

Spectrophotometric Study on the Interaction of Water with Chloranilic Acid and its Analytical Application

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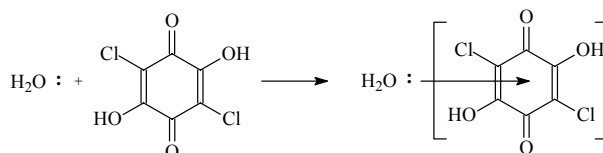
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Abstract: The reaction between chloranilic acid and water in alcohol was studied spectrophotometrically. The conditions of reaction were investigated in detail. The stable purple complex with an absorption wavelength at 530 nm was produced from the reaction between chloranilic acid and water. As a method for determination of H₂O, Beer's law was obeyed in range of 0-6.0 % or 0-8.0 % (V/V) with the detection limit of 0.13 %. The relative standard deviation (RSD) was less than 2 %. The proposed method has been applied to determination of trace amount of water in ethanol, flour and food flavoring, respectively. The recoveries of water in samples were 97~102 %.

Keywords : Water, chloranilic acid, charge-transfer reaction, spectrophotometry.

The determination of water is routine analytical requirement in chemical industry and food industry. To measure moisture in chemical products, Karl Fischer method (GB-6283-86) is usually employed as a reference method in China and many other countries^{1,2}. The method has several limitations: it is time-taking; the reagents are expensive; Karl Fisher reagent needs to be calibrated daily. In order to improve the accuracy of titration, dead-stop endpoint method of potentiometric titration is usually used. However, the method is less sensitive and reagents are toxic. Furthermore, the operation procedure is complicated. To determine the moisture in food industry, oven-drying method and azeotropic distillation are often used^{3,4}. These methods are time-consuming and the reagent of benzene or toluene is toxic.

Chloranilic acid is an electron-deficient agent (electron acceptor) and can react with electron-rich agent (electron donor) to form charge-transfer complex. For example, it



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can react with electron donor medicines to determine pharmaceuticals⁵. Water is an electron-rich compound and can react with chloranilic acid to form a purple complex. The charge transfer reaction is shown to happen between chloranilic acid and water. This paper discussed the charge-transfer reaction between chloranilic acid and water.

Experimental

Chloranilic acid(chemical purity, Beijing Chemical Factory, China) of 0.0200 mol/L solution in absolute ethanol, methanol, *n*-propyl alcohol, *n*-butyl alcohol, *n*-heptanol and 1-hexanol, *etc.* (Analytical grade, Beijing Chemical Factory, China). All the alcohols were dehydrated in laboratory before using.

A Shimadzu Model UV-265 double-beam spectrophotometer with 1 cm cell (Kyoto, Japan), HHS-2-NI constant temperature water-bath (Beijing Jingwei Science Instrument Factory), KQ3200E ultrasonic washing appliance (Kunshan,China).

A certain amount of sample solution containing water was pipetted into a 10 mL volumetric flask, 2.00 mL chloranilic acid solution was added and the solution was diluted to volume with anhydrous solvent and mixed thoroughly. The flask was placed at room temperature for 10 min. The absorbance of the solution was measured at 530 nm against the reagent blank prepared in the same way simultaneously.

Solid sample of 1.5~2 g was weighed and put into a conical flask with a stopper, and 30 mL absolute alcohol was added. The mixture was then ultrasonically extracted for 40 min. The supernatant was collected. Then 20.0 mL absolute alcohol was added into the conical flask and the mixture was ultrasonically extracted for 20 min. The supernatant was collected and mixed with the first collection. The collection was distilled to near dry and the distillate was used for determination.

Results and Discussion

A certain amount of chloranilic acid was weighed and dissolved in water, methanol, absolute ethanol, 2-propanol, heptanol, dimethyl sulfoxide, ethyl acetate, methyl methacrylate, acetone and dioxane, respectively. Corresponding solvents were used as blank. The absorption spectra are presented in **Figure 1**. Solvent has a significant effect on absorption spectrum of chloranilic acid. λ_{\max} and absorbance of chloranilic acid changes with solvent used for dissolving chloranilic acid. As the polarity of solvent (dielectric constant ϵ) increases, the λ_{\max} value shifted to longer wavelength to different degrees.

The absorption curves of chloranilic acid-water complexes in methanol, absolute alcohol, 1-propanol, 2-propanol, 1-butanol, 1-heptanol, 1-hexanol, dioxane, acetone and ethyl acetate were recorded, respectively. The results showed that polarity of solvent affected λ_{\max} and absorbance value of chloranilic acid-water complexes. In solvent with higher polarity, the absorbance sensitivity of chloranilic acid-water complex became higher. In alcohol solvents, the absorption peak of chloranilic acid was at 440 nm, λ_{\max} of chloranilic acid-water complex moved to a longer wavelength at 530 nm with a shift of 90 nm. In acetone, ethyl acetate and dioxane, the absorbance sensitivity

was low and the maximum absorbance wavelength moved to shorter wavelength. It may be that the drawing electron effect of carbonyl group in acetone and ethyl acetate reduced electron supplement capability of solvents. In this experiment, absolute ethanol was used as solvent and the absorbance of chloranilic acid-water complex was measured at 530 nm.

