1-(4-Antipyrine)-3-(2,4,6-tribromophenyl)triazene and its Chromogenic Reaction with Cadmium

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(Received: 16 March 2013;

Accepted: 14 November 2013)

AJC-14403

The chromogenic reagent 1-(4-antipyrine)-3-(2,4,6-tribromophenyl)triazene (ATTBPT) was synthesized and its colour reaction with cadmium has been investigated in the presence of the microemulsion OP. In the Na₂B₄O₇-NaOH medium of pH 10.5, the reagent reacts with Cd(II) to form an orange-yellow complex with a molar ratio of 2:1. The complex has a maximum absorption at 460 nm. The apparent molar absorptivity of the complex was $1.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Beer's law was obeyed in the range of 0-12 µg/10 mL for cadmium. The method has been applied to the direct determination of cadmium in real samples with satisfactory results.

Key Words: 1-(4-Antipyrine)-3-(2,4,6-tribromophenyl)triazene, Cadmium.

INTRODUCTION

The structure of three triazenes reagents can be expressed as R¹-1N=2N-3NH-R², is a kind of organic reagent widely used in photometric analysis of cadmium. The method has the advantages of high sensitivity, good selectivity and synthesized easily¹. The apparent molar absorption coefficient by spectrophotometric analysis method established for the determination of some metal ions is in generally 10⁵ orders of magnitude, which relative to some other photometric analysis reagents have a high colour sensitivity². There are many reports about three new triazene reagents in recent years, not only in the determination of Cd²⁺, Mg²⁺, Hg²⁺, Ni²⁺ ions with satisfactory results and used for the determination of anionic, cationic surfactant also achieved good results. Cadmium is not the essential elements of human. The cadmium is absorbed in human body from the external environment, mainly accumulated through food, water and air into the body. Cadmium can stimulate the respiratory tract, long-term exposure can cause anosmia, gingival macular or become yellow ring, cadmium compounds are not easy to intestinal absorption, but the being absorbed into the body through the respiratory, stored in the liver or kidney and damaged them. Cadmium can lead to osteoporosis and softening. Method for the determination of cadmium in environmental monitoring *e.g.*, spectrophotometry, anodic stripping voltammetry and polarography and so on³. The chromogenic agent which spectrophotometric method commonly used include for class A, pyridine^{4,5}, pyridine azo^{6,7}, three triazenes, fluorescence ketone, *etc*⁸. This work

described the synthesis of a new chromogenic reagent 1-(4-antipyrine)-3-(2,4,6-tribromophenyl)triazene (ATTBPT), studied on the condition of colour reaction of the reagent and cadmium and being applied to determine cadmium in environmental water samples. On this basis, established the spectrophotometric on determination method of determination of trace cadmium.

EXPERIMENTAL

UNICO WFJ 7200 spectrophotometer (Shanghai Analytical Instrument Factory V); pH-3C pH meter (Shanghai Precision kore Magnetic Co., Ltd.). Cadmium(II) standard solution (10 µg/mL): weigh 0.21032 g cadmium nitrate. In a 50 mL beaker, add a small amount of distilled water to dissolve it, shift-in a 100 mL volumetric flask, with distilled water dilute to volume with distilled water, Stir it. This is the 1 mg/mL cadmium standard stock solution, when using it, it is diluted to 10 µg/mL standard working solution. Borax-NaOH (Na₂B₄O₇-NaOH) buffer solution: pH 10.5, 0.05 mol/L of Na₂B₄O₇ solution with 200g/L NaOH solution tune to the required value in pH meter; ATTBPT solution: weighed 0.25 g colour reagent, dissolved with ethanol then moved into 250 mL volumetric flask, diluted with ethanol to scale and shake.

Reagents all above were of analytical grade, water used in the test was double distilled water.

Synthesis and test of reagents

Diazotization and coupling reaction: 3 mL aniline is dissolved in 100 mL acetic acid. The 4 mL of Br₂ elements

dissolved in 30 mL acetic acid, Then drop in acetic acid solution into the drip of aniline in the stirring and ice, immediately produce a white precipitate, Mixing reaction 2 h then filtering, With 1:1 acetic acid and water washing, dry to receive white powder 7 g, m.p.73 °C^o.

Take 1 g of 4-antipyrine dissolved in 10 mL 6 mol/L hydrochloric acid and cooling into the ice bath. Another take 0.35 g NaNO₂ dissolved in a small amount of water and slowly added into 4-amino antipyrine hydrochloric acid solution, stirring reaction, Until KI-starch paper unchanged blue and obtain clear orange red diazonium salt solution.

