Replacement of the diazonium group by hydroxyl is best accomplished by running the diazotized amine into a solution of sulfuric acid and sodium sulfate at 130–140°, and continually distilling out the cresol with superheated steam.

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THE ANALYSIS OF BROMINATED CRESOLS

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Previously described methods which were being employed for analyzing mixtures of brominated cresols were found to be troublesome enough to justify further investigation in the hope that improvements could be made. In the bromide-bromate titration method of Francis and Hill[1] there is, after acidification, a slow reaction between the standard solution and the alcohol used as solvent. In the method of halogen determination proposed by Robertson[2] the end-point of the final titration is difficult to determine because hydrogen peroxide present in the solution reacts with the thiocyanate.

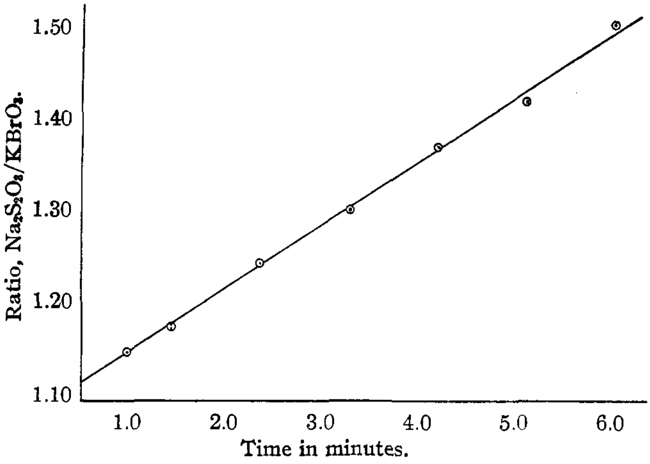

Fig. 1.—Effect of alcohol upon standard bromate solution in 1 N H_2SO_4.

The Bromide-Bromate Titration.—In the method of Francis and Hill it was found that the reaction between alcohol and bromate in acid solution decreased the amount of thiosulfate required for back titrations. Fig. 1 shows how the ratio of 0.1005 N thiosulfate to 0.091 N bromate changes

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[1] Francis and Hill, THIS JOURNAL, **46**, 2499 (1924).

[2] Robertson, *J. Chem. Soc.*, **107**, 902 (1912).

with time when 15.00 cc. of standard bromide-bromate solution stands with 50 cc. of water, 15 cc. of alcohol and 5 cc. of 18 N sulfuric acid. This reaction may not ordinarily be bothersome in the procedure recommended by Francis and Hill since the solution is not made acid until all of the bromate is introduced. However, any variations in time, temperature or concentration from the standard conditions might introduce errors. It has been found that by substituting glacial acetic acid for alcohol the undesirable side reaction between the solvent and the bromate solution is eliminated.

The following is the method finally adopted: approximately 0.10 to 0.15 g. of the phenol or substituted phenol is dissolved in 25 cc. of glacial acetic acid in a glass-stoppered conical flask and diluted with 50 cc. of water. Standard bromide-bromate solution of about 0.1 normality is introduced slowly until there is an excess of 2 to 4 cc., as shown by the development of the bromine color. This liberation of free bromine when the bromate is in excess is a convenience since it is not necessary to know in advance the bromine requirement of the sample. The solution is shaken thoroughly and allowed to stand for about one minute, at which time approximately 0.5 g. of potassium iodide is added and the liberated iodine is titrated with standard thiosulfate. The method was checked against pure 2-bromo-*p*-cresol, m. p. 55.2–55.4,[3] with the following results.

Wt. of 2-bromo-*p*-cresol taken, g.	Cc. of 0.100 N bromate	Wt. found, g.	Percentage error
0.1254	26.79	0.1252	0.16
.1698	36.03	.1684	.82

A sample of 3-bromo-*p*-cresol which distilled at 104–105.5° under 20 mm. on a second distillation gave the following results on analysis.

Wt. of sample taken, g.	Cc. of 0.0986 N bromate	Wt. found, g.	Percentage error
0.1715	18.68	0.1721	0.35
.2047	22.10	.2037	.49

Mixtures of known amounts of 2-bromo- and 3-bromo-*p*-cresol gave

Wt. of 2-bromo-, g.	Wt. of 3-bromo-, g.	Cc. of 0.0986 N bromate	% of 3-bromo- Present	% of 3-bromo- Found
0.0317	0.1732	26.02	84.5	83.0
.0253	.2188	28.98	89.6	90.6
.1018	.1683	40.14	62.3	63.0

The per cent. of each isomer was calculated according to the following equations

$$x = \frac{9.35\,nc}{w} - 100 \quad \text{and } y = 200 - \frac{9.35\,nc}{w}$$

where x and y are the per cent. of 2-bromo and 3-bromo-*p*-cresol, respectively, w = weight of sample, n = normality of the bromate solution

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[3] Lucas and Scudder, THIS JOURNAL, **50**, 244 (1928).

and c = number of cc. used. Since 2-bromo-*p*-cresol may be obtained quite pure by the method described elsewhere[3] its use as a means of standardizing the bromide-bromate solution is here suggested.

