Synthesis of a new chromogenic reagent, 1-(p-azophenyl)-3-(2-thiazol)triazene, and its application to determination of zinc(II)

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Synthesis and characterization of a new chromogenic reagent, 1-(p-azophenyl)-3-(2-thiazol)triazene (APTT), are described. The reagent has been used for spectrophotometric determination of zinc(II). APTT forms a red colored complex with zinc(II) in alkaline medium in the presence of Triton X-100. The optimum conditions for the colour reaction have been described. The molar absorptivity of the complex is $9.6 \times 10^3$ l.mol$^{-1}$ cm$^{-1}$ at 543 nm. Beer's law is obeyed over the range 0 - 24 µg/25ml Zn(II). Interference due to several ions has been studied. The recommended method has been applied to the determination of zinc(II) in aluminum alloys.

Zinc(II) is an essential trace element for human beings. Several spectrophotometric methods for determination of zinc(II) have been described$^{1-7}$. However, most of these have poor selectivity, and require prior separation.

In the present note, the synthesis, physico-chemical characteristics and application of a new chromogenic reagent, 1-(p-azophenyl)-3-(2-thiazol)triazene (APTT), have been reported. It was observed that APTT showed high selectivity and sensitivity for determination of zinc(II). The present note describes a method for the determination of Zn(II) using APTT in the presence of Triton X-100 at pH 13.0-14.0. The method has been used for direct determination of zinc(II) in alloys, and the results were found to be in good agreement with the certified values.

Experimental

A WFZ-25 UV-vis spectrophotometer (Tian jing, China), PHS-2 model pH-meter (Shang hai, China) and 721 model spectrophotometer (Shang hai, China) were used.

Stock solution containing 1.0mg/ml Zn(II) was prepared by dissolving 0.1000g pure zinc (99.99%) in 20 ml of (1:1) HCl solution and diluting to 100 ml with distilled water. Working solution (10.0µg/ml Zn(II) ) was prepared by suitable dilution with distilled water. Buffer solution was prepared by dissolving 76g tetraborate and 109 sodium hydroxide in distilled water, diluting to 1 litre with distilled water. The pH was adjusted with HCl and 1M NaOH. Triton X-100 (1% aqueous) and 0.03% (w/v) solution of APTT in dimethylformamide was used.

Synthesis of APTT

$p$-Aminoazobenzene (5.0g) was slowly dissolved in 15 ml of conc. sulphuric acid with constant stirring and cooled to below 10°C. Sodium nitrite (1.9g) was dissolved in 15 ml of conc. sulphuric acid with stirring, and heated (temp<°C) until sodium nitrite dissolved completely, and then cooled to below 10°C. The two solutions were mixed well with stirring, and kept in a refrigerator for 2 h to get the diazotate. The diazotate was poured into a 1 litre beaker with 300 ml ice-water, and to it a 15% of sodium carbonate solution was added dropwise with stirring to adjust the pH between 3 and 5. Then 30 ml of 15% sulphuric acid containing 2.5 g of 2-aminothiazole was added with constant stirring. After mixing well, 10g of sodium acetate was added, and the solution was kept in the refrigerator overnight. The brown crystals which precipitated were filtered off and washed with ethanol-water. The product was dissolved in dimethylformamide and recrystallized from water to give red-brown needles. [m.p. 181-182°C; yield 64%; Found(%): C 59.26, H 4.11, N 26.58; ClsH12N6S requires(%): C 58.42, H 3.92, N 27.25; IR (KBr cm$^{-1}$) - NH (3415), C=C of benzene (1598,1494), N=N (1440,1184); NMR(6,ppm): NH(3.67), benzene H(7.46,8.06), thiazole H(5.9,5.1).]
General procedure

An aliquot containing up to 24 μg of zinc(II) was taken in a 25-ml standard flask. To it, was added 2.0 ml buffer solution of pH 13.5, APTT solution (0.03%, 2.0 ml) and Triton X-100 solution (1%, 2.0 ml), mixed well and diluted to the mark with distilled water. The absorbance was measured at 545 nm in a 1 cm cell against reagent blank.

