

Colorimetric Determination of 5-Nitro-2-furfuridene Aminoguanidine

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It has been often reported on the color reaction of 5-nitro-2-furfural derivatives. In this paper, the following two methods are applied to find whether they are useful for the detection and the colorimetric determination of its aminoguanidine derivative: one¹⁾ is to detect nitrosoradical which is obtained by reduction of nitroradical and the other²⁾ is the same method as 5-nitro-2-furfural and its semicarbazone derivative whose color is changed into red with caustic alkali.

(I) *Coloration by sodium nitroprusside after reduction in neutrality.*

Aqueous solution of 5-nitro-2-furfuridene aminoguanidine (Guanofracin, the commercial name, G.F. is abbreviated in this paper) is filtered after reduction with zinc dust. To the filtrate are added sodium nitroprusside solution and KOH solution, and it turns reddish brown color. Its detectability is so weak that the limit is in 10 mg% (1/10,000) solution, and the distilled water which does not contain G.F. turns deep yellow by the same treatment as mentioned above. It is therefore difficult to apply this color reaction to the colorimetric determination for our purpose.

(II) *Coloration with caustic alkali.*

By the addition of caustic alkali, G.F. aqueous solution turns orange or red or makes fine red crystal in strong alkalinity, corresponding to G.F. concentration. To the reaction mixture are added dioxane, carbowax, acetone or other various solvents, respectively, in order to increase the stability and intensity of this coloration, and, as the result, acetone is the best one for this purpose. Using Beckmann's spectrophotometer, it is found that no strictness is required in the quantity of alkali to be added, 1 cc of N-NaOH solution being enough for 10 cc of test solution, and that the absorption maximum is observed approximately at 410 m μ . Further studies clarified that the following method is the most suitable one for the determination: the test solution is prepared in a proportion of 8 cc of G.F. solution, 2 cc of acetone and 0.1 cc of 10N-NaOH, and then the absorption spectrum is measured at 410 m μ after kept standing for 1.5 hours.

So the optical density of 0.1-2 mg G.F. aqueous solution is measured by Beckmann's spectrophotometer. The result (Fig. 1) shows that the optical density is measurable at this range of concentration and there is a proportional relationship between the concentration of G.F. and the optical density at 410 m μ . (In Fig. 1 the lines show the optical density of G.F. solution of various concentrations at 410 m μ and the dotted lines show the relationship between the wave length and the optical density.) The result of the measurement of 0.1-100 mg% G.F. aqueous solution by the Duboseq colorimeter (Fig. 2) shows an approximately proportional relation. (In Fig. 2 the dotted line indicates the values of the same test solution which are measured by Beckmann's spectrophotometer.)

