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A Simple Photometric Method for the Determination of Hydrazinophthalazines

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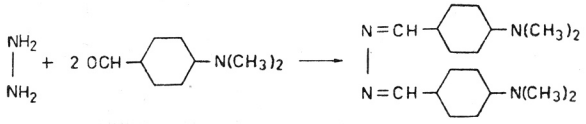
An accurate and sensitive photometric method for the determination of hydrazinophthalazines is described. The method is based on the formation of the yellow azine by the action of the acid solution of *p*-dimethylaminobenzaldehyde.

The proposed method is successfully applied on the determination of 1-hydrazinophthalazine hydrochloride (I) and 1,4-dihydrazinophthalazine sulphate (II).

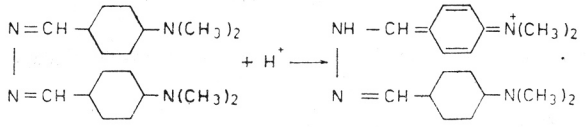
For the determination of hydrazine Watt and Crisp[1] describe a spectrophotometric method based upon the observation by Pesez and Petit[2] that a characteristic colour results upon addition of a solution of *p*-dimethylaminobenzaldehyde in ethyl alcohol and hydrochloric acid to hydrazine in dilute hydrochloric acid solution. The optimum concentration range is 0.06 to 0.47 p. p. m. over which the relative error does not exceed 1%. The maximum of absorption is at 458 mμ.

Wood[3] presents a method for the determination of maleic hydrazide whereby the hydrazide is reduced and hydrolized to split off hydrazine which is then determined spectrophotometrically using a 4% solution of *p*-dimethylaminobenzaldehyde in 2 *N* sulphuric acid as a reagent.

The colour reaction involves a condensation of hydrazine with aldehyde:



The aldazine formed is soluble in acids and rearranges to a quinoid structure possessing an intense colour:



Ruggieri[4] reports a spectrophotometric and a colorimetric method for the determination of hydrazinophthalazine and dihydrazinophthalazine. In the spectrophotometric method Ruggieri describes the use of 1% solution of

p-dimethylaminobenzaldehyde in hydrochloric acid and not in alcoholic-hydrochloric acid as propose the above mentioned authors[1,2].

In the colorimetric method the same author uses a 1% solution of β-naphthoquinone sulphonate sodium in water. The colorimetric method is less sensitive than the spectrophotometric one.

The photometric method proposed in this paper is not known although some modifications of the primary reaction of hydrazines with *p*-dimethyl-aminobenzaldehyde have been published. A notable addition is the introduction of this method and its use with the photoelectric colorimeter.

The interferences shown by the photometric measurements of I are due only to the smaller sensitivity of the photometer. Our method was confirmed by extinction measurements of I and II with the spectrophotometer.

Suggestions for the use of sulphuric acid instead of hydrochloric acid[1,2,4] in the preparation of the reagent and standard solution are made.

EXPERIMENTAL

Effect of reagent concentration on colour density

To determine the optimum concentration of *p*-dimethylaminobenzaldehyde solution for maximum colour development, samples containing 16 μg (I), i. e. 14 μg (II) per ml. with varying amounts of reagent were run against blanks containing equal amounts of reagent. The maximum colour intensity is reached with 0.1 ml. of *p*-dimethylaminobenzaldehyde solution (Fig. 1).

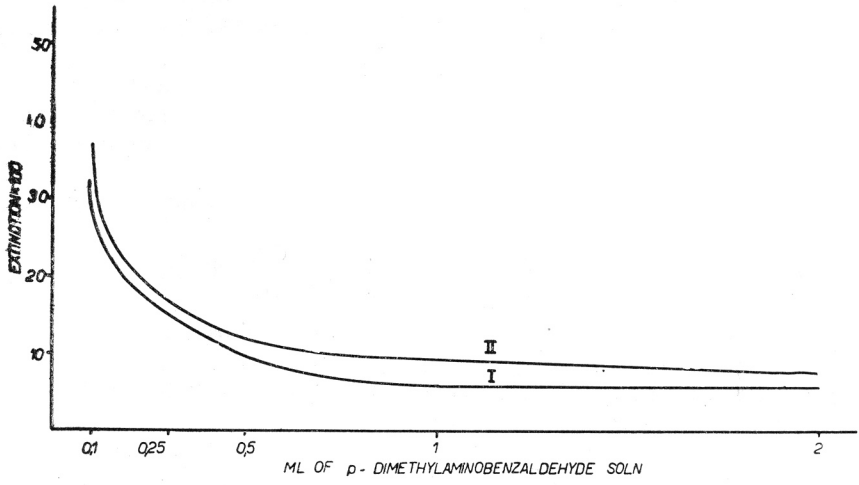


Fig. 1. Effect of reagent concentration on colour density

Stability of the yellow colour produced

The maximum colour intensity is reached after approximately 10 minutes (I) and 15 minutes (II) (Fig. 2).

