ges.*, **4**, 770 (1871).

[2] *Centrbl.*, 1898, 1, 1309 (from *Rev. Chim. Anal. Appl.*, **6**, 138 (1898)).

[3] *Ztschr. anal. Chem.*, **15**, 233 (1876).

[4] *J. prakt. Chem.*, N. F., **17**, 390 (1878).

[5] *Bull. Soc. Chim.*, **38**, 69 (1882).

[6] *Chem. News.*, **83**, 51 (1901).

[7] *Ibid.*, **43**, 152 (1881).

[8] *Ber. d. chem. Ges.*, **14**, 1581 (1881), (from *Arch. Pharm.*, **15**, 321).

[9] *J. Soc. Chem. Ind.*, **5**, 546 (1886) (from *Arch. Pharm.*, **24**, 561 (1886)).

in the precipitate, but assumed that it was quantitatively converted into tribromphenol by potassium iodide.

The following table may serve as a synopsis:

Gravimetric:
(1) Landolt, Chabrie.
Volumetric:
(2) *Bromine and phenol in acid solution.*
(*a*) End-point determined by color, or by potassium-iodide-starch paper.
Degener—Bromine water.
Telle —Hypochlorite and potassium bromide.
Waller —Bromine water and alum.
Seubert —Bromide-bromate mixture.
(*b*) Excess bromine determined by potassium iodide.
Koppeschaar—Bromine water or bromide-bromate mixture.
Beckurts—Bromide-bromate mixture.
(3) *Bromine and phenol in alkaline solution.*
Chandelon.

Various modifications for use in the estimation of phenol in tar-oil, urine, soaps, etc., have been suggested by Tóth,[1] Kleinert,[2] Fedeli,[3] Giacosa,[4] Endemann, Neuberg,[5] Kossler and Penny,[6] Partheil,[7] Ditz and Cedivoda,[8] Stockmeier and Thurnauer[9] (who used chloroform in the titration), and others.

Some idea of the accuracy of the results obtainable by these different methods of procedure may be gleaned from the test analyses published by their authors. Landolt's numbers show variations of 0.5 per cent. or more, Koppeschaar's (bromine water) 2.5 per cent. (bromide-bromate) 0.5 per cent., Degener's 3 per cent., Chandelon 2 per cent., Seubert's 1.5 to 3 per cent. No test analyses have been published by Waller or Telle. According to Frerichs,[10] Beckurt's modification is the best, but as his paper, in its original form, is not accessible to me, I am unable to quote the results of this author's analyses.

These discrepancies are due, in part at least, to the formation

[1] *Ztschr. anal. Chem.*, **25**, 160 (1886).
[2] *Ibid.*, **23**, 1 (1884).
[3] *Ber. d. chem. Ges.*, **28**, 1060 R (1895), (from Moleschott's *Untersuchung.*, **15**, 583).
[4] *Ztschr. physiol. Chem.*, **6**, 43 (1878).
[5] *Ibid.*, **27**, 123 (1899).
[6] *Ibid.*, **17**, 117 (1889).
[7] Meyer's *Jahrbuch d. Chemie*, 1896, p. 237 (from *Apoth. Ztg.*, 1896).
[8] *Ztschr. angew. Chem.*, 1899, pp. 873 and 897.
[9] Mohr: *Titrirmethode*, 7th ed., p. 386 (1896) from *Chem. Ztg.*, 1893, pp. 119 and 131.
[10] *Centrbl.*, 1896 (II), 2141.

of tribromphenolbromide, which, as I have shown in a previous paper,[1] is produced by the action of bromine water on the precipitated tribromphenol, and once formed is not quantitatively reconverted into tribromphenol by potassium iodide.

The present paper, after dealing with the loss of bromine by evaporation during the analysis, the use of volumetric solutions containing bromates, and the formation of a new product of the action of bromine on phenol, contains the results of a number of test-analyses in which the precautions suggested by the previous experiments were adopted, and closes with an enumeration of the conditions under which phenol may be accurately determined.

SOLUTIONS EMPLOYED.