Take 1.7 g (0.01 mol) 2,4,6-tribromo aniline to dissolve in 20 mL acetone, slowly dripped into the diazonium salt solution, Immediately precipitate orange precipitate, adjust the pH 5-6 by saturated Na₂CO₃ solution. Remove the ice bath, reaction temperature 2 h, adjust pH to 8, standing overnight, filter to obtain red brown powder.

The main reaction equation as follows:

Fig. 1. Main coupling reaction equations

Purification and identification: Dissolved the crude product in an appropriate amount of ethanol-water, recrystallized 2 times and obtained a red-brown product, its melting point is 145 °C. Element analysis results to the experimental value (theoretical value) is expressed as: C 37.44 (37.50), H 2.62 (2.57), N 12.78 (12.87).

IR spectra data of product (KBr tablet, cm⁻¹) as: 3426 cm⁻¹ is the stretching vibration absorption peak for N-H; 3308 cm⁻¹, 3082 cm⁻¹ is the stretching vibration absorption peak for C-H in benzene ring; 1731 cm⁻¹ is the asymmetric stretching vibration absorption peak for C=O; 1562, 1542 and 1453 cm⁻¹ are stretching vibration absorption peak for the benzene ring framework (*i.e.*, 1532 cm⁻¹ is the stretching vibration absorption peak for C=C; 1619 cm⁻¹ is the stretching vibration absorption peak for N=N); 667, 545 and 485 cm⁻¹ are the stretching vibration absorption peak for the C-Br.

RESULTS AND DISCUSSION

Absorption curve: The absorption spectra of the reagent ATTBPT and Cd(II)-ATTBPT complex were shown in Fig. 2. It was evident that the maximum absorption of ATTBPT was at 390 nm while that of the Cd(II)-ATTBPT and Cd(II)-ATTBPT-OP complex were at 458 and 460 nm. The contrast of the two peaks was 70 nm and can be obviously distinguished. So the absorption peak 460 nm was chosen as determination wavelength.

Fig. 2. Absorption spectra. 1. Reagent blank/water, 2.10 μg Cd(II)-ATTBPT/reagent blank, 3.10 μg Cd(II)-Triton X-100-ATTBPT/reagent blank

Effect of system acidity: A series of solution with different values of pH were prepared to determine the influence of pH solutions (HCl, H₂SO₄, Na₂SO₃, H₃PO₄, NaOH, HOAc-NaOAc, H₃BO₃-NaOH, NH₃·H₂O-NH₄Cl, Na₂B₄O₇-HCl, Na₂B₄O₇-NaOH) on the absorbance of the complex. The results show that the complex was almost unchanged in the pH range of 9.6-10.8, therefore the buffer solution of Na₂B₄O₇-NaOH with pH 10.5. From 1.6-2.4 mL the absorbance of the complex was largest and kept constant, in this study 2 mL was chosen.

Effect of amount of reagent ATTBPT: With the increase of the volume of ATTBPT solution, the absorbance increased rapidly, followed by remaining almost at a maximum and unchanged. In 10 mL of solution, the addition of 1.2-1.8 mL solution gave maximum and constant absorbance, thus an addition of 1.5 mL ATTBPT solution was recommended.

Surfactant types and the range of the amount: Effect of the surfactants, it was found that in the presence of cationic, anionic and nonionic surfactant all have good solubilization on system, but non-ionic surfactants has the most significant effect on the sensitizing of system. In this study, it was found that OP solution has better stability, solubility and sensitivity. The amount of it was in the range of 1.2-1.8 mL, absorbance was the maximum and stability, so chose 1.5 mL.

Influence of reagent adding order and colour reaction time and the stability of complex: The proposed method was used for determination the effect of the order of joining the reagent on system absorbance, the results shown the effect of absorbance was largest and accorded the experimental method was better. The maximum and constant absorbance was obtained After 10 min and keep unchanged for 8 h.

Determination of complex components: By the mole ratio, continuous variation and mobile equilibrium method the composition of the complex was determined to be n(Cd(II)): n(ATTBPT) = 1:2 as shown in Figs. 3 and 4.