The obtained yellow colour does not change within 5 minutes (II) and 60 minutes (I) (Fig. 3).

Reagents

p-*Dimethylaminobenzaldehyde solution.* A 4% solution of *p*-dimethylaminobenzaldehyde C. P. grade in 2 *N* sulphuric acid. The reagent should be freshly prepared.

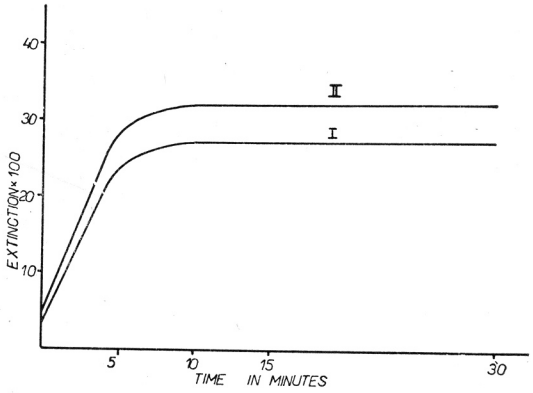


Fig. 2. Rate of colour development

Standard 1-hydrazinophthalazine hydrochloride solution. A solution containing 0,4 mg. of I per ml. in water.

Standard 1,4-dihydrazinophthalazine sulphate solution. A solution containing 0,4 mg. of II per ml. in water.

Apparatus

Fisher Electrophotometer AC Model, cylindrical absorption cells 2.3 cm. thickness, filter 425 B.

Beckmann Model DU Spectrophotometer using Corex cells of 1.003 cm. light path.

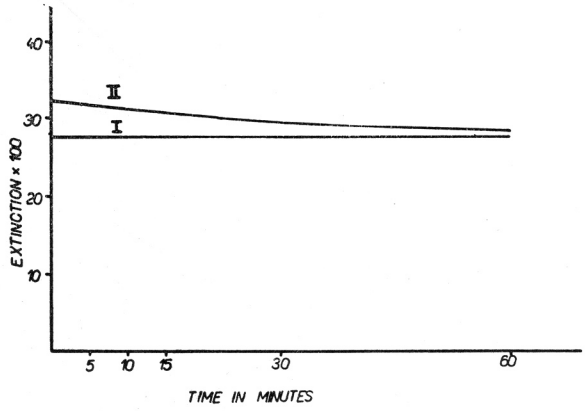


Fig. 3. Stability of the yellow colour

Preparation of standard concentration curves

Aliquots of standard solution containing 0.C to 1.4 mg. of I, i. e. 0.1 to 0.7 mg. of II were transfered to 50 ml. volumetric flasks. The yellow colour is developed with 0.1 ml. of *p*-dimethylaminobenzaldehyde solution; after 10 minutes (I) and 15 minutes (II) the mixture is brought to 50 ml. with water. Curves plotting concen-

trations I and II against extinction × 100 at 425 mμ (electrophotometer) are shown in Fig. 4. Excellent conformity to Beer's law is evident in the range from 12 to 28 μg. per ml. (I) and from 2 to 14 μg. per ml. (II).

Curves plotting concentration I (1.12 mg. to 2.40 mg.) and II (1.20 mg. to 2.80 mg.) against extinction at 410 mμ (spectrophotometer) are shown in Figure 5.

