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DETERMINATION OF PHOSPHORUS BY PHOSPHORUS MOLYBDENUM BLUE SPECTROPHOTOMETRY BY BISMUTH ANTIMONY SENSITIZATION

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ABSTRACT. The determination of phosphorus in rain water is of great significance. In this paper the optimum conditions of phosphorus molybdenum blue spectrophotometric method for the determination of phosphorus content were obtained. At the maximum absorption wavelength 690 nm, the apparent molar absorptivity is $\varepsilon_{690\ nm} = 1.44 \times 10^4 L \cdot mol^{-1} \cdot cm^{-1}$. Beer's law is followed over the range of 0.02-1.8 $\mu g \cdot mL^{-1}$ for phosphorus(V) content. Bismuth(III) and antimony(III) as the sensitizer has a sensitization effect on the phosphomolybdenum blue photometry. The addition of both simultaneously increases the sensitivity by 71.3%. The present method has been used for the determination of phosphorus in water samples. The recovery of method is between 99.20 - 100.1% and the relative standard deviation is between 1.31-1.33% for eleven determination. The results determined by the present method were in agreement with those of atomic absorption spectrometry. This method can avoid the harm of organic reagent to human body and to environmental pollution without organic solvent extraction. This method does not need heating with room temperature color development. Compared with other methods, it has the advantages that the operation is simple, fast and the sensitivity is high.

KEY WORDS: Phosphorus, Spectrophotometry, Phosphorus molybdenum blue, Sensitizer, Bismuth (III), Antimony (III), Rain water

INTRODUCTION

The phosphorus is abundant in nature, and the abundance in the crust is about 0.12%. Usually it exists in a variety of all kinds of minerals in the form of phosphate, the main minerals have calcium phosphate, apatite and so on. Phosphorus also exists in cells, proteins, bones and teeth of animals and plants. Therefore, it is also an important element consisting of life. Although phosphorus is one of the essential elements for biological growth, too high phosphorus content in the water body can cause the excessive multiplication of algae until a harmful level is reached in quantity, making the water quality worse. PO_4^{3-} is mainly derived from animal excreta, sewage and industrial wastewater. The content of PO_4^{3-} in natural water is not high, and the presence of PO_4^{3-} is generally not allowed in drinking water. Its appearance can be used as a sign of water pollution degree [1-5]. Therefore, phosphorus is one of the important indexes to evaluate water quality and the phosphate concentration limit in the water quality standard is 0.5 mg/L [6-7]. The traditional analytical methods of phosphate determination are gravimetric and titrimetric methods. The analytical methods of micro amount of phosphate mainly include spectrophotometry [8-18], atomic absorption spectrometry [19], inductively coupled plasma-emission spectrometry [20] and X-ray fluorescence spectrometry [21] and so on. Gravimetric determination of phosphorus is a long operation. Spectrophotometric method has the advantages of simple operation, rapidity and accurate results. The stability of many methods for the determination of low phosphorus content is poor and the conditions are not easy to be grasped [22-24]. Other analysis methods are expensive, inconvenient to operate, and not easy to be widely used. Rain water affects the composition of soil, and then affects the growth of related crops and the absorption of soil components. Therefore, the determination of phosphorus in rain water is of great significance. The method of common use for the spectrophotometric determination of phosphorus is

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phosphomolybdenum blue photometry, but its sensitivity was low [25]. To the best of our knowledge, the report is not found that bismuth(III) and antimony(III) are simultaneously used as sensitizers to sensibilize phosphomolybdenum blue photometry.

This paper explores spectrophotometric determination of phosphorus with ascorbic acid as a reductant of phosphomolybdate blue. The effects of bismuth(III) and antimony(III) on the determination of phosphorus are focused on. It is found that their sensitizing effects are good. The complete developing can be carried out at 20 min in this method and is fast, while the phosphorus(V) spectrophotometric system generally takes a long time [10, 26]. P(V)-Mo(VI)-Bi(III)-Sb(III)-ascorbic acid is a new system for the determination of phosphorus not reported in literature. This method has the advantages that the operation is simple, fast and the sensitivity is high [27-31]. The determination of phosphorus in rain water samples has been successfully carried out and satisfactory results have been obtained.