According to the experimental procedure, the absorbance of complex was determined at 18-65°C. The results indicated that the reaction speed of chloranilic acid with water was not influenced by temperature. The absorbance of complex reached maximum in 10 min and kept unchanged in 3 h.

Ten aliquots of distilled water were tested in ethanol solvent to evaluate repeatability of the method. The result indicated that the relative standard deviation was 1.56%. The detection limit was $\varphi(\text{H}_2\text{O}) = 0.13\%$ (V/V) (3σ).

Different volumes of distilled water were added into 2.0 mL chloranilic acid solution, respectively, and the solution was diluted to volume with different alcohols. Absorbance at 530 nm was measured after 10 min. The results are shown in **Table 1**.

Figure 1 Absorption spectra of chloranilic acid in some organic solvents
 $c(\text{chloranilic acid}) = 4.0 \times 10^{-3} \text{ mol/L}$

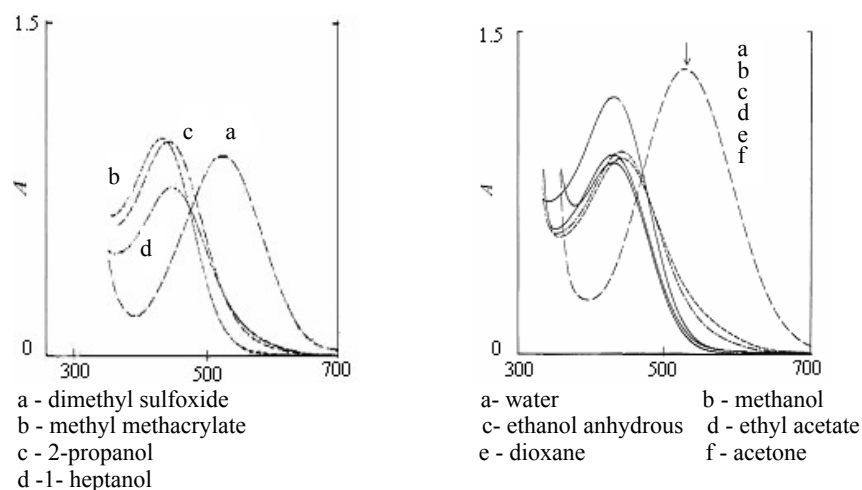


Table 1 Regression equations for standard curves in alcohols

Solvent	Regression equation	Correlation coefficient	Linear range [$\varphi(\text{H}_2\text{O})/\%$]
methanol	$A=0.018+19.7\varphi(\text{H}_2\text{O})$	0.9999	0~8.0
ethanol	$A=-0.005+25.4\varphi(\text{H}_2\text{O})$	0.9999	0~6.0
<i>n</i> -propyl alcohol	$A=0.041+22.4\varphi(\text{H}_2\text{O})$	0.9984	0~6.0
<i>n</i> -butyl alcohol	$A=-0.008+19.1\varphi(\text{H}_2\text{O})$	0.9982	0~6.0
glycol	$A=0.071+19.7\varphi(\text{H}_2\text{O})$	0.9992	0~6.0
glycerol	$A=-0.023+22.0\varphi(\text{H}_2\text{O})$	0.9981	0~6.0

Analytical Application

Determination of moisture content in ethanol

According to the experimental section, 5.0 mL ethanol (95.5 %) was added into a 10 mL flask, and 2.0 mL chloranilic acid ethanol solution was added, and then the mixture was diluted to volume with absolute ethanol. The absorbance of the solution was measured at 530 nm against the reagent blank. The moisture content in ethanol was 4.45 %, RSD = 1.6 %, the relative error $E_r = 1.0$ %; Two milliliters of chloranilic acid and 0.1 mL ~ 0.4 mL of distilled water were mixed, and diluted to volume with absolute ethanol. The absorbance of the solution was measured for recovery test at 530 nm against the reagent blank. The recoveries were 98.0 %-101.7 %.

Determination of moisture content in flour and in food flavoring

The test solution 8.0 mL was mixed with 2.0 mL chloranilic acid solution. The mixture was diluted to volume with absolute alcohol. The absorbance of the solution was measured at 530 nm against the reagent blank. The moisture of flour was determined with GB method⁴ simultaneously. The moisture content in flour was 10.82 %, RSD = 2.0%, E_r was 1.6 %. The recoveries were 98.0 %-102.0 %.

Moisture contents of 3 food flavoring were measured by the suggested method. The results were comparable with that from standard method⁴, E_r was 1.0 %-2.0 %. The recoveries were 97.0 %-101.0 %.

The experimental results indicated that the reaction of chloranilic acid with water could produce charge-transfer complex, it could be used not only to determine trace amount of water in alcohol, but also to determine trace amount of water in solid samples. This method is simple, reproducible and sensitive. The toxicity of reagent is low. No special appliance is needed. This method could be a efficient procedure to determine moisture in samples.

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