NOTES

The Determination of Formaldehyde by Means of 3-Methyl-2-benzothiazolone Hydrazone. A New Procedure, Involving Extraction

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A new solvent extraction procedure for the determination of formaldehyde with 3-methyl-2-benzothiazolone hydrazone (MBTH)[1] will be described. This procedure is particularly advantageous in the determination of a minute amount of the aldehyde in colored and/or turbid sample solutions.

Experimental

Reagents.—*A Standard Solution of Formaldehyde.*—The stock solution of formaldehyde is standardized by the dimedon method.[2] The aliquot portion of the stock solution is then diluted in order to prepare the standard solution (1 μg./ml.).

3-Methyl-2-benzothiazolone Hydrazone Hydrochloride (MBTH) Reagent.—0.4% aqueous solution.

1% Ferric Chloride Solution.

Saturated Sodium Chloride Solution.

Anhydrous Sodium Sulfate.

A Mixed Solvent, (1+1) Acetone-Chloroform.

Instruments.—A Beckman model DU spectrophotometer. A Coleman model 14 spectrophotometer.

Procedure.—To 9 ml. of test solution, 1 ml. of a saturated sodium chloride solution is added, and then 2 ml. of a 0.4% MBTH aqueous solution is added. After the mixture has stood for 20 min., 0.5 ml. of a 1% ferric chloride solution is added. After an additional 10 min., 12.5 ml. of a (1+1) acetone-chloroform solvent is added to the mixture. Then the mixture is transferred into a separatory funnel and shaken twenty times.* The extract is poured into a 10 ml. measuring flask, and the flask is filled up to the mark with the solvent. Then the extract is quickly dehydrated in a stoppered test tube with 6 g. of anhydrous sodium sulfate.** The extract is filtered through a dry filter paper. The absorbance is read at the wavelength of 670 mμ. The color is stable for at least two hours.

Results and Discussion

In the reaction of MBTH with formaldehyde, a maximum coloration is obtained in the range of the concentration of sodium chloride from 0.5 mol. to 1.0 mol. The molar absorptivity is 6.9×10^4 in the sodium chloride solution, while it is 6.1×10^4 in a solution without sodium chloride. The absorbance is increased by 1.13 times in the sodium chloride solution. On the other hand, Sawicki et al.[1] give 6.5×10^4 as the molar absorptivity in a solution without

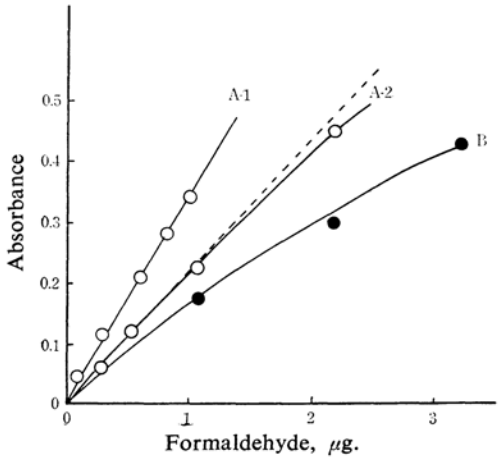

Fig. 1. Calibration curve fromaldehyde.

A. Extraction from 0.54 mol. sodium chloride solution. pH of the aqueous phase, 2.5.
   1. 16 mm. light path at the wavelength of 670 mμ. (Coleman spectrophotometer).
   2. 10 mm. light path at the wavelength of 670 mμ. (Beckman spectrophotometer).

B. Extraction from a solution without sodium chloride. pH of the aqueous phase, 2.45. 10 mm. light path at the wavelength of 670 mμ. (Beckman spectrophotometer).

1) E. Sawicki, T. R. Hauser, T. W. Stanley and W. Elbert, *Anal. Chem.*, 33, 93 (1961).

2) J. H. Yoe and L. C. Reid, *Ind. Eng. Chem., Anal. Ed.*, 13, 238 (1941).

* After shaking the solvent decreases in volume to about 9.8 ml.

** The color is not stabilized for a longer period by using a smaller amount of sodium sulfate. Any decrease of the absorbance is not noticed by treating the extract with sodium sulfate and then a filter paper.

sodium chloride, while Hünig et al.[3] gives 7.6 $\times 10^4$ as the molar absorptivity of the pure product in acetone. A similar increase in the absorbance is also noticed in the reaction of acetaldehyde with MBTH. Sodium chloride seems to be effective in raising the yield of the color reaction of MBTH with aldehyde. Potassium chloride is less effective than sodium chloride for the enhancement of the sensitivity of the present method.

The addition of sodium chloride to the reaction mixture has another advantage. In the presence of sodium chloride, the extraction of the colored product is quantitative, while in a solution without sodium chloride more than 10% of the colored product remains in the aqueous phase (Fig. 1). Extraction is also advantageous for the determination of a minute amount of aldehyde in colored or turbid solutions, because the colored product of aldehyde is concentrated in a small volume of the organic phase. A prolonged contact of the organic phase with the aqueous phase reduces the absorbance. The extract must be rapidly dehydrated after extraction; delayed dehydration also causes a decrease in the absorbance.

The presence of 20 mg./l. of ferrous ions or 50 mg./l. of manganese ions does not interfere. The presence of 1 mg. of sugar gives only a minimum detectable absorbance. This is one of the advantages of the MBTH method here presented. By means of the method using chromotropic acid, a small amount of formaldehyde in the presence of a larger amount of sugar cannot be determined because sugar and formaldehyde are likely to react with the reagent.

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3) S. Hünig and K. H. Fritsch, *Ann.*, **609**, 172 (1957).