Sensitive Spectrophotometric Determination of Aromatic Aldehydes Based on Their Reaction with Diphenylamine

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Because of the industrial uses of aldehydes, on one hand, and their toxicity1, on the other, their determination is of special interest. Various techniques, including polarographic2, amperometric4-9, thermometric10, fluorometric11 and spectrophotometric12-17 methods, have been reported for the determination of aromatic aldehydes. They are either not sensitive enough, require complicated and expensive instruments, and are subject to interference from other compounds or have high detection limits. The need for a sensitive, simple and reliable method for the determination of aromatic aldehydes is therefore clearly recognized.

In this paper we wish to report on a simple, sensitive and reliable method for the determination of aromatic aldehydes based on their reaction with diphenylamine in the presence of Te(IV) in hydrochloric acid media.

Experimental

Reagents

All of the chemicals were of analytical grade, and triply distilled water was used throughout. A diphenylamine solution (0.2 M) was prepared by dissolving 1.6923 g of diphenylamine (Merck) in ethanol (Merck) in a 50-ml volumetric flask. Aldehyde solutions were prepared in ethanol. A 0.175 M Te(IV) solution was prepared by dissolving 1.3966 g TeO2 (Merck) in 6 M HCl and diluting to the mark in a 50-ml volumetric flask by 6 M HCl. A 6 M HCl solution was prepared by appropriate dilution of concentrated HCl (Merck).

Apparatus

Absorption spectra were recorded on a Shimadzu UV-265 Model UV-Visible recording spectrophotometer with 1-cm glass cells. A Shimadzu Model UV-120-01 spectrophotometer with a 1-cm glass cell was used for absorbance measurements.

Procedure

A 5-ml aliquot of a solution containing an appropriate amount of desired aromatic aldehyde was transferred into a test tube. Then 1.7 ml of 0.20 M diphenylamine followed by 1.0 ml of a 0.175 M Te(IV) solution was added. The mixture was heated at 75° C in a thermostated water bath for 2 h. After cooling, 2 ml of 6 M HCl was added and the solution was diluted to the mark in a 10 ml volumetric flask by ethanol. A blank solution was also prepared in the same way, except that 5 ml ethanol was used instead of aldehyde solution. The absorbance of the solution was measured against the blank solution at corresponding wavelengths (Table 1).

Results and Discussion

A colored product was formed by the reaction of aromatic aldehydes with diphenylamine. As Table 1 shows, A_{max} of the product depended on the utilized aldehyde. Tellurium(IV) catalyzed the reaction effectively.

Effect of variables

Various experimental parameters, including the reagent concentrations, temperature and reaction time, were studied in order to obtain optimized systems. These parameters were optimized by setting all parameters to be constant and optimizing one each time; benzaldehyde was used as model aldehyde.

The effect of the diphenylamine concentration was studied over the range of 5.0×10^{-3} - 5×10^{-2} M. As Fig. 1 shows, A_{max} of the product depended on the utilized aldehyde. Tellurium(IV) catalyzed the reaction effectively.

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and then nearly remained constant. A final concentration of 0.0175 M was selected as the most suitable.

The effect of the reaction temperature was studied over the range of 50–95°C. Figure 4 shows that the optimum temperature is 75°C. Thus, 75°C was used for this study.

The effect of the reaction time was investigated in the range of 1–24 h. As Fig. 5 shows, the reaction is nearly completed after about 2 h. Thus, a reaction time of 2 h was selected.

**Analytical parameters**

Calibration graphs were obtained under the optimum conditions. Table 1 shows a linear regression of the calibration data for the investigated aldehydes.

![Fig. 1 Effect of the diphenylamine concentration on the absorbance intensity. Conditions: HCl, 0.1 M; Te(IV), 5×10^{-4} M; benzaldehyde, 10 µg/ml; temperature, 75°C; time, 1 h.](image1)

![Fig. 2 Effect of the hydrochloric acid concentration on the absorbance intensity. Conditions: diphenylamine, 0.03 M; Te(IV), 5×10^{-4} M; benzaldehyde, 5 µg/ml; temperature, 75°C; time, 1 h.](image2)

![Fig. 3 Effect of the Te(IV) concentration on the absorbance intensity. Conditions: diphenylamine, 0.03 M; HCl, 1.0 M; benzaldehyde, 10 µg/ml; temperature, 75°C; time, 1 h.](image3)

![Fig. 4 Effect of the temperature on the absorbance intensity. Conditions: diphenylamine, 0.03 M; HCl, 0.6 M; Te(IV), 0.0175 M; benzaldehyde, 5 µg/ml; time, 1 h.](image4)

![Fig. 5 Effect of the time on the absorbance intensity. Conditions: diphenylamine, 1×10^{-4} M; HCl, 0.6 M; benzaldehyde, 10 µg/ml; temperature, 75°C.](image5)
Selectivity

The effect of several organic compounds on the determination of the aromatic aldehydes was studied following the proposed procedure. Benzophenone, acetoephonone, pyridine, acetone, formamide, acetamide and propanol did not interfere even when present in 1000-fold excess over aromatic aldehydes, however more than 50-fold of acetaldehyde and 5-fold of formaldehyde interfered.

References


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