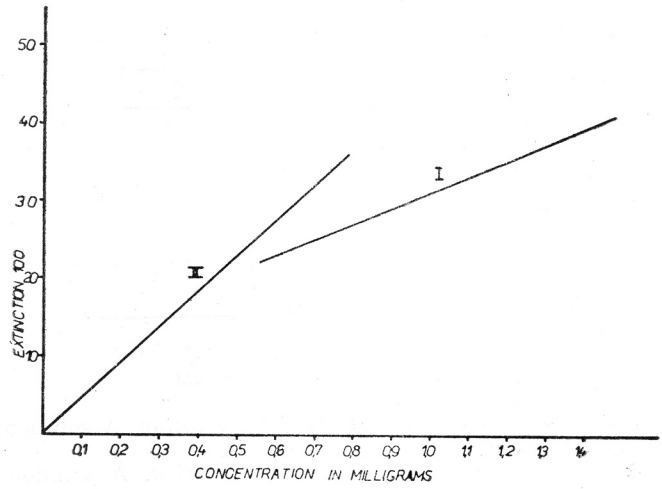


Fig. 4. Standard calibration curves (Electrophotometer)

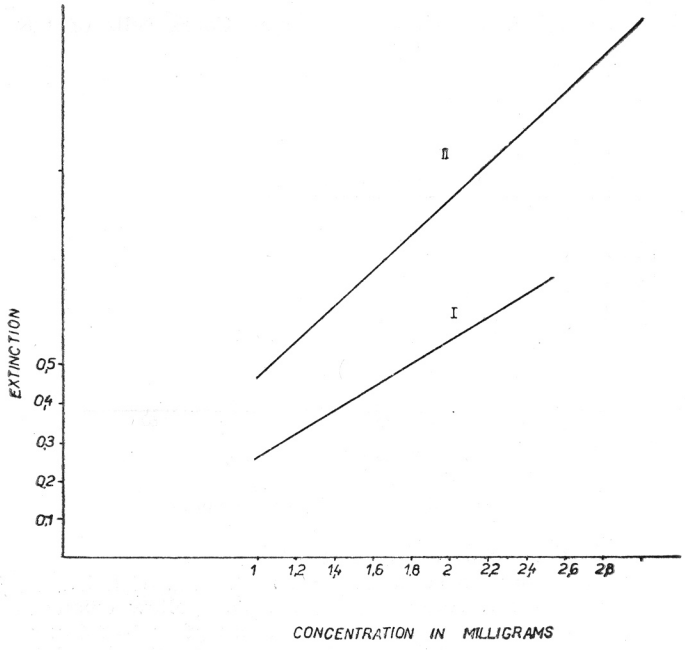


Fig. 5. Standard calibration curves (Spectrophotometer)

A blank containing an equal concentration and 0.1 ml. of *p*-dimethylaminobenzaldehyde solution is used as a reference solution.

All the measurements concerning II are to be performed within 5 minutes after dilution (Fig. 3).

Procedure for the determination of 1-hydrazinophthalazine hydrochloride

Dissolve from 60 to 140 mg. of 1-hydrazinophthalazinehydrochloride in 20 ml. of water and dilute to 100 ml. Pipette 1 ml. of the solution to a 50 ml. volumetric flask, add 0.1 ml. of *p*-dimethylaminobenzaldehyde solution. Mix well, let stay for 10 minutes and dilute with water. Correct the results for the reagent blank.

Procedure for the determination of 1,4-dihydrazinophthalazine sulphate

Dissolve from 10 to 70 mg. of 1,4-dihydrozinophthalazine sulphate in 20 ml. of water by haeting to boiling point and dilute to 100 ml. Pipette 1 ml. of the solution to a 50 ml. volumetric flask, add 0.1 ml. of *p*-dimethylaminobenzaldehyde solution, mix well, let stay for 15 minutes and dilute with water. Correct the results for the reagent blank.

The measurements are to be performed within 5 minutes after dilution.

REFERENCES

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2. M. Pesez and A. Petit, *Bull soc. chim. France* **1947**, 122.
3. P. R. Wood, *Anal. Chem.* **25** (1953) 1879.
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IZVOD

Jednostavna fotometrijska metoda za određivanje hidrazinoftalazina

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Opisana je točna i osjetljiva fotometrijska metoda za određivanje hidrazinoftalazina. Metoda bazira na stvaranju žuto obojenog azina — djelovanjem kisele otopine *p*-dimetilaminobenzaldehida.

Predložena je metoda uspješno primijenjena kod određivanja 1-hidrazinoftalazin hidroklorida (I) i 1,4-dihidrazinoftalazin sulfata (II).

Intenzitet apsorpcije linearan je u području koncentracije 12—28 μg/ml (I) tj. 2—14 μg/ml (II) kod 425 mμ. Mjerenja su vršena na Fisherovu elektrofotometru, model AC, u kivetama 2.3 cm. Relativna pogreška ne prelazi 1%.

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