EXPERIMENTAL

Chemicals and reagents

Phosphorus(V) standard solution: 0.0426 g of $(NH_4)_2HPO_4$ was dissolved in a small amount of water, fixed volume to 100 mL with water. 0.1 mg·mL^{-1} P(V) stock solution was obtained and the working solution concentration was 10 μg·mL^{-1} containing P(V). Ammonium molybdate solution: 10.0000 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in 100 mL water, and the solution with concentration of ammonium molybdate 9.42% (w/v) was obtained. Bismuth nitrate solution: 5 g of $Bi(NO_3)_3\cdot 5H_2O$ were dissolved in 5 mL concentrated nitric acid (15.5 mol·L^{-1}) and diluted to 100 mL with water to obtain a solution containing 4.07% (w/v) of bismuth nitrate. Antimony(III) solution: 0.0274 g of potassium antimony tartrate ($KSbC_4H_4O_7\cdot 1/2H_2O$) was dissolved and made to a volume of 100 mL with water to obtain a reserved solution containing Sb(III) 0.1000 mg·mL^{-1}. The working solution containing Sb(III) 1 μg·mL^{-1} was obtained by dilution of this reserve solution 100 times with water. 10% (w/v) ascorbic acid solution was obtained by dissolving 10.0000 g of ascorbic acid was dissolved in a small amount of water, and the water capacity was fixed at 100 mL. Concentrated perchloric acid (12.38 mol·L^{-1}) was used to regulate the acidity of the chromogenic system.

All the reagents were purchased from Beijing Chemical Reagents Factory, China and had analytical pure grade. The water was deionized water.

Instrumentation

722S model spectrophotometer (Shanghai Third Analytical Instrument Factory, China) was used for the determination of absorbance.

Procedure

An appropriate amount of P(V) standard solution was added to 25 mL volumetric bottle, adding proper amount of water to keep the total volume at about 15 mL. In turn 3.0 mL of 12.38 mol/L concentrated perchloric acid, 0.6 mL of 9.42% (w/v) ammonium molybdate solution, 0.6 mL of 4.07% (w/v) bismuth nitrate solution, 3.0 mL of 0.0274% (w/v) potassium antimony tartrate solution and 1.0 mL of 10% (w/v) ascorbic acid solution, were added. After water was used to fix the volume to the mark, the solution was placed for 20 min. The absorbance was determined with the corresponding reagent blank as reference at the wavelength of 690 nm using 1 cm cells.

RESULTS AND DISCUSSION

Absorption spectra

Figure 1A and B show the absorption spectra of phosphorus molybdenum blue and reagent blank solution, respectively. It can be seen that the maximum absorption wavelength of phosphorus molybdenum blue heteropoly acid is 690 nm and the maximum absorption wavelength of reagent blank is 610 nm. In the following experiments, 690 nm is used as the determination wavelength.

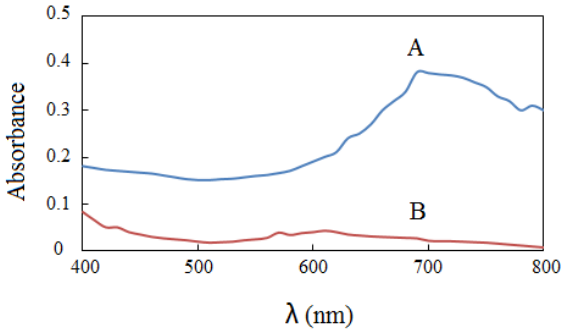

Figure 1. Absorption spectra: (A) phosphorus molybdenum blue against reagent blank; (B) reagent blank against water: [P(V)] = 2.53×10^{-5} mol·L^{-1}; [ammonium molybdate] = 1.94×10^{-3} mol·mL^{-1}; [ascorbic acid] = 2.27×10^{-2} mol·L^{-1}; [Bi(III)] = 2.47×10^{-3} mol·L^{-1}; [potassium antimony tartrate] = 9.86×10^{-7} mol·L^{-1}; [$HClO_4$] = 1.44 mol·L^{-1}.

