THE ASSAY OF CARBOLIC SOAP.

BY ALFRED H. ALLEN.

THE great and increasing use of soaps to which carbolic acid and other coal-tar acids and products have been added, has rendered the determination of the active or *quasi*-active ingredients a matter of some practical interest. A year or two since I had occasion to examine a considerable number of such soaps, and found the published information on the subject very incomplete. In fact, the only method, so far as I am aware, that has been hitherto published, is that described in Volume I. of the first edition of my "Commercial Organic Analysis," which method was communicated to me by Mr. Charles Lowe. The process of Mr. Lowe is gravimetric, and in my experience unreliable, owing to the ready volatility of the brominated phenols, to the indefinite nature of the compound weighed, and to some unexplained causes apparently connected with their unstable nature. The method I have now to describe is based on Mr. Lowe's, but is modified in several respects, which are more or less important.

I may point out here, however, that although the coal-tar acids are added to the soap in a free state, the free alkali so frequently present prevents them from continuing to exist wholly in that condition. This is important, as the antiseptic virtues of the alkaline carbolates and cresylates are of a very doubtful nature. Analytically, also, the fact is of interest, for phenols existing in combination will not be dissolved out on treating the dried soap with petroleum ether, in the manner recommended by Professor Leeds and Dr. Wright.

The process for determining phenols which I now employ is as follows:—Five grammes weight of the sample is dissolved in warm water, with addition of from 20

to 30 c.c. of a 10 per cent. solution of caustic soda, according to the proportion of phenols believed to be present. The cooled solution is then agitated with ether, and the ethereal layer separated and evaporated at a low temperature. The weight of the residue gives the amount of hydrocarbons, &c., in the quantity of the sample taken. The odour towards the end of the evaporation and that observed on heating the residue will give considerable information as to the nature of the admixture. Odours suggesting gas-tar and burning gutta-percha are very common. The alkaline liquid separated from the ether is then treated in a capacious separator with an excess of strong brine, which completely precipitates the fatty acids as sodium salts. The liquid is well agitated to cause the soap to filter, and is then passed through a filter. In cases where the soap does not readily coagulate, an addition of a small quantity of tallow or palm oil soap, previously dissolved in water, will usually overcome the difficulty. The precipitated soap is washed twice by agitating it with strong brine, the washings being filtered and added to the main solution, which is then diluted to one litre. 100 c.c. of this solution (= 0.5 gramme of the sample of soap) is then placed in a globular separator, and acidulated with dilute sulphuric acid, when it should remain perfectly clear. Standard bromine water is then added from a burette, the stopper of the separator inserted, and the contents shaken vigorously. More bromine water is then added, and the agitation and addition of bromine solution repeated alternately until the liquid acquires a faint but permanent yellow tint, showing that a slight excess of bromine has been used. If crystallised carbolic acid has been employed for making the soap the bromo-derivative is precipitated in snow-white, crystalline flocks, which allow the faintest yellow tint due to excess of bromine to be observed with great facility. If cresylic acid be the chief phenol present, as in the case of soaps made with an article of a quality similar to Calvert's "No. 5, Carbolic Acid," the precipitate is milky, and does not separate well from the liquid, but the end of the reaction can still be observed. The addition of a solution containing a known amount of crystallised phenol is a useful device in many cases, as the precipitate then curdles readily, and the yellow coloration can be easily seen.

The bromine solution is made by mixing in a separator one measure of saturated bromine water with two measures of water. This solution is approximately 1 per cent. and should be run out from the tap of the separator into the Mohr's burette used for the titration. The burette should be closely covered, and the last few c.c. of the solution contained in it should never be employed for the titration, as it is apt to have become weak. The bromine water must be standardised immediately before or after use, by a solution of Calvert's No. 2 or No. 5 carbolic acid, according to the kind of acid the titration has indicated to have been present in the soap. This solution is made by dissolving 0.5 gramme of the coal-tar acid in 20 c.c. of a 10 per cent. of caustic soda, together with 5 grammes of a non-carbolic soap. The solution is then precipitated with brine in the same manner as the sample, the filtrate diluted to 1 litre, and 100 c.c. acidulated and titrated with the bromine solution used for the sample. The volume of bromine solution used is that required by 0.050 gramme of coal-tar acid of approximately the same quality as that contained in the soap.

