

## TESTING OF COMMERCIAL TOLUIDINE.\*

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EVEN in the aniline trade the necessity has been felt of late years to sell pure products with guaranteed analysis, particularly in the case of aniline and toluidine. At one time most of the toluidine offered for sale was tested by the buyers as to its specific gravity and boiling point, but now they demand a specified percentage of *p* toluidine. The estimation of this body in presence of *o* toluidine and aniline often leads to disputes with the manufacturers, because the testing is not always done precisely in the same manner.

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The aniline works which obtain their benzol, 50-90 per cent., from England, know that they must exactly stick to the specification or contract. This provides for the size of the retorts, length of the condenser, distance of thermometer from bottom of retort, etc., etc., in order to get concordant results. To prevent as much as possible analytical differences in the testing of toluidine, it is absolutely necessary for the buyers to agree with the manufacturers on a definite method of testing. As I have lately been often consulted as to a reliable process for the estimation of *p* toluidine, I will now communicate the various methods from time to time proposed. In testing toluidine, one must take particular notice of its appearance, which should be as clear as a brewer likes to see his ale. The colour may, however, be spoiled to some extent when the sample has been stored in iron barrels. To ascertain the boiling point, and consequently the presence of higher homologues, 100 c.c. of the oil are fractioned in a retort holding about 180° C., the heat being so regulated that about two drops distil over every second. The specific gravity is taken with the bottle, or also very accurately with a large hydrometer, by preference the one devised by Lunge. To get the temperature exactly at 15° C., the oil is put into a cylinder, which is then put into a second cylinder, filled either with warm or, if necessary, iced water.

For the estimation of *p* toluidine many processes have been proposed, and the method to be chosen ought to be such a one as can be readily mastered by the most inexperienced who works on not too small quantities of the sample. Merz and Weith take advantage of the little solubility of *p* toluidine in water, which process was further worked out by Schoop. Rosenstiehl noticed the little solubility of *p* toluidine oxalate in ether, which process was simplified by Nietzki, and particularly by Lorenz. Lunge recommends the taking of the specific gravity, and has published an excellent table; whilst Schön treats the sample with potassium dichromate and hydrochloric acid, and then tests colorimetrically. I have tried a totally new idea, which consisted in dissolving *pure p* toluidine in the sample and ascertaining the solidifying point of the mixture. I cannot recommend the colorimetric process, as this is too much influenced by the personal equation in working.

The specific gravity process is very much influenced by slight alterations in temperature, and also by the presence of small quantities of aniline. Schoop's acetyl process may be used when the sample is of at least 30 per cent. strength, by operating as follows:—The toluidine must have been dried with calcium chloride or potassium carbonate. Ten grams. of the sample are boiled, under a reflux condenser, with 10 c.c. of acetic anhydride. After cooling, 30 c.c. of glacial acetic acid are added, and the mixture poured into 400 c.c. of hot water, the flask being rinsed with another 200 c.c. of water. The liquid is then kept for twenty-four hours at a temperature of 0° C., which causes the separation of acetoluidine, which may be collected on a weighed filter, slightly washed with dilute acetic acid, dried first by pressure between blotting paper, and finally at a temperature of 98° C. 149 parts of the precipitate correspond with 107 parts of *p* toluidine.

The oxalate process is most conveniently performed according to Lorenz's directions. If applied in an empirical sort of way, the results are very good. What is wanted is pure ether, free from alcohol and water; a solution of 1.062 grams. of dry oxalic acid in

250 c.c. of ether; deci-normal solution of carbonate of soda; pure *o* and *p* toluidine, and also very delicate litmus paper. First of all, 10 c.c. of the ethereal oxalic acid solution are put into a flask containing 25 c.c. of water, and, after removing the ether by distillation, the residue is titrated with the sodium carbonate, litmus paper serving as indicator. Two grams, of pure *p* toluidine are now dissolved in 70 c.c. of ether, with two drops of *o* toluidine and so much of the oxalic acid solution added until all the *p* toluidine is precipitated, which may be easily recognised by the turning red of litmus paper. After adding another 2 c.c. of the acid, the whole is allowed to stand for four hours at a temperature of 158 C., when the precipitated oxalate is filtered off and washed with about 30 c.c. of ether, both filtrate and washings being collected in a flask containing 25 c.c. of water. The ether is distilled off, and the residue again titrated with the soda, when the difference between the two titrations will give us the check on the oxalic acid, which may then be used to test the commercial sample. I have tried to use a watery solution instead of the ethereal one, and have obtained very satisfactory results when analysing samples containing from 25-40 per cent. of toluidine. The acid must, however, be added in large excess, and the precipitate weighed. After a few more experiments, I hope to say something more on the subject. The solidifying or crystallisation process is, however, a much quicker one. When the sample is fused with from 1-3 parts of pure toluidine, a mixture is obtained which may be tested by taking its solidifying point. With the same weight of pure *p* toluidine, the percentage of the mixture is got accurate within .5 per cent., with double the weight .33 per cent., with treble the weight .25 per cent. For instance:—

						Difference.	
10	Toluidine of	50	per cent.	<i>p</i> + 10	pure <i>p</i> = 20	Toluidine 75	per cent. .5
10	"	50	"	+ 10	" = 20	" 75.5	" —
10	"	30	"	+ 20	" = 30	" 76.66	" .33
10	"	31	"	+ 20	" = 30	" 77	" —
10	"	30	"	+ 30	" = 40	" 82.5	" .25
10	"	31	"	+ 30	" = 40	" 82.75	" —

A 30 C.M. thermometer, running from 30-50° C. and graduated in  $\frac{1}{2}^{\circ}$ , shows a difference of .2 per cent. of paratoluidine. The process is, therefore, very suitable for being daily used by manufacturers.

It is as well to have at hand a number of standard samples, containing, say, 82.5, 83, 83.5, 84, 84.5, and 85 per cent. of *p* toluidine, to be compared with any given sample. I will later on communicate in how far the crystallisation point is influenced by the presence of any moisture.