Phenol.—Merck's "absolute phenol" was distilled three times, the first and last fractions being rejected in each case, and the portions boiling between 182° and 183° collected. In the last fractionation the distillate was received in a tared and stoppered weighing-glass, cooled, weighed (20.5340 grams) and dissolved to 1 liter. The solution used in the following analyses was made by diluting 100 cc. of this solution to 1 liter.

Hypobromite.—About 9 cc. of bromine were dissolved in 2 liters of N/4 caustic potash, and the solution was standardized by adding potassium iodide and hydrochloric acid, and determining the iodine with decinormal thiosulphate.

One hundred cc. of the phenol solution were equivalent to 71.95 cc. of the hypobromite.

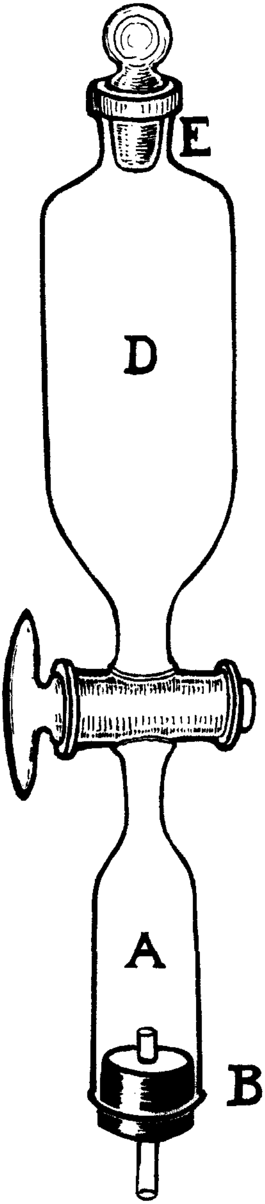
Sodium Thiosulphate.—One liter of an approximately N/10 solution was prepared and standardized with iodine which had been ground with potassium iodide, sublimed from the mixture, and dried for three days in a vacuum desiccator over sulphuric acid. The value was found to be 0.1045 N. This solution was used to fix the titre of the alkaline solution of bromine as stated above, and in turn was repeatedly standardized against the latter solution; it showed a slight falling off in normality from 0.1045 to 0.1042 in two weeks.

For use in the phenol determination the decinormal thiosulphate was diluted to five times its volume and the ratio controlled by comparison with an iodine solution.

Iodine, approximately N/50 for use in "titrating back."

---

[1] This Journal, **27**, 7 (1905).



Acid, hydrochloric, "strictly chemically pure" (sp. gr. 1.2).

Potassium Iodide, 17 grams in 100 cc.

The solutions were prepared and standardized with every care, the buretres were calibrated before using, and a special burette reader was employed, by means of which hundredths of a cubic centimeter could readily be distinguished.

LOSS OF BROMINE BY EVAPORATION.

The test analyses published at the close of this paper were carried out in a 0.25 liter long-necked glass-stoppered measuring flask. In order to assure myself that there was no loss of bromine by evaporation, two measurements were made in the apparatus sketched in the accompanying figure (made by sealing an adapter to a separating funnel).

The chamber *A* was closed by the perforated rubber stopper *B*, the tap opened and the whole exhausted with a filter-pump; the tap was then closed, *B* removed, and the apparatus fixed in a stand, *A* upwards. Fourteen cc. of the hypobromite (or bromide-bromate solution) were then pipetted into *A* and sucked into *D* by slightly opening the tap; this was followed by 25 cc. of acid and then 20 cc. of phenol solution; the vessel *A* was rinsed out with 10 cc. of water between each addition and the rinsings sucked into *D*. After shaking and allowing to stand for five minutes, 5 cc. of the potassium iodide solution were added in the same manner; the tap was then opened to restore atmospheric pressure in *D* and the contents poured through *E* into a beaker containing 150 cc. of water, where the iodine was titrated by sodium thiosulphate. From the thiosulphate required the excess of bromine was calculated, and by subtracting from the original 14 cc. the "KOBr used" of the table was obtained.

Experiments identical in every respect, except that the 250 cc. flask was used instead of the apparatus just described, were carried out at the same time; as is shown in Table I, the results differ only by one or two parts per thousand. It is thus proved that the operation may be carried out in a flask without loss of bromine. Some care, however, is necessary; in one case where the bromine vapor was purposely blown out of the flask, an error of 2 per cent. in the analysis resulted.

