(7) Capps, J. D., Thesis (University of Nebraska) 1938.
(8) Knueppel, C. A., *Ann.*, 310, 76 (1900).
(9) Ziegler, *Ber.*, 21, 863 (1888).
(10) *Ibid.*
(11) Bostick, O., Thesis (Alabama Polytechnic Institute) 1937.
(12) Claus, Ad., *J. Pr. Chem.*, (2) 53, 335 (1896).

THE ASSAY OF SPIRIT OF CAMPHOR.*

BY O. GISVOLD.**

The U. S. P. XI method of assay for camphor in spirit of camphor has proven very unsatisfactory. E. M. Plein and C. F. Poe[1] report studies of this assay, show that the official method is unsatisfactory and recommend a method that is very similar to the one presented in this paper. Since this problem was under investigation at the time Plein and Poe reported their results, it seemed desirable to present the findings in this laboratory.

The dinitrophenylhydrazine reagent when prepared according to the U. S. P. XI is very unstable. About one-half of the reagent crystallizes out upon standing over night. When this half-strength reagent was used in the assay of spirit of camphor, very low results were obtained. *First*, because the camphor sublimed into the reflux condensor and *second*, because an insufficient amount of dinitrophenylhydrazine was present to insure complete combination with all camphor. A freshly prepared one and one-half per cent reagent also gave very unsatisfactory results.

The addition of either methyl or ethyl alcohol increased the yield of the dinitrophenylhydrazone. It was found that 25 per cent methyl alcohol was a very satisfactory solvent for the preparation of the one and one-half per cent dinitrophenylhydrazine reagent of the U. S. P. XI. This reagent is stable for some time.

The following procedure gave good results. Two cc. of the spirit of camphor were pipetted into 75 cc. of the reagent. The mixture was refluxed on a steam-bath for two hours. A Hoffmann distilling head was attached to the flask and the mixture heated at such a rate that 15 to 17 cc. of alcohol were distilled in a period of one-half hour. Fifty cc. of 5 per cent sulfuric acid were added to the flask and the mixture allowed to cool. An additional 150 cc. of 5 per cent sulfuric acid were added and the mixture allowed to stand over night. The derivative was collected in a tared fritted-glass filter funnel (No. 3) and dried to constant weight at 100°.

The derivative can readily be washed from the fritted-glass filter funnel with chloroform and the funnel can be used repeatedly without retaring.

This procedure was used in the analyses of accurately prepared 8, 10 and 12 per cent spirits. These results, together with those obtained using the U. S. P. XI and the Plein and Poe methods, are tabulated below.

U. S. P. XI Method.	Plein and Poe Method.	Modified Method.
	Eight per cent spirit.	
6.44	7.91	7.88
7.66	7.92	7.81
6.49	8.00	7.95
7.72	8.02	7.85
Av. 7.08	Av. 7.96	Av. 7.87

* Presented before the Scientific Section, A. PH. A., Minneapolis meeting, 1938.

** From the Department of Pharmaceutical Chemistry, College of Pharmacy, University of Minnesota, Minneapolis, Minn.

[1] *Ind. Eng. Chem.* (Analyt. Ed.), 10, 78 (1938).

	Ten per cent spirit.	
7.84		9.86
9.58		9.85
10.42		9.87
10.68		9.84
Av. 9.63	9.80*	Av. 9.86
	Twelve per cent spirit.	
8.45	11.63	11.75
7.68	11.68	11.77
7.80	11.60	11.80
8.80	11.60	11.82
Av. 8.38	Av. 11.63	Av. 11.79

* Average of fifty determinations by five analysts.

A few assays were conducted using a 5-cc. sample and a 2 per cent reagent. Satisfactory results were obtained when the reagent was freshly prepared. Upon standing over night some of the dinitrophenylhydrazine crystallized out of the 2 per cent reagent, thus indicating its instability. It is the opinion of the author that the percentage yield of hydrazone is dependent upon two factors, *i. e.*, the solubility of the derivative and the equilibrium obtained between the reactants. By increasing the amount of dinitrophenylhydrazine, the reaction can be driven more nearly toward completion, and thus decrease the error.

SUMMARY.

1. It is shown that the official method of preparing dinitrophenylhydrazine reagent and also the assay of camphor in spirit of camphor is unsatisfactory.

2. The results of Plein and Poe have been confirmed and what is considered to be an improvement on their procedure is submitted.

3. In the Plein and Poe method fifteen cc. of ethyl alcohol is added and the sample refluxed for four hours. In the method submitted in this paper the dinitrophenylhydrazine reagent contains twenty-five per cent methyl alcohol which stabilizes the reagent. The time consumed in refluxing is reduced from four to two and one-half hours. The yield of dinitrophenylhydrazone was increased thus reducing the error of the procedure.

THE PREPARATION OF EMODIN FROM CHRYSAROBIN.*

BY JOHN H. GARDNER.[1]

In an earlier paper from this laboratory (1), it was shown that chrysophanic acid can be obtained from chrysarobin by a process consisting in reducing to convert dianthrones into anthrones, boiling under reflux with hydrobromic and acetic acids to demethylate the emodin-anthrone-monomethyl ether, acetylating and crystallizing the chrysophanic acid-anthranol triacetate from acetic acid. From this compound, chrysophanic acid may be prepared by oxidation followed by saponification. Since chrysarobin contains large amounts of reduction products of emodin-

* Presented before the Scientific Section, A. PH. A., Minneapolis meeting, 1938.

[1] From the Chemical Laboratory of Washington University, St. Louis.