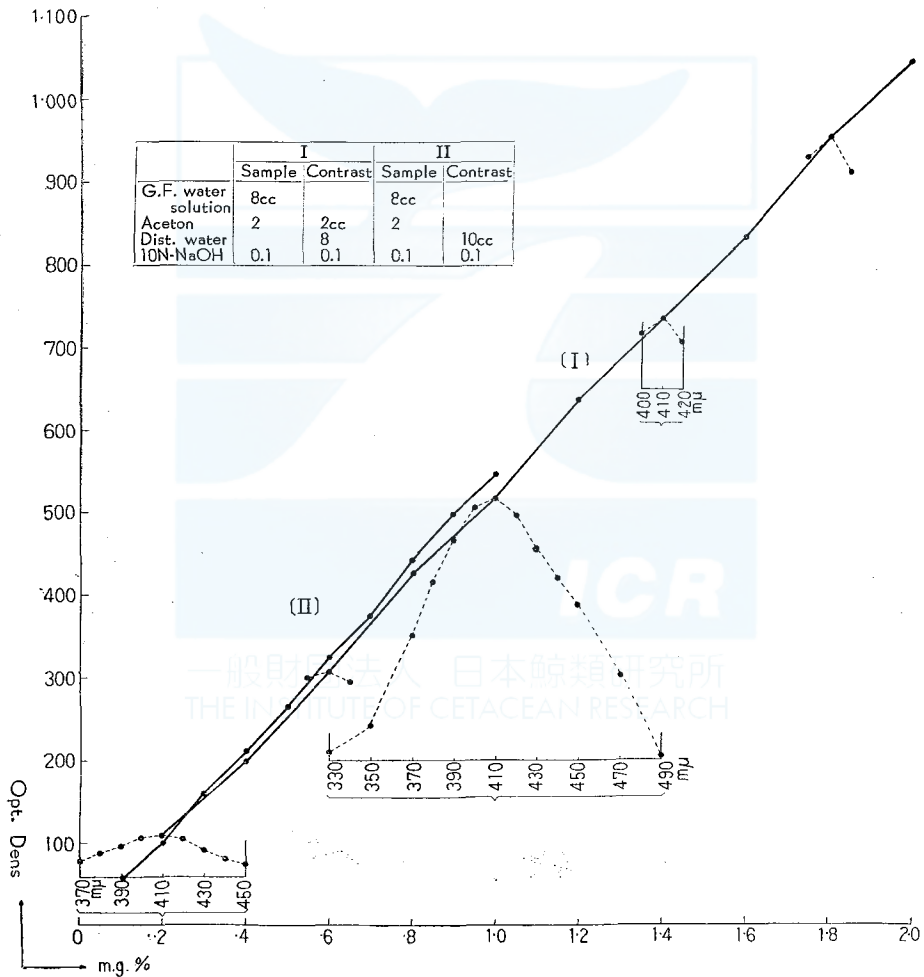


Fig. 1.

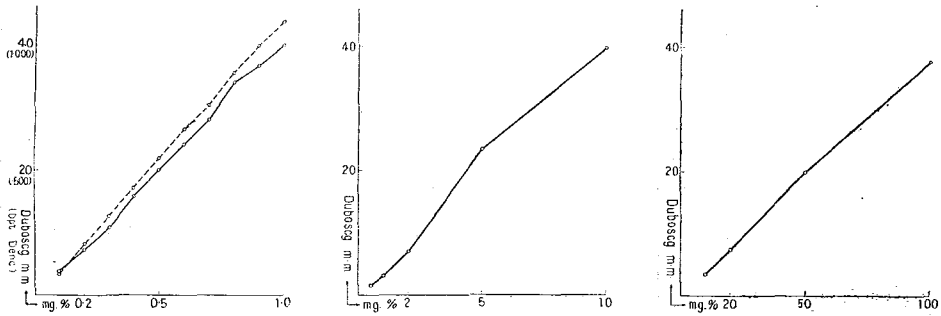


Fig. 2 a.

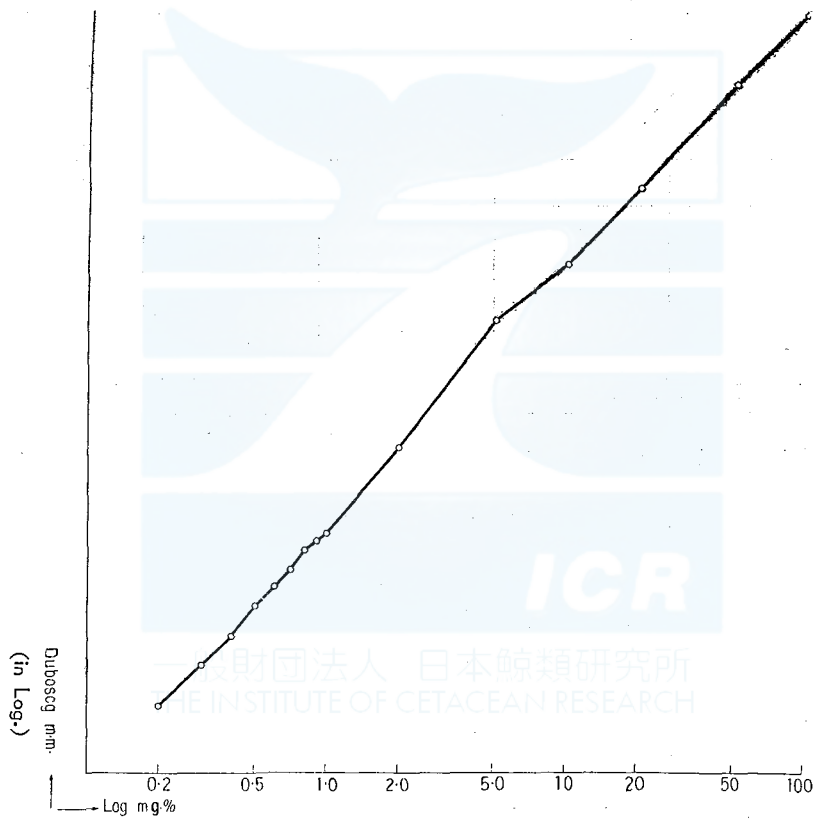


Fig. 2 b.

