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# Colour Reaction of *p*-Acetylchlorophosphonazo with Strontium(II) and Analytical Application

QING-ZHOU ZHAI

Research Center for Nanotechnology, Changchun University of Science and Technology, 7186 Weixing Road, Changchun 130022, Jilin Province, P.R. China

Corresponding author: Fax: +86 431 85383815; Tel: +86 431 85583118; E-mail: zhaiqingzhou@163.com, zhaiqingzhou@hotmail.com

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A simple and sensitive spectrophotometric method for the determination of strontium has been developed using *p*-acetylchlorophosphonazo (CPA*p*A) as chromogenic agent and optimum reaction conditions along with analytical properties parameters have been established. CPA*p*A with strontium(II) forms a blue complex in $CH_3COOH$-$CH_3COONa$ buffer solution at pH = 3.5. At maximum absorption wavelength of the complex of 600 nm, absorbance being determined, a good linear relationship is presented over the range 1-20 μg of strontium(II) in 10 mL with a correlation coefficient of 0.9996. Its regression equation is: A = 0.0499C (C: μg/10 mL) + 0.0211. The apparent molar absorption coefficient of the method is $\varepsilon_{660\,nm} = 4.45 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ and its detection limit is 0.126 μg/mL. The composition of complex is $n_{(CPAPA)} : n_{Sr}{}^{2+} = 2:1$ determined respectively by molar ratio method and the equimolar continuous variation method. The method has been successfully applied to the determination of strontium content in KCl and $Na_2SO_4$ chemical reagents. The results were compared favourably with those obtained by atomic absorption spectrometric method.

**Key Words: *p*-Acetylchlorophosphonazo, Strontium, Spectrophotometry.**

## INTRODUCTION

Strontium is a necessary microamount element for human body. If strontium lacks in human body, many disadvantageous symptoms cause. These symptoms include metabolism foul-up in body and at the same time extremity and body lacks force and virtual sweat comes out and the growth of bones slows. The lack of strontium can also bring osseous severe after effect, *etc*. In addition,when strontium in human body is excessive, gentle alimentary canal reaction can appear such as naupathia, discomfort of stomach, *etc*. It can also bring an egregious rapidness of bones growth, behaving that arthrosis is thick and large and aching and at a grave time bones are deformable and flimsy and muscles shrink and anaemia appears, *etc*. Analysis of strontium content has a very important significance in medicine, geology domain, *etc*.[1]. At present, in the methods for the determination of strontium for the normal amount of strontium titration method, gravimetric method is used[2]. For micro and trace amount of strontium, atomic absorption spectrometry (AAS)[3], inductively coupled plasma-mass spectrometry (ICP-MS)[4], inductively coupled plasma-atomic emission spectrometry (ICP-AES)[1], atomic fluorometric spectrometry (AFS)[1] and spectrophotometry, *etc*. Spectrophotometric determination of strontium has the advantages of operation simplicity, cheap instrument price, *etc*., which caused people's great interests[5,6]. In recent years, although some spectrophotometric methods for the determination of strontium have been already proposed and the chrmogenic agents dealt with arsenazo III[5], xylenol orange[6], *etc*., selectivity of the methods is poor. Thus, establishment of a new spectrophotometric method for the determination of strontium is still an interesting groping study.

This article uses *p*-acetylchlorophosphonazo (CPA*p*A) as a chromogenic agent and develops a spectrophotometric method for the determination of strontium. Chemically *p*-acetylchloro-phosphonazo is 2-(4-acetylphenyl)azo-6-(4-chloro-2-phosphonophenylazo)-4,5-dihydroxy-2,7-naphthalene disufonic acid (Fig. 1):

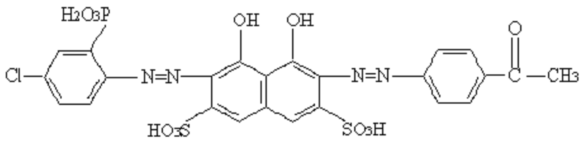

Fig. 1. Molecular structure of CPA*p*A

It can be known from Fig. 1 that the aromatic ring in CPA*p*A carries -OH, $-SO_3H$ and $-PO_3H_2$ and multiligands containing N, O. The reagent has stronger complex ability and can form the complexes of water-solubility with metal ions. This paper investigated the colour reaction of the reagent with strontium(II) and developed a simple, fast and sensitive spectrophotometric method for the determination of strontium. The proposed method has been satisfactorily applied to the determination of the strontium contents in chemicals KCl and $Na_2SO_4$.

