

## On the Quantitative Determination and Qualitative Characterization of Organic Compounds through their Salts or Addition Compounds with Picric Acid

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Two methods for preparing picrates of unknown substances are given, the first to be used when the picrate is stable and the solubilities of the components are almost equal, the second to be used when the picrate is unstable and the solubilities of the components are different.

It is shown that equivalent weights of picrates may be determined by acid titration.

Of anisole and *p*-cresyl-methylether picrates were obtained which do not seem to have been previously reported. Of anthracene picrate a new modification was obtained.

It is well known that some organic substances can be characterized through their compounds with picric acid (picrates)<sup>1-3</sup>. It is less widely known that the equivalent weights of these compounds may be determined by acid titration of the picrates after decomposition with an excess of sodium hydroxide.

The limitations of the method are that it is sometimes difficult to prepare picrates — salts as well as addition compounds — of unknown substances. The common methods<sup>1,3</sup> of preparation are not always ideal and postulate that the molecular weights are known. When the latter are unknown these methods cannot be used as described. The acid titration of picrates has been used in a special course in organic identification for graduate students in this laboratory. The methods described below have been employed.

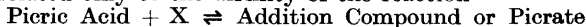
### EXPERIMENTAL

*Preparation of picrates.* Many substances form picrates but a number of picrates have a very limited stability range and may not be congruently soluble in many solvents. The stability increases with the size of the aromatic ring system in the partner component, and with the number of methyl, methoxyl, hydroxyl, and amino groups. The stability is diminished by nitro groups<sup>4</sup>.

If the inequality below is satisfied, a picrate will — according to Dimroth and Bamberger<sup>5</sup> — be formed when equimolar quantities are dissolved in the necessary amount of boiling solvent, and then allowed to crystallize:

$$\frac{\text{Solubility of the more soluble component}}{\text{Solubility of the less soluble component}} < G. \quad (1)$$

$G$  is a constant related only to the affinity of the reaction



Solubility means solubility at room temperature. If (1) is not satisfied it is necessary to use an excess of the more soluble component. When an excess is not used the less soluble component will contaminate the picrate.

When the picrate is stable, and the molar solubilities of the components are sufficiently close together the following method of preparation may be used. 0.75 g of the unknown component and 1.15 g (5 millimoles) of picric acid are dissolved in the necessary amount of boiling solvent and then allowed to crystallize. These quantities are chosen on the assumption that the molecular weight of the unknown substance is 150.

If the solubilities of the components are not sufficiently close together an excess of the more soluble component is taken, equal to the difference between the solubilities, in the amount of solvent used.

If the picrate is not very stable or if the solubilities of the components in the pure solvents are far from equal, a mixture of two solvents must be used. In the latter the components must have almost the same solubilities or at least have limited solubilities. The following procedure may be used.

A mixture of solvents (for instance ethanol-water) is prepared. The mixture should dissolve almost the same amounts of the components (if 5 ml of ethanol-water mixture is used, a mixture dissolving *ca.* 0.35 g of the unknown component will fit, since 0.35 g is the average solubility of picric acid in 5 ml of ethanol-water mixtures). The mixture can be prepared by the following method.

A convenient amount of the unknown component (in the case of ethanol-water, 0.35 g) is dissolved by adding increments of the two solvents, in turn, until a convenient volume is reached (if ethanol and water are used, 5 ml), and then adding the solvent with poorer solvent action drop by drop until the solute precipitates. — To this saturated solution there is added 0.75 g of the unknown component and 1.15 g (5 millimoles) of picric acid plus an amount of picric acid corresponding to the solubility in the mixed solvent. The substances are dissolved by heating and then allowed to crystallize. In this way equimolar amounts plus an excess of the more soluble component — corresponding to the difference between the solubilities of the components — are used, assuming the molecular weight of the unknown substance to be 150.

The picrates are separated from the solvent by suction on a suction funnel and then dried at room temperature between sheets of filter paper. Since the picrates rarely are congruently soluble washing and recrystallization are not advisable.

*The Acid Titration of Picrates.* It is important to have the picrate completely decomposed in the titration. The following method may be used.

