

Citation:

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Chemistry. — “*On the preparation of pure o-toluidine and a method for ascertaining its purity.*” By Prof. A. F. HOLLEMAN.

(Communicated in the meeting of November 26, 1904).

Whilst *p*-toluidine being a solid, well crystallised substance may be very readily obtained in a perfectly pure state from the commercial product by recrystallisation and distillation, this is by no means the case with the liquid *ortho*-toluidine. The latter stands a good chance of containing its *para*-isomer as it is prepared from *o*-nitrotoluene, which is rather difficult to completely separate from the *p*-nitrotoluene simultaneously formed in the nitration of toluene, particularly because the *ortho*-nitrocompound is liquid. It is further stated that *o*-toluidine sometimes contains aniline.

Of the various ways mentioned in the literature on the subject for the purification of *o*-toluidine, the conversion into oxalate seemed to me the most appropriate. According to BEILSTEIN'S Handbuch, the solubility of *ortho*-toluidine oxalate amounts to 2.38 parts by weight in 100 parts of water at 21°, that of the acid oxalate of *p*-toluidine (the neutral compound does not exist) 0.87 parts in 100 parts of water at 10°. If, therefore, the *o*-toluidine contains a few per cent of *para*, the oxalate thereof must remain in the aqueous mother-liquor when the mixture is submitted to recrystallisation, and the use of ether, which is given as an accurate method of separating the oxalates, becomes superfluous. Even any aniline which happens to be present, may be removed in this manner.

In order to see whether a complete purification might indeed be attained in this way, it was necessary to first obtain a characteristic test for ascertaining the purity; for the processes found in the literature for ascertaining the purity of *o*-toluidine, of HAUSERMANN (Fr. 26,750), REINHART (Fr. 33,90) and LUNGE (Fr. 24,459) appeared but little suitable for the detection of very small amounts of impurities.

For this purpose the determination of the solidifying point of the acetyl compound proved serviceable. By determining a portion of the solidifying point curve of *o*- and *p*-acetotoluidide the amount of the impurity could then be ascertained quantitatively at the same time.

The following solidifying point figures were found :

Percentage of <i>para</i> .	Solidifying point.
0	109.°15
1.12	108.°45
2.42	107. 75
9.58	103.°2
13.6	100.°8

That 109°.15 is the solidifying point of pure aceto-*o*-toluidide was proved by recrystallising the oxalate prepared from a "chemically pure" *o*-toluidine and then recovering the toluidine, which was then treated once more in the same way.

After each crystallisation of the oxalate a small quantity of *o*-toluidine was converted into the acetocompound; the observed solidifying points were both the above figure, which moreover did not suffer any change when the acetocompound was again recrystallised.

In order to ascertain how far small quantities of *para*-toluidine and aniline may be detected by means of the solidifying point figures, the above purified *o*-toluidine was mixed with 2% of aniline and another portion with 2% of *p*-toluidine and tested as follows:

25.2 grams of oxalic acid ($\frac{1}{5}$ mol.) are dissolved in a litre of boiling water and to this are slowly added 42.8 gram of toluidine ($\frac{2}{5}$ mol.). On cooling, the oxalate crystallises out; after placing the flask in ice the liquid is thoroughly removed by suction and the crystals washed once with a little water; the toluidine is then recovered from the crystals as well as from the motherliquor by adding alkali and distilling in a current of steam. In order to avoid loss it is necessary to extract the water, which has also distilled over, twice with ether. The toluidine so obtained is converted into the acetocompound by adding per gram a mixture of 2 cc. of glacial acetic acid and 1 cc. of acetic anhydride. The mass is now evaporated on the waterbath and the dry residue once distilled in *vacuo* when everything passes over leaving but a small black residue. The solidifying point of both products is then determined. We found:

	Added	
	2% <i>p</i> -toluidine	2% aniline
Solidifying point of the acetotoluidide from the crystals:	109°.15;	109°.15
" " " " " " " " motherliquors:	103°.2 ;	103°.0

This shows that while the oxalate crystallised out, the added impurities remained completely in the motherliquor and that the acetocompound prepared from the latter shows the serious depression of about 6°. If now we consider that the determination of the solidifying point is accurate to 0°.2 and with practice even to 0°.1 it follows that we may detect in this way $\frac{1}{100}$ part of the impurities now present, viz. $\frac{2}{100}$ or 0.02%.

Using this method I have examined two samples of *o*-toluidine from different makers and both marked "chemisch rein" as to their purity with the following result.

I. Converted into oxalate in exactly the same manner as described. Flask cooled in ice water.