The Determination of Total Bromine.—In Robertson's[2] method of halogen determination the end-point of ferric thiocyanate fades rapidly due to the presence of hydrogen peroxide. To one who has developed considerable familiarity with the titration the fading may not be bothersome, but to one who is using the method for a short time only this complication may give much trouble. The removal of the hydrogen peroxide may be accomplished by boiling the solution while still alkaline with some of the iron salt which is needed for the end-point, for under these conditions the peroxide decomposes completely. If more than 1 cc. of 1 *N* ferric nitrate solution is added before boiling, the ferric hydroxide dissolves very slowly after acidifying.

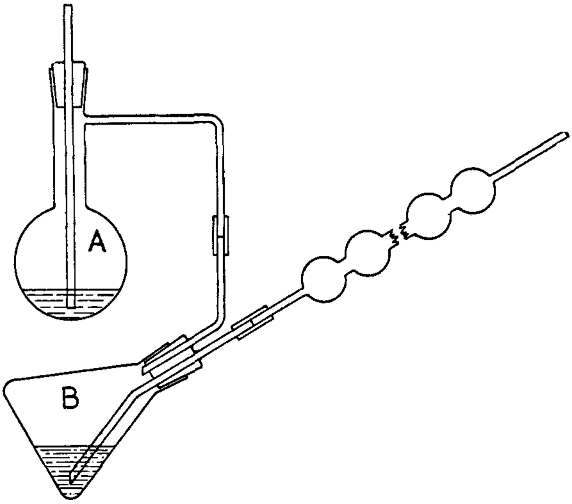

Fig. 2.—Absorption apparatus for bromine determination.

The apparatus of Robertson, Fig. 2, was modified for the sake of convenience by building it in separate units which could be joined together by heavy pieces of rubber tubing well lubricated with sirupy phosphoric acid. The modified method follows: sufficient sample to give the equivalent of 9 cc. of 0.1 *N* silver nitrate is weighed into the reaction flask A and covered with 30 cc. of cold concentrated sulfuric acid which should be free from chloride. The acid is added by means of a funnel while the flask is kept surrounded by an ice-salt bath. After the sample has dissolved and the temperature of the contents has dropped to zero, 10 g. of c. p. chromic anhydride is added and the connection is made to the absorption flask B, which should contain 40 cc. of 1 *N* sodium hydroxide and

20 cc. of 3% hydrogen peroxide, both free of halides. Heat is applied slowly to flask A, care being taken not to increase the temperature rapidly, otherwise the reaction may become too vigorous and lead to the production of smoke, the presence of which should be avoided since low results invariably accompany it. After the end of the reaction, which usually requires about forty-five minutes, a slow stream of air is passed through the apparatus in order to sweep the vapors of bromine and hydrogen bromide over into the absorption apparatus and at the same time the mixture is heated more strongly so as to decompose most of the excess chromic acid. After about fifteen minutes longer the apparatus is disconnected, the solution is washed out of the absorption tube into the flask and 1 cc. of 1 *N* ferric nitrate is added to the solution. It is boiled for ten minutes in order to decompose the hydrogen peroxide and after cooling is acidified with 20 cc. of 6 *N* nitric acid. In order to have a good end-point, 9 cc. more of ferric nitrate is added. The titration is made by adding 10 cc. of 0.1 *N* silver nitrate, filtering, washing the precipitate and back titrating the filtrate and washings with 0.1 *N* potassium thiocyanate.

The reliability of the method is indicated by the results obtained with a pure specimen of 2-bromo-*p*-cresol,[3] for which the bromine content was found to be 42.95 and 43.02%, compared to the calculated value of 42.50%.

Summary

The bromide-bromate titration method of Francis and Hill as applied to brominated cresols is best carried out in water-acetic acid solution.

A procedure has been suggested for obtaining a better end-point when determining bromine in brominated cresols by the method of Robertson.

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NOTE

Improved Lighting Source for Melting-Point Apparatus.—A melting point determination, when taken on a dull day or at night under artificial light, is both difficult to accomplish and a strain on the eyes. If a light is placed directly above or behind the melting-point apparatus, considerable reflection from the glass surface results, and the intensity of light directed at the melting point tube is very small. In order to avoid these obstacles, a simple device has been developed.

A short length of tube or rod of any clear glass, fused quartz being desirable but not essential, will transmit practically the entire intensity of light with very little loss of light transversely, and this property is utilized in an apparatus constructed as follows. A small box built of aluminum, or of wood lined with tin foil, holds an electric light bulb (about 100 watts). In the wall opposite the bulb is a hole through which a piece of quartz tube, 8 mm. in diameter and 4 cm. long, is pro-