Results and discussion

APTT was found to be insoluble in water, carbon tetrachloride and cyclohexane and sparingly soluble in ethanol, benzene, toluene, formic acid, acetone, chloroform, dimethylsulphoxide, ethyl acetate, methyl isobutyl ketone and absolute ether. It was soluble in dioxane and dimethylformamide. In the presence of Triton X-100, the colour of APTT solution was yellow at pH<5, orange at pH 5-10, and red at pH >14, the maximum absorptions being at 400, 455 and 500 nm respectively.

The absorption spectra of the red zinc(II) complex and of APTT itself in aqueous alkaline medium shows that λmax of the complex has a red shift of 82 nm relative to that of APTT (545 and 463 nm respectively). The absorbance of the complex was found to be maximum and constant at pH 13.0-14.0. Further experiments were therefore carried out at pH 13.5.

It was found that anionic and non-ionic surfactants enhanced the colour considerably and improved solubility of the complex, while cationic and amphoteric surfactants had very little effect. The absorbance of the complex was found to be maximum and constant on addition of 1.5-5.0 ml of 1% Triton X-100; 2.0 ml of 1% Triton X-100 was used in further studies.

For estimation of 10 μg Zn(II), 1.5-4.0 ml of 0.3% APTT solution was found to be sufficient. Hence, 2.0 ml of the reagent is recommended. The colour development of the complex was found to be complete in 15 min. The colour was found to be stable for at least 48 h. Beer’s law was obeyed over the range 0-24 μg/25 ml Zn(II). The linear formula is:

$$A = 0.04893m + 0.01955 \quad (m=\text{conc of zinc(μg)})$$

The molar absorptivity of the complex was found to be 9.6×10^4 1 mol^-1 cm^-1.

The mole-ratio and continuous variation methods indicated the Zn(II): reagent ratio to be 1:3. By the equilibrium shift method the apparent stability constant was found to be 1.8×10^16.

Effect of diverse ions

The effect of forty cations and anions on the determination of 10 μg Zn(II) was studied. A change of ±5% in absorbance was set as the tolerance limit. The tolerance limits (in mg) are given in parentheses:

- SiO₃²⁻ (5), Ca²⁺ (3), NH₄⁺ (2), Al³⁺ (1), Sn²⁺ (1), Bi³⁺ (1), Sn²⁺ (0.2), Zr⁴⁺ (0.3), As⁺ (0.2), Pb⁴⁺ (0.1), Mn²⁺ (0.1), Be²⁺ (0.1), Mg²⁺ (0.06), Fe³⁺ (0.05), Ti⁴⁺ (0.05), Au³⁺ (0.05), Tl⁴⁺ (0.03), Co²⁺ (0.02), Ag⁺ (0.01), Pb⁻ (0.01), Cr³⁺ (0.01), Ni²⁺ (0.01), Cl⁻ (15), NO₃⁻ (10), Br⁻ (10), NO₂⁻ (10), F⁻ (10), SO₄²⁻ (10), SO₃²⁻ (10), C₂O₄²⁻ (20), I⁻ (5), S₂O₃²⁻ (1), SCN⁻ (200), H₂O₂ (200), CH₃COO⁻ (20), citrate (80), ascorbic acid (2), dimethylglyoxime (20), phenanthroline (40), tartrate (50), sulphosalicylic acid (100), thiourea (100). Interference due to Cd(II), Hg(II) and Cu(II) was removed by adding sulphosalicylic acid and NH₄SCN as masking agent.

Analysis of alloys

A sample of aluminium alloy (0.5-1.0 g) was decomposed in a 100 ml beaker with 10 ml of 1:1 HCl, and then heated to boiling for min. Hot water (30 ml) was added, and the contents were heated to boiling. After cooling, the insoluble material was filtered off and washed. The filtrate was transferred to a 250 ml standard flask, and diluted up to the mark with distilled water and mixed well. An aliquot (2.0 ml) of this solution was transferred to a 25 ml standard flask, and 2.0 ml of 5% sodium fluoride was added. The amount of Zn(II) was estimated by the
recommended procedure. The results for analysis of two aluminium alloy samples are given in Table 1. The coefficient of variation are 3.7% and 1.2% for samples (seven determinations) respectively.

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References


