

Synthesis and Spectrophotometric Studies of 2-(1, 3, 4-Triazolylazo)-5-Diethylamino Phenol and 2-(5-Carboxy-1, 3, 4-Triazolylazo)-5-Diethylamino Phenol

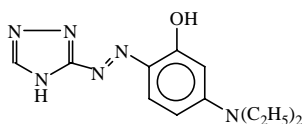
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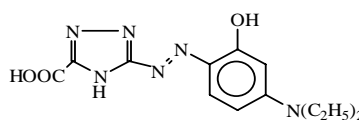
Abstract: In this paper, 2-(1, 3, 4-triazolylazo)-5-diethylamino phenol (TZAPN) and 2-(5-carboxy-1, 3, 4-triazolylazo)-5-diethylamino phenol (CTZAPN) were prepared, the protonation behaviour and the condition of spectrophotometric determination of cobalt with the reagents are reported. The results show that the new colour reagents react with cobalt to form a stable purple red complex (1:3). However, the complex formed could be changed into another species of stable absorptivity by addition of mineral acid (1+1). The method is highly selective and sensitive and has been applied to the direct determination of cobalt in some alloys with satisfactory results.

Keywords: Synthesis, triazolylazo reagent, spectrophotometry, cobalt.

In a search for new sensitive and selective organic reagents, a thorough study of some of the quinolyazo, pyridylazo compounds has been reported¹⁻⁵. But triazolylazo compounds have not been studied. In this paper, 2-(1, 3, 4-triazolylazo)-5-diethylamino phenol (TZAPN) and 2-(5-carboxy-1, 3, 4-triazolylazo)-5-diethylamino phenol (CTZAPN) were prepared, the conditions of this reaction with cobalt were studied. It was found that the reagents had high sensitivity and selectivity in the determination of microgram amounts of cobalt under the conditions established. The structures of the reagents are:



TZAPN



CTZAPN

Experimental

High-purity (99.99%) cobalt was dissolved in nitric acid (1+1). The solution was finally diluted to 10 mg/L. Ammonium acetate was used for pH7 adjustment. The

solutions (1+1) of mineral acids were made from high-purity sulphuric, hydrochloric, nitric and perchloric acids. Concentration of **TZAPN** or **CTZAPN** solutions was 1×10^{-3} mol/L, in ethanol. All other reagents were of A. R. grade. Carlo Erba 1106 elemental analyzer (Italy), UV-265Fw spectrophotometer (Japan). IR-408 spectrophotometer (Britain) and pHS-3C pH meter (China) were used for analysis.

Preparation of 2-(1, 3, 4-triazolylazo)-5-diethylamino phenol (**TZAPN**)

To a solution of 1.5 g (0.065 mol) of metal sodium in 30 ml of absolute ethanol, 2-amino-1, 3, 4-triazoly 4.2 g (0.050 mol) in 100 ml of anhydrous ether and 18 g (0.154 mol) of isopentyl nitrite were added, and the mixture was refluxed for 6 h. 3-N,N-diethylamino phenol 8 g (0.048 mol) in ethanol and hydrochloric acid (1+3) were added at 0-5°C until the mixture was slightly acidic and the deep red color appeared. Crude reddish brown crystals were formed upon dilution with water (200 ml), which were filtered off and washed with water and the crude material was recrystallized from ethanol-water.

Analysis: $C_{12}H_{16}N_6O$ found: 55.59% C, 6.23% H, 32.10% N; calculated: 55.37 % C, 6.20% H, 32.29% N; IR (KBr, ν / cm^{-1}): 1630 (N=N), 1530 (), 3500 (OH), 1200-1300 (C_2H_5); 1H NMR (ppm) δ_H : 1.1-1.2 (6H), 3.3-3.6 (4H), 6.4 (1H), 6.1 (2H), 7.5 (2H), 8.3 (1H); Reddish brown powder (m.p. 206°C).

The preparative method of 2-(5-carboxy-1, 3, 4-triazolylazo)-5-diethylamino phenol (**CTZAPN**) was similar to that for **TZAPN**.

Analysis: $C_{13}H_{16}N_6O_3$ found: 55.20% C, 5.12% H, 27.72% N; calculated: 55.31 % C, 5.30% H, 27.62% N; IR (KBr, ν / cm^{-1}): 1600-1610 (N=N), 1500 (), 2500-3500 (OH, COOH), 1720 (C=O), 1200 (C_2H_5); 1H NMR (ppm) δ_H : 1.1-1.2 (6H), 3.3-3.4 (4H), 6.2 (1H), 6.5 (1H), 7.5 (2H), 8.3 (1H), 11.7-12.2 (1H); Reddish brown powder (m.p. 252°C).

Protonation behaviour of the reagents

The reagents are insoluble in water, but soluble in various organic solvents including ethanol, acetone and dioxane. The **TZAPN** proton-dissociation constants have values of $pK_{a1}=7.4$ and $pK_{a2}=9.9$. The absorption spectra of the reagent at different pH values are shown in **Figure 1**. The **CTZAPN** proton-dissociation constants have values of $pK_{a1}=3.1$, $pK_{a2}=7.5$ and $pK_{a3}=9.6$. The absorption spectra of **CTZAPN** at different pH values are similar to those of **TZAPN**.