TABLE I.

Hypobromite, 14 cc.; acid, 25 cc.; water, 30 cc.; phenol, 20 cc.; iodide, 5 cc.; time, five minutes.

Hypobromite.	Apparatus.	KOBr used.	Differences.
Fresh	Flask	13.91	0.0
Fresh	See figure	13.91	
Evaporated	Flask	13.96	0.02
Evaporated	See figure	13.94	

ACTION OF BROMIC ACID ON PHENOL AND THE USE OF THE BROMIDE-BROMATE MIXTURE.

If a little potassium bromate be mixed with a solution of phenol and acid be added, the solution turns red and a red precipitate is deposited which contains bromine and does not liberate iodine with hydriodic acid. It is obvious that the formation of this substance, during the determination of phenol, would vitiate the result.

As old solutions of potassium hypobromite are liable to contain bromate, two pairs of experiments were undertaken to see whether errors could be introduced into the analysis from this source; in one of each pair 14 cc. of fresh hypobromite solution were used and in the other a solution of bromide and bromate made by evaporating 14 cc. of the same hypobromite to dryness and dissolving the residue. In one experiment of each of the pairs the reagents were mixed in the order *A*, hypobromite (or bromide-bromate mixture), acid, phenol, and in the other in the order *B*, acid, phenol, hypobromite (or bromide-bromate). The results with the bromide-bromate mixture were 3 or 4 parts per thousand higher than the others, while the order of mixing made no difference (see Table II). It is thus clear that the presence of a little bromate in the hypobromite solution can exert no influence whatever on the result.

TABLE II.

Hypobromite, 14 cc.; acid, 25 cc; water, 30 cc.; phenol, 20 cc.; iodide, 5 cc.; time, five minutes.

Hypobromite.	Order of mixing.	KOBr used.
Fresh	*A*	13.91
Fresh	*B*	13.94
Evaporated	*A*	13.96
Evaporated	*B*	13.96

NEW PRODUCT OF THE ACTION OF BROMINE ON PHENOL.

If solutions of phenol and potassium hypobromite be mixed and the mixture be acidified, the precipitated tribromphenol is mixed with a red powder. What seems to be the same compound was obtained as a by-product in the preparation of tribromphenolbromide, and by the action of alkaline solutions of bromine on tribromphenol. It melts at about 91° C. and contains about 64 per cent. of bromine, but does not liberate iodine with an acid solution of potassium iodide. It is insoluble in water, alcohol, ether, and in glacial acetic acid; soluble in carbon bisulphide, chloroform and benzene, giving red solutions. Its molecular weight in chloroform solution (boiling-point determinations) is 508 to 514. On warming with a 10 per cent solution of caustic potash, or with concentrated sulphuric acid, it is apparently unaltered, but by heating to a temperature above its melting-point it is converted into a substance resembling hexabromphenoquinone.

I propose, if possible, to determine the constitution of this substance. Its formation during an analysis would, obviously, introduce errors into the result, hence the analytical method of group 3 (page 18) cannot be recommended.

THE DETERMINATION OF PHENOL.

Four of the most likely sources of error in the present methods of determining phenol by bromine having been studied in detail, it remained to inquire whether determinations carried out under the conditions suggested by the foregoing experiments, would give accurate results. The test-analyses undertaken with the object of deciding this question were made in acid solution in order to avoid the formation of tribromphenolbromide;[1] they were carried out at room temperature in a long-necked, glass-stoppered 0.25-liter flask (page 20), and the bromine was introduced in the convenient form of a solution in caustic potash (page 22). The

---

[1] This Journal, **27**, 7 (1905).

phenol solution was run into the flask from a burette, the acid added, and then the hypobromite from a pipette. The flask was closed, shaken for thirty seconds, and allowed to stand for the time given in the table after "t." Five cc. of potassium iodide solution were then added, followed by 100 cc. of water, and in some cases 10 cc. of chloroform. The whole was shaken for fifteen seconds, allowed to stand for two minutes, and the iodine determined with the N/50 thiosulphate.

