

A MODIFIED METHOD FOR THE PREPARATION OF PICRAMIC ACID.

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The importance of picramic acid as a standard for Benedict's blood sugar determination and the present shortage of picric acid suggested to the writer that the small yield of picramic acid obtained by working in accordance with the instructions in the literature might be improved.

One method commonly used for the preparation of picramic acid is that of Girard,¹ which states: If a cold saturated alcoholic solution of picric acid is neutralized with ammonium hydroxide and then saturated with hydrogen sulfide the liquid turns red and small red crystals are deposited. On distilling off the alcohol, sulfur and additional red crystals are deposited. They are the ammonium salt of picramic acid from which picramic acid can be obtained on addition of acetic acid to the hot aqueous solution.

The other method reported by Lea² reads as follows: An alcoholic solution of picric acid treated with an excess of ammonium sulfide is evaporated on the water bath, the residue extracted with boiling water, and in the filtrate the picramic acid is precipitated with acetic acid. 63 per cent is claimed as yield. The writer was unable to confirm this last statement.

As to Girard's methods, if one follows the instructions literally, that is, if one uses a cold saturated solution of picric acid neutralized with ammonium hydroxide, the larger proportion of the crystals deposited on passing hydrogen sulfide into the solution consists of unchanged picric acid. It takes at least from 1 to 1½ hours to deposit any crystals of the reduction product and these are greatly contaminated with the diamino salt due to the heat resulting from reduction. The product obtained when using Lea's method is also contaminated to a great extent with the diamino salt.

¹ Girard, A., *Compt. rend. Acad.*, 1853, xxxvi, 421; *Ann. Pharm.*, 1853, lxxxviii, 281.

² Lea, C., *Jahresbr. Fortschr. Chem.*, 1861, 637; *Am. J. Sc. and Arts*, 1861, xxxi, 188; xxxii, 210; *Chem. News*, 1861, iv, 193; *J. prakt. Chem.*, 1862, lxxxvi, 319.

Picric acid remains in solution in the presence of an excess of ammonium hydroxide, and the formation of the ammonium salt of the diamino-acid is almost excluded by cooling the solution.

The following modification of the procedure proved satisfactory.

20 gm. of finely powdered picric acid are heated in 300 cc. of alcohol in an Erlenmeyer flask of 600 cc. capacity (boiling the solution should, however, be avoided so as not to decrease unnecessarily the quantity of liquid). When dissolved, 125 cc. of concentrated ammonium hydroxide are added and the contents of the beaker cooled to 30°C. with running water. A very rapid stream of washed hydrogen sulfide gas is passed into the solution until the thermometer shows a temperature of 50–55°C. This temperature is reached in about 10 or 15 minutes, depending on the rapidity with which hydrogen sulfide is passed in, and should not be exceeded. Without discontinuing the stream of hydrogen sulfide the flask is placed in crushed ice and hydrogen sulfide allowed to pass through for 45 minutes more. The delivery tube should be at least 1 cm. wide.

The crystals of the ammonium salt of picramic acid which have now been deposited in large quantities are freed from all mother liquor by filtration on a Buchner funnel, transferred to a porcelain dish, and treated with 60 cc. of acetic acid (1 part of glacial acetic acid to 4 parts of water) to decompose the ammonium salt. The mixture is vigorously stirred so as to bring all solid substance into reaction with the acid. The picramic acid is filtered off on a Buchner funnel and washed with two portions of water, using 10 cc. each time. The yield should be from 14 to 15 gm. The acid is purified as follows: 500 cc. of distilled water are heated to boiling, and 2 gm. of the crude picramic acid are added and boiled in the water with stirring. Not more than 50 cc. of the water should be allowed to evaporate. The undissolved part, consisting chiefly of sulfur and a trace of diamino-acid, is filtered off through a folded filter. The filtrate is allowed to cool in an ice box or in ice to a temperature of from 10–12°. The picramic acid is filtered off by suction and air dried.

The picramic acid thus obtained has a melting point of 168°C. as required of the pure acid. The yield from 20 gm. of picric acid is 13.3 gm., which is 76.5 per cent of the theoretical value.

If the residue, obtained by concentration of the alcoholic filtrate from the ammonium picramate, is treated with 500 cc. of boiling water, filtered, and acidified with 5 cc. of glacial acetic acid, cooled with ice to about 10–12°C., an additional yield of picramic acid is obtained. It is filtered on a small Buchner funnel, washed with two portions of water of 5 cc. each. The yield is increased about 5 per cent of the theoretical value.

The writer wishes to express appreciation for assistance in the experimental work to Miss Frances Ford.

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