[SIXTH CONTRIBUTION FROM THE COLOR INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A METHOD FOR THE RAPID ANALYSIS OF MIXTURES OF CHLORINATED TOLUENE.

BY HERBERT A. LUBS AND ARTHUR B. CLARK.

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There are several methods for the analysis of aromatic compounds containing side-chain chlorine, but to each there are objections. The most commonly used method for the quantitative determination of side-chain chlorine in such compounds is that of Schulze,[1] which consists in heating the compound with alcoholic silver nitrate. In studying the side-chain bromination of toluene, Jackson and Field[2] used a method very similar to that of Cannizzaro.[3] It consists in heating the halogenated compound with alcoholic ammonia, decomposing the ammonium halide with barium hydroxide and titrating the halogen by Volhard's method. The first procedure naturally involves a gravimetric determination and hence is comparatively slow. Moreover, neither method permits of a simple and direct determination of the relative amount of the various constituents of the chlorinated compound but merely gives the total side-chain chlorine. The advantages of a rapid volumetric method for factory control of the chlorination of toluene are obvious. With such a purpose in mind, we have developed a method in which a mixture of benzyl chloride, benzal chloride, and benzotrichloride can be hydrolyzed by pure water,[4] and the resulting hydrochloric acid and benzoic acid separately determined in a single titration with standard alkali as described in the previous paper.[5]

The amount of benzotrichloride may be calculated from the benzoic acid titer and the other two components by a calculation similar to that used in the quantitative estimation of mixed alkalis. The accuracy of the method depends on the accuracy of the titration of benzoic acid in the presence of hydrochloric acid and is reliable to ± one to two per cent. This question is fully discussed in the previous paper. Experiments have shown that hexachlorobenzene, *p*-dichlorobenzene, *o*-chloronitrobenzene and *o*-chlorotoluene are not appreciably hydrolyzed under the conditions used for the analysis of side-chain chlorine.

[1] Schulze, *Ber.*, **17**, 1675 (1884).

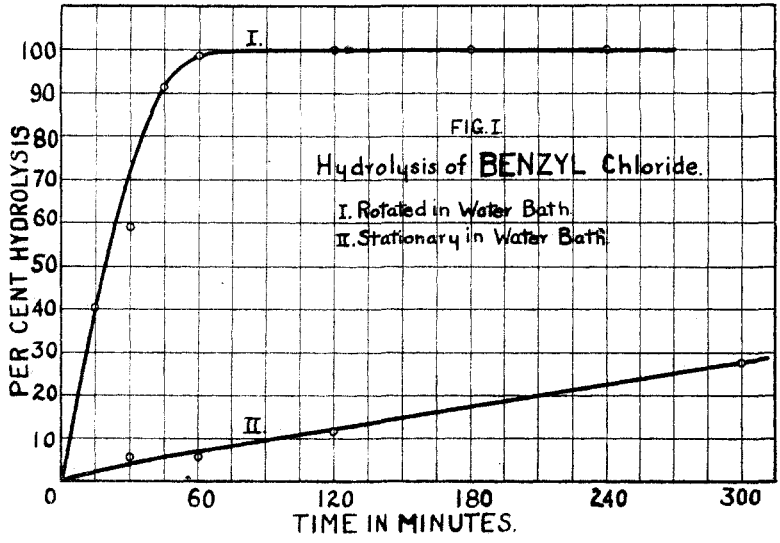
[2] Jackson and Field, *Am. Chem. J.*, **2**, 1 (1880).

[3] Cannizzaro, *Ann.*, **141**, 198 (1867).

[4] Since the method described was developed, it has been found that German patents (D. R. P. 82,927 and 85,493) have been granted on the method of hydrolyzing these compounds on a large scale with water at 100° in the presence of iron salts. Since the introduction of these salts would interfere with the titration, no attempt was made to use the method.

[5] THIS JOURNAL, **40**, 1443(1918).