TABLE III.

Hypobromite, 25 cc.; acid, 15 cc.

		10 cc. chloroform.		No chloroform.		
Phenol. cc.	Excess Br. cc.	$t = 0$. Per cent.	$t = 2$ minutes. Per cent.	$t = 0$. Per cent.	$t = 2$ minutes. Per cent.	$t = 5$ minutes. Per cent.
5	21.40	....	114.0	105.6	105.6	106.2
10	17.80	....	109.6	103.9	103.7	103.9
15	14.21	....	100.10	....	....	....
20	10.61	100.0	99.95	....	99.97	100.11
20	10.61	....	....	....	101.51*	102.71*
20	10.61	....	....	....	....	101.92†
25	7.01	....	100.05	99.62	99.83	99.83
25	7.01	....	....	....	100.35*	....
25	7.01	....	....	....	99.85	....
30	3.42	99.9	99.95	99.56	97.7	99.83
30	3.42	....	....	99.6	99.65	99.85
31	2.70	99.8	99.8	99.44	99.55	99.97
32	1.98	....	99.85	99.25	99.35	99.97
33	1.26	....	98.99	98.7	99.35	99.7
34	0.54	....	98.62	98.1	98.9	99.42
35	0.18	....	97.63	96.9	....	98.74

Under "Excess Br" is given the difference between the volume of the hypobromite employed, *viz.*, 25 cc. and the volume equivalent to the phenol taken (volume of phenol solution multiplied by 0.7195, see page 19). The results of the determinations are expressed as percentages of the amount of phenol actually present.

In the experiments marked with a star (*), 10 cc. of carbon bisulphide were used instead of chloroform, and in that marked dagger (†), 5 cc. of acid were used instead of 15 cc. In this experiment the precipitate, dissolved in chloroform, gave a distinct green with benzidine solution, indicating the presence of tribromphenolbromide.

Table IV contains the results of a few measurements in which sulphuric acid was used instead of hydrochloric. It is obvious that Koppeschaar[1] was mistaken in saying that the presence of sulphuric acid spoils the titration.

---

[1] *Ztschr. anal. Chem.*, **15**, 237 and 240.

TABLE IV.

Hypobromite, 25 cc.: sulphuric acid (sp. gr. 1.84), 11 cc.; chloroform, 10 cc.

Phenol. cc.	Excess Br. cc.	$t = 2$. Per cent.
20	10.61	99.91
25	7.01	99.85
30	3.42	100.11

The above experiments lead to the following:

DIRECTIONS FOR THE DETERMINATION OF PHENOL BY BROMINE.

The following solutions are needed.—Fiftieth-normal thiosulphate and iodine; starch; hydrochloric acid (sp. gr. 1.2); potassium iodide, 17 grams in 100 cc.; hyprobromite, prepared by dissolving 9 cc. of bromine in 2 liters of a solution containing 28 grams of caustic potash. The hypobromite must be compared with the thiosulphate by adding acid and potassium iodide and titrating the iodine set free.

To carry out the analysis.—Introduce the phenol solution into a glass-stoppered flask and add a volume of acid equal to about one-third or one-fourth of the combined volumes of the phenol solution and the hypobromite thar will probably be added during the analysis.

Run in the hypobromite from a burette, shaking the flask, until the solution becomes permanently yellow. Then add an excess of the hypobromite (10 to 20 per cent. of that used already) and shake well. Finally add an excess of potassium iodide, dilute with water, add 10 cc. of chloroform, and determine the iodine with the volumetric thiosulphate. The object of diluting is to prevent the acid from acting on the potassium iodide or on the thiosulphate; if 10 cc. of water be added at this stage for every cubic centimeter of acid previously added, the solution will be sufficiently dilute. The use of chloroform may be dispensed with, if the mixture be allowed to stand five minutes before adding the potassium iodide; it is, however, better to use the chloroform,—carbon bisulphide is not satisfactory.

If these directions be adhered to, the phenol can be determined within 1 or 2 parts per thousand.

In conclusion, the author wishes to express his thanks to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

THE UNIVERSITY OF TORONTO,
March, 1904.