## EXPERIMENTAL

***p*-Acetylchlorophosphonazo(CPA*p*A):** $1.46 \times 10^{-3}$ mol/L aqueous solution. $Sr^{2+}$ standard solution: 0.1685 g of $SrCO_3$ (Beijing Chemical Plant, China) was placed in 30 mL of distilled water. 1 mL of concentrated hydrochloric acid (Beijing Chemical Plant, China) was carefully added to dissolve it. After the mixture was stirred to eliminate $CO_2$, water was used to dilute to 100 mL and 1 mg/mL stock solution of $Sr^{2+}$ was obtained. The working solution was obtained by dilution of the stock solution with distilled water. Its mass concentration was 6 µg/mL. pH 3.5 $CH_3COOH$-$CH_3COONa$ buffer solution. All the reagents used in this study were of analytical grade. Distilled water was used throughout the experiment.

A 722S spectrophotometer (Shanghai Linggunag Technique Co. Ltd., China) equipped with 1.0 cm cell was used for measuring the absorbance.

In a 10-mL volumetric flask, 12 µg of $Sr^{2+}$ working solution, 3.0 mL of a $CH_3COOH$-$CH_3COONa$ buffer solution of pH 3.5, 2.0 mL of $1.46 \times 10^{-3}$ mol/L CPA*p*A solution was added in turn. The solution was diluted to the mark with water, shaken well. After 15 min, the absorbance of colour solution was measured at 660 nm with 1 cm cell against reagent blank.

## RESULTS AND DISCUSSION

**Absorption spectra of complex:** CPA*p*A and $Sr^{2+}$ form a blue complex in the acid medium. Over the range of 400-800 nm wavelength, absorption spectrum of the complex was drawn. The results showed (Fig. 2) that the complex has a maximum absorption peak at 660 nm. The maximum absorption peak of reagent blank is 580 nm. Therefore, 660 nm was selected to perform absorbance measurement.

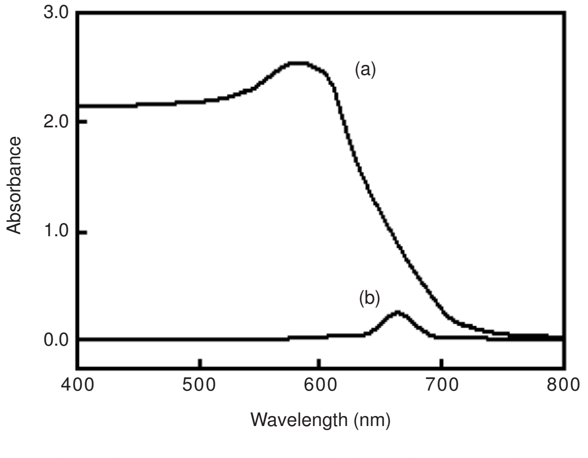

Fig. 2. Absorption spectra: (a) Regeant blank (against water); (b) complex (against reagent blank); $[Sr^{2+}] = 1.37 \times 10^{-5}$ mol/L; [CPA*p*A] = $2.92 \times 10^{-4}$ mol/L; pH = 3.5

**Optimization of experimental conditions:** Effects of different acidic medium on the reaction were reviewed, respectively. Under the conditions that other experimental conditions were kept optimum, different buffering systems on the reaction were investigated using pH = 1.8, 2.8, 3.1, 3.3, 3.5, 3.8, 4.1, 5.0, 6.0, 8.0, 9.2, 10.0, respectively. The results indicated that the absorbance was the largest over the range of pH = 3.3-3.8 and the reaction sensitivity was the highest. The present study selected pH = 3.5 of HAc-NaAc buffer solution as the reaction medium. When amount of buffer solution was between 2.5-3.5 mL, the absorbance was maximum. 3.0 mL of the buffer solution was used for adjusting of the pH of solutions.

The experimental results of CPA*p*A amount indicated that amount of the chromogenic agent was in the range of 1.8-2.2 mL, the absorbance was largest and steady. Therefore, a volume of 2 mL of 1 g/L CPA*p*A solution was selected for further studies.

Order of addition reagent has not effect on the experimental results of complex formation. The order employed in the experiment was: $Sr^{2+}$ + ($CH_3COOH$-$CH_3COONa$) + CPA*p*A.

**Composition and stability of complex:** CPA*p*A and $Sr^{2+}$ form a blue complex in the acid medium. Molar ratio method and equal molar continuous variation method were respectively used to determine the composition ratio of complex to be $n_{Sr^{2+}}:n_{DBC\text{-}CPA} = 1:2$.

At room temperature, the complex of CPA*p*A and $Sr^{2+}$ forms within 15 min and the abosrbance reached a maximum. Within 20 h a change of absorbance was less than 5 % and the complex kept stable.