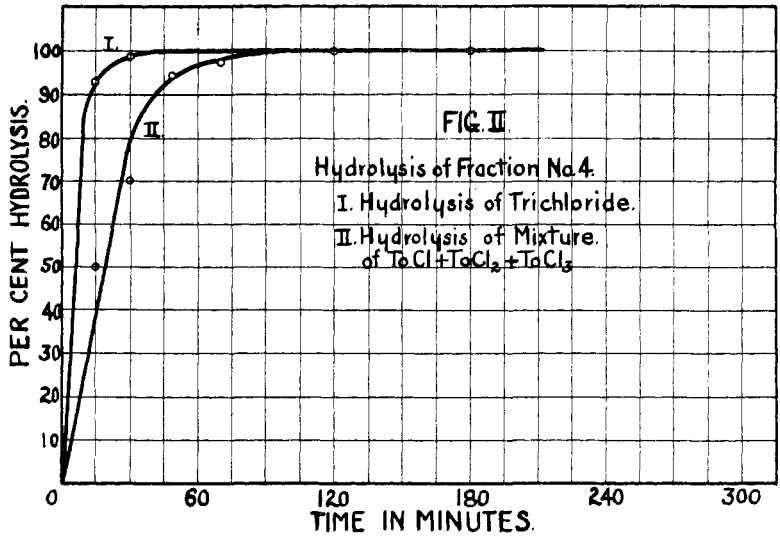
In order to determine the best conditions for carrying out the hydrolysis, half-gram samples of chlorinated toluene were weighed into test tubes, 10 cc. of distilled water added and the tubes sealed. These were then placed in the apparatus described below and heated at the temperature of the boiling water bath, successive tubes being removed and the acids titrated after intervals of 15, 30, 45, 60, 120, 180, and 240 minutes. The data obtained by hydrolysis of benzyl chloride are shown in the upper curve of Fig. 1, in which 100 times the ratio to hydrochloric acid (found



by titration) to total theoretical hydrochloric acid are plotted as ordinates with time as abscissas. The determination of the rate of hydrolysis of a sample of mixed chlorides of the following composition: 63.0% benzyl chloride, 21.7% benzal chloride, 15.3% benzotrichloride, was carried out in the same way. The data are presented in Fig. 2, from which it will be seen that benzotrichloride hydrolyzes much more rapidly than benzyl chloride, and that hydrolysis is complete in less than two hours if the mixture is continually agitated. That such vigorous stirring is absolutely necessary is shown by the lower curve of Fig. 1. It is to be noted that hydrolysis has proceeded to the extent of only 27.7% in 5 hours when the tubes were not agitated while hydrolysis of the same mixture was complete in less than two hours with thorough agitation.

The test tubes containing the products to be hydrolyzed are held by spring clips on a rotating shaft immersed in a water bath. The shaft is rotated by a motor at the maximum speed at which the contents of the tube would fall from one end to the other twice during each revolution.[1]

[1] The apparatus described above was designed and constructed by G. Orange of the mechanical staff of the Color Investigation Laboratory.



Method of Analysis.

The method of analysis may be briefly summarized as follows: After rotating the tubes for two hours in the boiling water bath the contents of a tube is transferred to a small assay flask and the tube washed out with water free from carbon dioxide. The tube is then rinsed out with a small amount of alcohol free from carbon dioxide, if any benzoic acid remains. The solution is then titrated according to the method described in the previous article for the determination of benzoic acid in the presence of hydrochloric acid, using thymolsulfophthalein as the indicator. The percentage of benzotrichloride (equivalent to the benzoic acid) is calculated from the titration designated by (x). The percentages of benzal chloride (y) and benzyl chloride (z) are calculated from the following relations:

$$x + y + z = 100 \qquad (1)$$

$$0.545\,x + 0.434\,y + 0.281\,z = \text{per cent. side-chain chlorine}^1 \qquad (2)$$

Total chlorine for calculation of ring chlorine may be determined on another sample while the hydrolysis is going on by the Stepanow method as modified by Drogin and Rosanoff.[2] Our experience indicates that this hydrolysis is best carried out in a flask similar to a Kjeldahl flask loosely closed at the mouth by a test tube condenser. The reaction proceeds more smoothly if the flask is heated by an oil bath rather than by a free flame, direct heat having a tendency to cause charring of the ethylate which collects on the bottom of the flask near the end of the reaction.

[1] 54.5, 43.4, 28.1 represent the percentage of chlorine in benzotrichloride, benzal chloride, and benzyl chloride, respectively.

[2] Drogin and Rosanoff, THIS JOURNAL, **38**, 711 (1916).

All of the analyses for total chlorine given in this paper were made by the method of Drogin and Rosanoff. After this work had been completed a modification of the Pringsheim method for the determination of halogens in organic compounds was used which is much easier to manipulate and far more rapid than the method of Drogin and Rosanoff. The modification of Pringsheim's method is described in a paper by Lemp and Broderson.[1]

The following analyses were made of two unknown mixtures, A and B. The samples were hydrolyzed as described above; two of each mixture were titrated with alkali and the third with silver nitrate by the Volhard method:

Mixture A.