To a weighed amount (*ca.* 0.25 g) of picrate there is added 20.00 ml 0.1 *N* sodium hydroxide and the mixture is heated to boiling. The mixture is then cooled, a soda-lime tube being attached to the flask to keep out carbon dioxide. Finally the excess of sodium hydroxide is determined by titration with 0.1 *N* hydrochloric acid and bromothymol blue indicator.

If the unknown substance  $X$  is an acid attention should be drawn to the fact that it is not always possible to titrate the picrate. When bromothymol blue indicator is used in the titration the acid dissociation constant of  $X$  must be less than  $10^{-8.5}$ . If the unknown substance is a base it is also not always possible to titrate the picrate. If bromothymol blue indicator is used in the titration the dissociation constant of the acid conjugate to  $X$  must be greater than  $10^{-8.5}$ .

## RESULTS

In Table 1 are recorded the melting points and the titration results for picrates prepared from pure solvents. It may be added that in two cases *viz.*, anthracene picrate and guaicol picrate, there were complications.

Table 1. Melting points and equivalent weights of picrates prepared from pure solvents.

	Solvent	Excess of	Melting points. °C		Equivalent weights	
			Litt. *	exp.	calc.	exp.
Naphthalene	ethanol		149 149.5 150.2 151.5	146	357	356
Phenanthrene	chloroform	picric acid	132.8 143 145	143— 145	407	402
Anthracene	ethanol	picric acid	138 139 151.8 152.5	139	407	399
Guaiacol	chloroform	guaiacol	80 86 88.6 88 89 90	87	353	349
Guaiacol	water		80 86 88.6 88 89 90	85	353	352
<i>p</i> -Chloro-aniline	chloroform	<i>p</i> -chloro-aniline	178 187	185— 186	357	355
Pyridine	»	pyridine	162 164 165 167 168	161	308	309

\* The melting points quoted are taken from Beilsteins Handbuch der organischen Chemie, and from 3, and 6.

Table 2. Melting points and equivalent weights of picrates prepared from alcohol water mixtures.

	Melting points. °C		Equivalent weights	
	Litt. **	exp.	calc.	exp.
1-Bromo-naphthalene	134—135 129.6	134	436	437
2-Naphthole	157 156	158	373	372
Anisole *		99	566	570
<i>p</i> -cresyl-methylether *		103	580	582
Anethole	70	69	377	380
<i>o</i> -Chloro-phenol	81	80	358	360
<i>o</i> -Toluidine	212—215 213 185	213	336	336
Aniline	175—180 181 182	181	322	325

\* These picrates contain 2 moles picric acid to 1 mole of the other component.

\*\* The melting points quoted are taken from Beilsteins Handbuch der organischen Chemie, and from 3, and 6.

When first prepared from chloroform the anthracene picrate had a melting range of 148—180° C. After recrystallization from chloroform it melted at 183° C. Anthracene picrate prepared from ethanol melted at 134° C which is in agreement with the literature. A batch of anthracene picrate prepared this time from chloroform as solvent gave the same melting point, 134° C. Several months later, another batch prepared from chloroform showed the wide melting range of the first lot, and after recrystallization from chloroform melted at 184°. The "equivalent weight" of this new picrate was 378 before and 429 after the recrystallization ( $C_6H_3O_7N_3 + C_{14}H_{10} = 407$ ). It was shown by X-ray diagrams that the high- and the low-melting picrates prepared from ethanol and chloroform were two definite modifications. Two modifications of guaiacol picrate were simultaneously obtained from chloroform: a red one consisting of six-sided prisms, and a yellow consisting of long needles. Both the picrates melted at 87° C and the equivalent weight was 349 for both.

In Table 2 are recorded the melting points and the titration results for some picrates prepared from ethanol-water mixtures. It should be mentioned that the picrates of anisole and of *p*-cresyl-methyl ether contain 1 mole of ether component to 2 moles of picric acid. In the preparation of these picrates it was necessary to change the amount of picric acid from 5 to 10 millimoles. The last two picrates do not seem to have been previously reported.

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