**Analytical characteristics:** Under the optimum experimental conditions described above, working curve was established from spectrophotometric measurements performed. Table-1 summarizes the analytical characteristics of the method, including regression equation, linear range and limit of detection and reproducibility. The limit of detection, defined as $C_L = 3S_b/m$, where $C_L$, $S_b$ and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was 0.126 µg/mL. The relative standard deviation (RSD) for eleven parallel determinations of 1.2 µg/mL of $Sr^{2+}$ was 1.21 %.

TABLE- 1
ANALYTICAL FEATURES OF THE PPROPOSED METHOD

| | |
|---|---|
| Linear range (µg/10 mL) | 1-20 |
| Regression equation | A = 0.0499C (C: µg/10 mL) + 0.0211, r = 0.9996 |
| Limit of detection ($3S_b/m$ blank, µg/mL) (n = 11) | 0.126 |
| Reproducibility (RSD, %) (n = 11) | 1.21 |

**Interference studies:** The effect of different ions on the determination of 10 µg $Sr^{2+}$ in a volume of 10 mL by the proposed method was studied. An ion was considered to be an interferent when it caused a variation greater than ± 5 % in the absorbance of the sample. Allowable amounts of the co-existing ions (mass multiple, m/m) are as follows: $NO_3^-$, (400); $Cl^-$(160); $Ni^{2+}$, $Si^{4+}$, $I^-$, $Br^-$, $NO_2^-$ (10); $Li^+$, $Hg^{2+}$, $B^{3+}$, $SO_3^{2-}$ (50); $S^{2-}$ (10); $Cd^{2+}$, $PO_4^{3-}$ (10); $Fe^{2+}$, $CO_3^{2-}$ (5); $F^-$ (2); $Cr^{3+}$, $Cr^{6+}$, $Mo^{6+}$ (1); $Mg^{2+}$ (0.5); $Ag^+$, $Zn^{2+}$, $Y^{3+}$, $Zr^{4+}$, $W^{6+}$ (0.5); $Hf^{4+}$ (0.25); $Mn^{2+}$, $Al^{3+}$, $Fe^{3+}$ (0.2); $Ba^{2+}$, $Pb^{2+}$, $Ti^{4+}$, $Th^{4+}$ (0.1); $Ca^{2+}$ (0.1); $Bi^{3+}$, $Be^{2+}$ (0.05); $Ce^{4+}$ (0.02); $Cu^{2+}$, $La^{3+}$ (0.01).

TABLE-2
ANALYTICAL RESULTS OF SAMPLES (n = 13)

| Sample | Found (ng/g) | Average (µg/g) | Relative standard deviation (%) | Added (ng/mL) | Recovered (ng/mL) | Recovery (%) | Atomic absorption spectrometric method (µg/g) |
|---|---|---|---|---|---|---|---|
| KCl | 2.79, 2.86, 2.67, 2.77, 2.76, 2.63, 2.64, 2.89, 2.84, 2.76, 2.74, 2.85, 2.81 | 2.75 | 3.64 | 0.5000 | 0.4816 | 96.32 | 2.75 |
| $Na_2SO_4$ | 15.3, 15.4, 15.9, 15.4, 15.7, 15.9, 15.9, 16.7, 16.7, 16.7, 15.9, 15.9, 15.3 | 15.9 | 0.51 | 0.3000 | 0..047 | 101.59 | 15.7 |

**Sample analysis:** 1 g of KCl or $Na_2SO_4$ were accurately weighed, respectively and was dissolved with water. The solution was diluted to the mark in 25-mL volumetric flask. 2 mL of the solution was taken and determined according to the general procedure. Then, revovery experiments were made and atomic absorption spectrometry was used for comparison. The results are given in Table-2. It can be seen that the analytical results of the method were in accord with those of the contrast method atomic absorption spectrometry. The addition standard recoveries were 96.32-101.59 % and the relative standard deviations of thirteen parallel determinations were 0.51-3.64 %. The analytical results were satisfactory.

## Conclusion

This work reports the use of CPA*p*A as chromogenic agent to establish a spectrophotometric method for the determination of strontium(II) and satisfactorily determined the strontium contents in $Na_2SO_4$ and KCl. $n_{(CPAPA)}:n_{Sr}^{2+} = 2:1$ was determined by molar ratio method and equal molar continuous variation method. Beer's law is obeyed over the range of 1-20 µg of $Sr^{2+}$ in a system of 10 mL at 660 nm. The apparent molar absorptivity of method is $\varepsilon_{660\ nm} = 4.45 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ and the limit of detection is 0.126 µg/mL.

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