Influence of coexisting ions: Determined 10 μg Cd(II) according to experimental method, the relative error ≤ ± 5 %, the allowed amount of coexisting ions (μg): K⁺ (50000), Na⁺ (40000), Mg²⁺, Fe²⁺ (1800), Ba²⁺ (1200), Ca²⁺ (800), Al³⁺ (600),

TABLE-1
 ANALYTICAL RESULTS OF Cd(II) IN SAMPLES (Cd(II), $\mu\text{g}/10\text{ mL}$) $n = 6$

Example	Recommended values AAS ($\mu\text{g}/\text{mL}$)	Found by the proposed method	Average	RSD (%)	Added Co (μg)	Recovery ratio (%)
River water 1	1.02	0.912, 0.961, 0.874, 0.954, 0.945, 0.959	0.934	1.10	1.00	—
River water 2	1.08	0.915, 0.974, 0.903, 0.885, 0.989, 0.951	0.936	1.28	1.00	98.4

Fig. 3. Molar ratio method

Fig. 4. Continuous change method

Ni^{2+} , Sn^{4+} (500), Ge^{2+} (400), Co^{2+} (80), Cr (f!) (60), In^{3+} (45), Cu^{2+} (35), Zn^{2+} , Pb^{2+} (30), Mo^{6+} (28), Pd^{2+} , Mn^{2+} (25), Pt^{2+} (22), Bi^{3+} , Ga^{3+} (20), W^{3+} , Ag^{+} (15), Sb^{3+} , Ti(IV) (12), Ru^{3+} (10), Rh^{3+} (3), Zr(IV) (2), Os(III) , V(V) (1.5), triethanolamine (4000), tartrate (3000), citrate (2500). SO_4^{2-} , PO_4^{3-} , NO_3^- , NO_2^- and EDTA have no influence on the determination of Cd (II). Experimental results showed that interference of 0.8 mg Fe^{3+}

could be eliminated efficiently and by addition of 2 mL of 1 % ascorbic acid solution and 0.3 mg Hg^{2+} could be eliminated efficiently and by addition of 0.5 mL 1 % EDTA. therefore the system exhibits good selectivity. As for other coexisting ions present in low content, appropriate amount of sodium pyrophosphate and sodium fluoride can be used as masking reagent.

Calibration curve and sensitivity: Prepared a series of 10 mL colorimetric tubes, followed by adding a certain amount of Cd(II) standard working solution for colour reaction determination, determined by experimental methods, Beer's law was obeyed in the range of 0.2-4.2 $\mu\text{g}/10\text{ mL}$ for Cd(II), linear regression equation: $A = 0.0152p + 0.0081$, correlation coefficient $r = 0.9999$, in the prepared experimental condition, measured the apparent molar absorption coefficient ϵ was $1.7 \times 10^4\text{ L mol}^{-1}\text{ cm}^{-1}$, the detection limit was 0.06 mg/L .

Sample analysis: Qiangwei water 2 couples, 1000 each for mL, HNO_3 , H_2O digestion and concentrated, add 2 mL mixed masking agent (100 mg sodium pyrophosphate + 50 mg thiourea + 20 mg sodium citrate). Colour by experimental methods and determination of absorbance, at the same time to do standard addition recovery experiment, calculate the Cd(II) content of the sample, the sample results in Table-1.

Conclusion

The method has been used for the determination of trace Cd(II) in water with satisfactory results and the result was in accordance with that of the atomic absorption spectrometry method.

REFERENCES

- Q.-H. Guo, Y.-Y. Zhou, H. Zou, C. Tai, X.-X. Gu and Y.-X. Wang, *Metallurgical Anal.*, **20**, 23 (2003).
- L. Xu and Z.-Y. Hu, *Shanxi Chem. Ind.*, **37**, 28 (2008).
- B.-C. Wu and S.-H. Yu, *Phys. Testing Chem. Anal. B (Chem. Anal.)*, **561**, 40 (2004).
- B.-C. Liu, S. Zhao and Z. Song, *Chem. Reagent*, **279**, 26 (2004).
- S.-H. Yu, S.-F. Chen and B. Wang, *Metallurgical Anal.*, **11**, 22 (2002).
- G.-H. Wang, *Chin. J. Anal. Chem.*, **1357**, 29 (2001).
- J.-K. Wu, S.-H. Yu and L.-S. Wang, *Chin. J. Anal. Lab.*, **64**, 24 (2005).
- Z.-G. Zhang, *Metallurgical Anal.*, **31**, 18 (1998).
- M.-H. Yang and Y. Wang, *J. Lishui Teachers College*, **19**, 23 (2001).