The mode of preparing the bromine solution, and the mode of conducting the titration may be modified in any of the various manners proposed by different chemists, but the method of operating just described is quite accurate enough for the purpose in view, and has several practical advantages. In any case, the bromine solution should be standardised by carbolie acid in the manner recommended, and not set in any other, and its power of brominating *calculated*.

The remaining portion of the liquid filtered from the precipitate of soap may be evaporated to a small bulk, acidulated with dilute sulphuric acid, and the separated phenols measured (see "Creosote Oils"), but the quantity is not sufficient to make the method satisfactory. It is generally better to employ the solution for the isolation of the bromo-derivatives. For this purpose it is acidulated with dilute sulphuric acid (without previous concentration), and bromine water added in slight excess. From 5 to 10 c.c. of carbon disulphide is then added, the liquid well agitated, and the carbon disulphide tapped off into a small beaker. The aqueous liquid is agitated with free quantities of carbon disulphide (of 5 c.c. each) till it no longer acquires a red or yellow colour. The carbon disulphide is then allowed to evaporate spontaneously, when a residue is obtained consisting of the brominated derivatives of the phenols present in the soap. If *crystallised carbolie acid* of fairly good quality was introduced into the soap, the bromo-derivative is obtained in fine long needles having very little colour, and, if all heating was avoided during the evaporation of the carbon disulphide, the weight of the residue multiplied by 0.281 gives a fair approximation to the amount of carbolie acid; but if a crude liquid article has been employed, consisting mainly of *cresylic acid* (e.g., Calvert's "No. 5, carbolie acid"), the bromo-derivative will be deep yellow, orange, or red, with little or no tendency to crystallise, and the weight will not afford even a rough indication of the amount of coal-tar acid present.

The following table shows some of the results obtained by the assay of representative samples of commercial carbolie soap. The suppression of the names of the firms manufacturing them unavoidably detracts from the interest attaching to the figures. The descriptions of the soaps given by the manufacturers are strictly adhered to, and in cases where two samples are described in the same words, they were manufactured by different firms:—

	Phenols.		Ether residue.	
	Percentage.	Nature.	Per cent.	Odour on heating.
1. Medical Carbolie Soap; 20 $\frac{1}{100}$ pure ..	30.5	pure phenol	..	
2. " " " 20 $\frac{1}{100}$ pure ..	17.0	pure phenol	..	4.2 .. gutta percha.
3. Carbolie Toilet Soap; 10 $\frac{1}{100}$..	3.6	pure phenol	..	2.0 .. cayenne.
4. " " " 10 $\frac{1}{100}$..	3.4	pure phenol	..	1.0 .. gutta percha.
5. Domestic Carbolie Soap ..	4.8	pure phenol	..	
6. " " " ..	6.4	common carbolie		
7. Carbolie Soft Soap; 10 $\frac{1}{100}$..	9.9	common carbolie		
8. " " " 10 $\frac{1}{100}$..	8.2	common carbolie		
9. " " " ..	0.16	common carbolie		
10. Transparent Carbolie Soap ..	3.2	pure phenol		
11. Transparent Coal Tar Soap ..	1.5	pure phenol		
12. No. 1 Carbolie Soap ..	2.5	common carbolie		
13. No. 1 " " ..	5.4	common carbolie		
14. No. 2 " " ..	4.4	common carbolie		
15. No. 2 " " ..	3.5	common carbolie		
16. Carbolie Soap ..	2.6	impure phenol		
17. " " ..	1.1	common carbolie ..	1.0	
18. " " ..	0.5	impure carbolie		
19. Disinfecting Soap ..	None		4.6 ..	coal tar oils.
20. Sanitary Soap ..	0.75	impure phenol	4.6 ..	coal tar oils.

No. 1 sample was described a medical carbolic soap, containing 20 per cent. of crystallised carbolic acid. It will be observed that 30.5 was the proportion actually found, and this result was fully verified on repeating the titration, and by the actual weight of the tribromo-phenol, which crystallised in beautiful colourless needles. In some other cases, the proportion of phenols found was notably less than the amounts stated to be present, and this is especially the case with each of the 10 per cent. toilet soaps, Nos. 3 and 4, though these soaps were made by different firms. It must, however, be borne in mind that a loss of 2 or even of 3 per cent. of carbolic acid is liable to occur through evaporation.

CONCLUSION OF THE SOCIETY'S PROCEEDINGS.