(b) is summarized from (a).

In case of color reaction using caustic alkali, the above described range of concentration (0.1–2 mg %, viz. 1/1,000,000–1/50,000) gives a very suitable condition for the determination by spectrophotometer, and

using the Duboscq colorimeter, colorimetric determination can be made easily at a wide range of concentration (0.1–100 mg%, viz. 1/1,000,000–1/1,000).

Table 1.

Wave length	15 min.	45 min.	1 hr.	1.5 hr.	2 hr.	3 hr.
360 m μ	—	—	0.232	0.243	—	—
380	0.327	0.360	0.373	0.380	—	—
400	0.470	0.490	0.498	0.502	0.500	0.502
410	0.502	0.515	0.522	0.515	0.515	0.515
420	—	—	0.505	0.502	0.495	0.488
430	—	0.475	0.468	0.461	—	—
460	—	0.330	0.360	0.366	—	0.360

Table 2.

Wave length	I	II	III	IV
390 m μ	0.465	0.470	0.465	0.448
400	0.522	0.525	0.512	0.495
410	0.528	0.531	0.530	0.518
420	0.510	0.510	0.510	0.495

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Experimental Part

(I) Coloration by sodium nitroprusside after reduction in neutrality.

1. Procedure

To 3 cc of G.F. aqueous solution in a test tube are added 6–7 drops of 10% CaCl₂ and about an spatulful of zinc dust. The reaction mixture is heated for a few minutes in a boiling water bath and then filtered through filter paper. After the filtrate is cooled, to it are added 6–7 drops of newly prepared 2.5% sodium nitroprusside solution. The mixture is vigorously shaken and then to it are also added 3 drops of 8% KOH solution, and the precipitate therein is removed by filtration. The filtrate turns reddish brown color in a few minutes.

2. Discussion

(1) The deep yellow, transparent filtrate is obtained by the above mentioned treatment from both whale blood and distilled water which do not contain G.F.

(2) This coloration is conspicuously observed in 100 mg% G.F. solution but not so in 10 mg% solution.

(II) Coloration by caustic alkali.

1. Procedure

To 8 cc of G.F. solution are added 2 cc of acetone and the mixture is vigorously shaken. And then to it is added 0.1 cc of 10N-NaOH and shaken vigorously again. 1.5 hours later, absorption is measured with a colorimeter. In case of using Beckmann's spectrophotometer, a mixture of 8 cc of water, 2 cc of acetone and 0.1 cc of 10N-NaOH or a mixture of 10 cc of water and 0.1 cc of 10N-NaOH is used as a control and the absorption at 410 $m\mu$ is measured.

2. Discussion

(1) Absorption spectra of acetone-alkali-aqueous solution

Absorption spectrum of various concentrations in acetone aqueous solution, to which alkali is added is measured with Beckmann's spectrophotometer between 330 $m\mu$ and 450 $m\mu$, and then the values obtained are almost constant, showing about 0.020 of optical density. The fluctuation of absorption by various quantities of acetone added is negligible.

(2) Effect of the reaction time

The results of the measurement for 15 minutes to 3 hours after preparation of test solution are shown in Table 1. The values are constant for 45 minutes to 3 hours after preparation of test solution (The value which is obtained for 1 hour after preparation is a little larger but the difference is only 1.3% from other values).

(3) Effect of various proportions of quantity between acetone and G.F. aqueous solution

	I	II	III	IV	Control
G. F. solution (in cc)	8.5	8	7.5	7	—
Acetone (")	1.5	2	2.5	3	—
10N-NaOH (")	0.1	0.1	0.1	0.1	0.1
Water (")	—	—	—	—	10.0

The result (Table 2.) shows that the mixture of proportion II gives the largest value in optical density. As the values for mixtures of proportion I and II fluctuate only 0.3-0.6% of the value of II, there is no necessity to change proportion more closely.

(4) In case of 100 mg% G.F. solution, there is no appearance of red precipitate even after the test solution is kept standing for several hours.

Summary

For the purpose of the colorimetric determination of aqueous solution of 5-nitro-2-furfuridene aminoguanidine, the two methods of coloration with sodium nitroprusside after reduction in neutrality and by caustic alkali were tried. The former was not suitable because of its dull sensitivity (10 mg% is the limit of detection). The latter was, on the contrary, applicable between in 0.1 and 100 mg% of G.F. concentration.

Literatures

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