Determination of optimum experimental conditions

Effect of acidity

pH can affect the polarity, physical chemical properties of a reagent. Using perchloric acid as medium, effect of the concentration range of 0.10 - 2.00 mol·L^{-1} on the formation of phosphorus molybdenum heteropoly blue was studied. The results showed that for the concentration of perchloric acid between 0.10 and 1.44 mol·L^{-1} with the increase of the concentration of perchloric acid, the absorbance is unceasingly increasing. When the concentration of perchloric acid was 1.44 mol·L^{-1}, the absorbance was the highest and sensitivity for the determination of phosphorus was the highest. After that, the sensitivity of determination phosphorus decreased. The acidity of perchloric acid was selected to be 1.44 mol·L^{-1}.

Effect of the dosage of reagent

The dosage of ammonium molybdate showed that the absorbance unceasingly increased with the increase of the amount of ammonium molybdate at 0 - 0.5 mL. At the time of 0.5 - 0.8 mL, the absorbance was the maximum. Then, the amount of ammonium molybdate was increased and the absorbance decreased. 0.6 mL of ammonium molybdate was chosen in the experiment. The sensitivity of determination of phosphorus can be improved by adding appropriate amount of bismuth nitrate. When the amount of bismuth nitrate added was 0 - 0.4 mL, the absorbance increases with the increase of its amount. The absorbance was a maximum at the time of 0.4 - 0.8 mL. Subsequently, the sensitivity of determination for phosphorus decreased, so the amount of bismuth nitrate solution selected was 0.6 mL. Under the conditions of this experiment, the

sensitivity of phosphorus determination can be increased by 66.7% by introducing bismuth(III). It is inferred that presumably because Bi(III) reacts with phosphomolybdate blue to form a new blue compounds with higher sensitivity and absorption was caused at the same absorption wavelength, thus increasing the sensitivity. The results of antimony(III) amount showed that when the amount of potassium antimony tartrate solution was 0 - 2.5 mL, the absorbance unceasingly increased with the increase of the amount of antimony(III) solution. When the amount of potassium antimony tartrate solution was 2.5 - 4.0 mL, the absorbance was the highest. Afterwards, the absorbance decreased. The dosage of potassium antimony tartrate solution was 3.0 mL. Antimony(III) is incorporated into phosphomolybdate blue to form a new blue compound with higher sensitivity and absorption at the same absorption wavelength is produced, thus increasing the sensitivity. The sensitivity is increased by 13.1%. The addition of both simultaneously increases the sensitivity by 71.3%. In this system, after P(V) and Mo(VI) formed phosphorus molybdenum yellow, ascorbic acid played a role in reducing phosphorus molybdenum yellow to phosphorus molybdenum blue [9, 10]. When the amount of ascorbic acid added was in 0 - 0.5 mL, the absorbance unceasingly was increased. At the time of 0.5 - 1.5 mL, the absorbance was stable and the highest and the sensitivity of determination of phosphorus was the highest. Therefore, the dosage of ascorbic acid selected in this article was 1.0 mL.

The following equation is used to indicate the generation of phosphorus-molybdenum blue [10]:

$$PO_4^{3-} + 12\ MoO_4^{2-} + 27\ H^+ \rightarrow H_3PO_4(MoO_3)_{12} + 12\ H_2O \quad (1)$$

$$H_3PMo(VI)_{12}O_{40} + \text{ascorbic acid} \rightarrow [H_4PMo(VI)_8Mo(V)_8O_{40} \quad (2)$$
(Phosphate molybdenum blue)

In the presence of Bi(III) and Sb(III), both participate in the formation of bismuth antimony phosphate molybdenum blue polyacid compound to generate a new product.

Effect of color temperature

The temperature was taken as a variable according to the experimental method and the experiment was carried out at 25, 35, 45, 55, 60, 80 ℃, respectively. The results show that the absorbance of the complex decreases with the increase of temperature during the range of 25 - 55 ℃. When the temperature exceeded 60 ℃, the color of the solution changed from blue to green. The phosphomolybdate blue was decomposed. Therefore, the experimental temperature is 25 ± 1 ℃ at room temperature.

