Colorimetric Determination of Formaldehyde Using 1,3-Diphenyl-2-thiohydantoin and Sodium Hydroxide

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A method for the determination of formaldehyde concentration in water is described. It is based on a coupling reaction of 1,3-diphenyl-2-thiohydantoin with formaldehyde. In this reaction an anionic pigment is formed by addition of sodium hydroxide solution. The color intensity and formaldehyde concentrations were linearly related in the range up to 100 μM . The minimum detectable concentration was 2 μM . The precision (R.S.D.) was 3.62%.

Keywords Formaldehyde, 1,3-diphenyl-2-thiohydantoin, anionic pigment, spectrophotometry

Several methods for determination and estimation of formaldehyde in water have been reported. They involve simple, sensitive, and reproducible methods such as spectrophotometric methods¹⁻¹¹, gas liquid chromatographic methods^{12,13}, and others.^{14,15} However, these methods exhibit various disadvantages with regard to sensitivity, detectable range, and troublesome operation.

2-Thiobarbituric acid (TBA) has been widely used for the determination of malonaldehyde (MA)¹⁶⁻¹⁸ produced from lipid peroxide in biological materials. TBA is reacted with carbonyl compounds, in the presence of catalysts such as alkalis and acids, to produce the coupled and colored compounds.¹⁹⁻²¹ 1,3-Diphenyl-2-thiohydantoin (DPTH) has a molecular structure similar to TBA, and is reactive also with aldehydes.

We have tested the reaction of DPTH with formaldehyde and sodium hydroxide, and here report a method for the determination of formaldehyde with DPTH and sodium hydroxide.

Experimental

Materials

DPTH was synthesized according to the method described by Shirai *et al.*²² Formaline was purchased from Nakakita Pharmaceutical Co., Nagoya, Japan; other chemicals were from Wako Pure Chemical Industries, Osaka, Japan.

DPTH solution was prepared by dissolving 600 mg of DPTH in 100 ml of acetone. Standard solutions of formaldehyde were prepared by diluting formaline with

water to give formaldehyde concentrations ranging from 2 to 100 μM ($\text{M}=\text{mol dm}^{-3}$), as determined by the iodine method.²³

Procedure for determination of formaldehyde

DPTH solution, 5 ml, was pipetted into test tubes. Formaldehyde standards, samples, or water as a blank, each 0.5 ml, and 1 M sodium hydroxide solution, 0.1 ml, were pipetted into each test tube and mixed well. The filled test tubes were incubated at room temperature for 30 min. The absorbances of these solutions were measured at 535 nm against the blank (Fig. 1).

Formaldehyde was determined by the 3-methyl-2-benzothiazolinone hydrazone method⁷ (the MBTH method), as previously described.

Results

Effect of reagent concentrations on extent of color formation

The color formation has been found to be optimum at a concentration of acetone solution containing 22 mM DPTH. Under the above conditions, the reacting solution contained DPTH in a molar ratio more than 2200 times that of formaldehyde. When volumes of the samples were tested between 0.2 and 4 ml, the reaction solution was turbid at a volume of under 0.3 ml. Thus the sample volume was set at 0.5 ml.

Reaction with other compounds

The effects of other compounds such as acetal, propionaldehyde, glutaraldehyde, malonaldehyde, dex-

Fig. 1 Visible absorption spectra. Formaldehyde concentrations in samples, 0 (---) and 78.6 (—) μM .

Fig. 2 Time-course of color reaction. Formaldehyde concentrations in samples, 0 (▲), 19.6 (◆), 49.1 (■), and 78.6 (●) μM .

Fig. 3 A typical calibration curve for formaldehyde by the proposed method. $n=11$, $r=0.998$, slope=0.0127, intercept = -0.0069.

trose, lactose, levulose, and maltose on colorimetry, were tested for the proposed method. Pigments produced from these compounds with DPTH were only under 0.01 absorbance unit at concentrations of these compounds about 10^4 times those of formaldehyde samples.

Time-course variation of color reaction

Figure 2 illustrates the time-course variation of color reaction of DPTH with formaldehyde and sodium hydroxide. The reaction was nearly completed within 30 min. Although a certain degree of variation in absorbance occurs in the absence of the sample, it does not interfere with linearity, because the absorbance of the blank can be subtracted from that of each sample.

Sensitivity and precision

As shown Fig. 3, good linearity was obtained between absorbances and formaldehyde concentrations (up to 100 μM). The lower limit of the concentration was 2 μM . Table 1 gives the within-run results for each concentration in 10 test tubes.

Comparison of methods

Figure 4 shows the formaldehyde concentrations of the identical samples measured by the proposed method and the MBTH method simultaneously. A good correlation was observed for the results of these two methods.

Table 1 Precision of the proposed method for the determination of formaldehyde

Added	Formaldehyde/ μM		R.S.D., %
	Measured		
	Mean	S.D.	
<i>Within-run</i> ($n=10$)			
9.8	10.3	0.24	2.31
39.3	38.8	0.65	1.67
78.6	74.4	1.76	2.36
<i>Between-run</i> ($n=10$)			
39.3	38.3	1.39	3.62

Fig. 4 Correlation between the proposed method (y) and the MBTH method (x). $n=27$, $r=0.994$, slope = 1.018, intercept = -0.193 , $\bar{x}=52.64$, $\bar{y}=53.41$.

Discussion

The product of the color reaction among DPTH, formaldehyde, and sodium hydroxide was found to be a red pigment. In the color reaction of TBA with MA, Sinnhuber *et al.*²⁴ showed that two molecules of TBA was coupled with one molecule of MA to produce a pigment. Similarly, in the reaction among DPTH, formaldehyde, and sodium hydroxide, we presumed that the structure of the red pigment produced in the proposed method was similar to that of the coupling compound of TBA with MA.

The method for the colorimetric determination of formaldehyde is sensitive, reproducible, and simple. The red pigment which resulted from DPTH, formaldehyde, and sodium hydroxide was sufficiently stable to allow reasonable precise measurement of formal-

dehyde. The absorbance varied very little within about 60 min after incubation at room temperature for 30 min.

A high degree of accuracy is shown, thanks to the good correlation between the proposed method and the MBTH method (Fig. 4).

Several methods for spectrophotometric determination of formaldehyde have been reported: for example, the acetylacetone method^{1,2}, the phenylhydrazine method³, the pararosaniline method^{4,5}, the MBTH method⁶⁻⁸, the chromotropic acid method⁹, and others.^{10,11} Among them, the most sensitive method is the MBTH method, which is affected by other aldehydes such as acetaldehyde, propionaldehyde, crotonaldehyde, and others.⁷ On the other hand, the sensitivity of the proposed method was almost similar to that of the MBTH method⁷ and the proposed method was affected neither by other aldehydes such as acetal, propionaldehyde, glutaraldehyde, and MA nor by aldoses such as dextrose, lactose, levulose, and maltose. Therefore, the proposed method is considered to be very useful for determining the concentrations of formaldehyde.

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