Cobalt was determined as follows: A suitable aliquot of sample solution containing up to 10 μ g of cobalt was transferred into flask and 2.0 ml solution of **TZAPN** or **CTZAPN** 1×10^{-3} mol/L was added, pH was adjusted to 7 with 5 ml of solution **NH₄Ac**. After 10 min, 5 ml of hydrochloric acid (1+1), or sulfuric acid (1+1) was added. The mixture was diluted to volume. The absorption of the cobalt complex was measured at 540 nm against a reagent blank with 1-cm cells.

Results and Discussion

Colour Reaction with Metal Ions

The coloured complexes are easily prepared by adding a few drops of a solution of **TZAPN** or **CTZAPN** in ethanol to solutions of the metal ions at pH7. However, the complex of cobalt can be changed to another species with stable absorptivity by addition of mineral acid (1+1), HCl, H₂SO₄, HNO₃ or HClO₄. Complexes of other ions were decomposed to the reagent upon addition of the acid, only palladium complex was not decomposed.

Figure 1. **TZAPN** Absorption spectra at different pH values **TZAPN** against H₂O blank [TZAPN] = 4×10^{-5} mol/L pH: 1, 3.2; 2, 4.0; 3, 5.0; 4, 6.0; 5, 7.0; 6, 8.0; 7, 9.0; 8, 10.0; 9, 11.0; 10, 12.0; 11, 13.0.

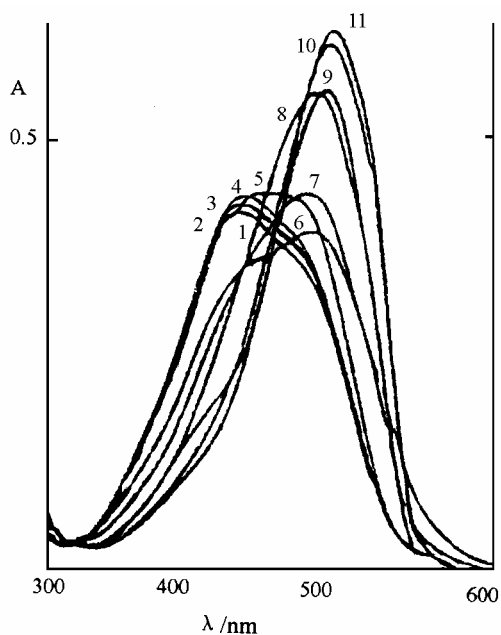
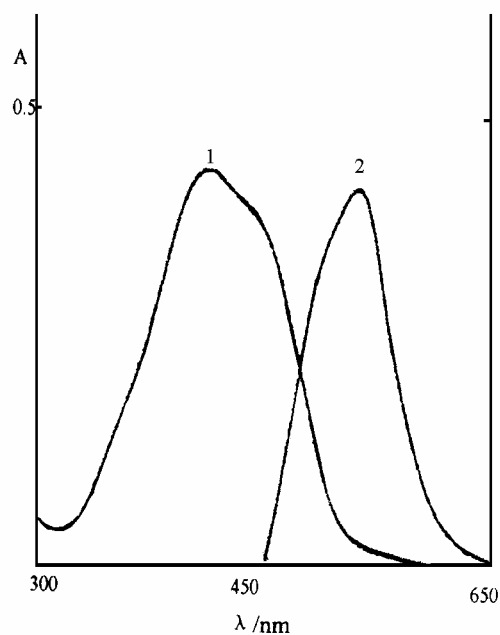


Figure 2. Absorbance curves of **TZAPN** and its cobalt complex in 1.2 M hydrochloric acid [TZAPN] = 4×10^{-5} mol/L, [Co²⁺] = 6.79×10^{-6} mol/L 1). **TZAPN** against H₂O blank. 2). Complex against **TZAPN** blank



The absorption curves of **TZAPN** and its cobalt complex in 1.2 mol/L hydrochloric acid are shown in **Figure 2**. The absorption maximum of **TZAPN** and **CTZAPN** are at 430 nm, but the complexes at 540 nm, $\Delta \lambda = 110$ nm.

Actually, 0.6 ml of 1×10^{-3} mol/L **TZAPN** or **CTZAPN** solution is sufficient to complex 10 μ g of cobalt.

The color was formed in 10 min at room temperature. The absorbance was stable for at least one day.

Beer's law is obeyed in the range of 0 – 0.4 mg/L of cobalt. The apparent molar

absorptivity is $6.23 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (TZAPN) and $5.7 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (CTZAPN) at 540 nm.

Numerous cations and anions were examined with the above mentioned method. The result showed, the most cations and anions have no effect at milligrams level, but palladium interferes with the determination, so the method is extremely selective and sensitive.

The empirical formula of the complexes were studied by the continuous and mole-ratio methods. The curves obtained indicate the formation of a complex 1:3 (metal: reagent) in the presence of NH_4Ac (pH 7.0) and 1.2 mol/L hydrochloric acid.

A sample of alloy (1 g) was dissolved in the usual way and cobalt was determined on an aliquot of the solution. Some results are shown in **Table 1**.

Table 1. Determination of cobalt in some alloys (n=6)

Alloy	Certificate (%)	found (%)	RSD (%)
35CrMoV-250	0.012	0.0119	2.4
38CrMoAl-251	0.011	0.0108	2.0

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