Stability of system

After mixed with various reagents according to the experiment procedure, for this system the absorbance reached stable at 20 min, the absorbance change was not more than 5% in 2.5 h and the system remained stable. Developing of the present system is rapid.

Working curve

The experimental results show that under the optimum experimental conditions when the content of phosphorus(V) is 0.02 - 1.8 μg·mL^{-1}, there is a good linear relationship between phosphorus content and absorbance and Beer's law is obeyed. According to the experimental results, the linear regression equation of the working curve found is: $A = 0.4512C + 0.0141$(C: μg·mL^{-1}), with a correlation coefficient $r = 0.9993$. The apparent molar absorptivity for the determination of phosphorus by present method was obtained by calculating from the working curve $\varepsilon_{690nm} = 1.44 \times 10^4$ L·mol^{-1}·cm^{-1}. According to the experimental method, 1.00 μg·mL^{-1}

P(V) standard solution was determined 11 parallel times, the average value determined was 1.01 μg·mL^{-1} and the relative standard deviation of the determination result was 0.33%. It can be seen that the method has good precision. The reagent blank was determined 11 times. According to D = 3S/K (D is detection limit, S is the standard deviation of 11 times parallel determination of the reagent blank and K is the slope of the working curve), the detection limit of this method calculated was 13 ng·mL^{-1}. The limit of quantification was 15 ng mL^{-1}.

Method selectivity

The experiment of the influence of coexisting ions was carried out under the best conditions. When 0.6 μg·mL^{-1} phosphorus(V) was determined and the relative error did not exceed ±5%, the following coexisting substances (in mass multiple) are allowed: Mg^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+} (800), Fe^{2+}, Al^{3+} (500), Fe^{3+} (300), Cu^{2+} (250), Ca^{2+} (200), Co^{2+}, Ni^{2+} (150), Ag^{+}, Cd^{2+}, Sn^{2+}, B(III), Ti^{4+}, Th^{4+} (100), Cr^{3+} (50), VO_3^-, NO_3^-, SiO_3^{2-} (300), F^-, Br^-, $S_2O_7^-$ (50), BrO_3^-, MnO_4^- (30) , I^-, NO_2^- (20).

Sample analysis

500 mL rain water was taken, heated and concentrated to about 50 mL. After cooling, 5 mL aqua regia was added to it, heated and evaporated to near dry on electric furnace. It was dissolved in a small amount of water, then transferred to a 25 mL volumetric flask. Phosphorus was determined according to the experimental method. At the same time, the atomic absorption spectrometry was used as a control method for the determination of phosphorus content in water samples. The above results are listed in Table 1. It can be seen from the Table that the measurement results of phosphorus content in rainwater determined by this method are consistent with those by atomic absorption spectrometry. The determination of phosphorus by the method has the advantages of high accuracy and good precision. The analysis results are satisfactory.

Table 1. Analytical results of samples.

Sample	Average concentration found (μg·g^{-1}, n = 5)	Relative standard deviation (%)	Added (μg·g^{-1})	Recovered (μg·g^{-1})	Recovery (%)	Average concentration found (μg·g^{-1}, n = 5)
No. 1	31.13	1.31	0.800	0.801	100.13	31.11
No. 2	55.53	1.33	0.500	0.496	99.20	55.53
No. 3	40.11	2.91	0.500	0.503	100.60	40.32
No. 4	51.21	0.26	0.500	0.491	98.20	51.09

CONCLUSION

A new phosphorus molybdenum blue spectrophotometric method for the determination of phosphorus in the perchloric acid medium has been established. It is found that adding bismuth(III) and antimony(III) simultaneously could make the sensitivity be increased by 71.3%. The maximum absorption and apparent molar absorptivity of this method are λ_{max} = 690 nm, ε_{max} = 1.44 × 10^4 L·mol^{-1}·cm^{-1}. The amount of phosphorus(V) obeys Beer's law in the range of 0.02 - 1.8 μg·mL $^{-1}$. The method has been successfully applied to the determination of phosphorus in rain water with satisfactory results. This method does not need heating with room temperature color development. The operation is simple, fast and the sensitivity is high. This method can be used for the determination of phosphorus in rain water samples.

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