Sample.	Weight.	Cc. 1.022 *N* NaOH for total HCl.	Cc. NaOH for benzoic acid.	Cc. 0.101 *N* $AgNO_3$.	% side-chain chlorine.	% $C_6H_5CCl_3$.
1.....	0.6012	5.9	0.47	...	35.5	15.6
2.....	0.6028	5.95	0.45	...	35.5	15.0
3.....	0.6033	..	..	61.05	36.4	..

Mixture B.

1.....	0.5927	5.50	0.30	...	33.6	10.0
2.....	0.5957	5.50	0.32	...	33.4	10.0
3.....	0.5829	..	..	55.25	33.9	..

The composition of the mixtures from these data are:

	% $C_6H_5CCl_3$.	% $C_6H_5CHCl_2$.	% $C_6H_5CH_2Cl$.	Total.
A.....	15.3	21.7	63.0	100
B.....	10.0	18.2	71.8	100

Determinations of total chlorine were made on each by the modified Stepanow method, the results being tabulated below:

Mixture A.

Sample.	Weight.	Cc. $AgNO_3$.	% chlorine.
1.....	0.2448	26.31	38.4
2.....	0.2476	26.94	39.0

Mixture B.

1.....	0.2434	24.42	36.0
2.....	0.2446	24.57	35.9

Assuming that there is not more than one atom of ring chlorine in any molecule, we may calculate from the difference (total chlorine less side-chain chlorine) the equivalent number of molecules having one atom of ring chlorine per molecule. The form of calculation is

$$100\,\frac{\%\text{ ring chlorine}/35.5}{x/196 + y/161 + z/127} = \text{Percentage of molecules containing one atom of chlorine.}$$

For mixture A the value is 13.2 and for mixture B it is 9.2 per cent.

In order to compare the results obtained by water hydrolysis, with alkali hydrolysis and with the gravimetric method, using alcoholic silver

[1] THIS JOURNAL, 39, 2069 (1917).

nitrate, the following analyses were made on a sample of benzyl chloride. The figures given are percentage of chlorine. Theory, 28.07.

Water hydrolysis. Titration with		Alkali hydrolysis. Titrated with 0.1 *N* $AgNO_3$ by Volhard method.	Alcoholic $AgNO_3$ gravimetric.	Drogin-Rosanoff method.
1.0 *N* alkali.	0.1 *N* $AgNO_3$.			
28.1	27.9	27.8	27.9	28.2
28.1	27.9	27.8	28.0	28.2

Summary.

This paper contains a description of a method for the determination of the composition of mixtures of the side-chain chlorination products of toluene. The accuracy attainable is such as to recommend the method for plant control work, although by observing certain precautions outlined in the preceding paper, the accuracy may be increased to such a degree that the method is suitable for a very exact quantitative analysis of these compounds. The analyses given in this paper were made with the object of obtaining rapid results rather than with the idea of securing the highest accuracy.

WASHINGTON, D. C.

[SEVENTH CONTRIBUTION FROM THE COLOR INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE.]

THE USE OF BENZALDEHYDE SULFITE COMPOUND AS A STANDARD IN THE QUANTITATIVE SEPARATION AND ESTIMATION OF BENZALDEHYDE AND BENZOIC ACID.

BY G. A. GEIGER.

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Prior to the work of Lubs and Clark, described in the two preceding papers, I attempted to develop methods for the analysis of side-chain chlorinated toluene, based upon the determination of benzaldehyde and benzoic acid. The procedure described in this paper is quite accurate and useful for check analyses, but for ease of manipulation and speed cannot be compared with the methods described by Lubs and Clark. The method is also useful for the determination of benzaldehyde and benzoic acid mixtures derived from other sources than chlorinated toluene. Many difficulties were experienced in obtaining and preserving pure benzaldehyde necessary for developing the analytical method, until the use of the benzaldehyde sulfite compound was suggested to me. This compound is very useful for obtaining benzaldehyde solutions of known concentration, since it is easily prepared pure, keeps well and decomposes quantitatively, giving known amounts of benzaldehyde.

The determination of benzaldehyde has been found by Denis and Dunbar[1] to be best effected by means of the phenylhydrazone compound which

[1] *J. Ind. Eng. Chem.*, **1**, 256 (1909). A review of the literature is given in this article.