

Catalytic Photometric Determination of Trace Hg in Environmental Water and Sewage Sludge Samples

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Abstract: Mercury is recognized as one of the most toxic elements, so the environmental water and sewage sludge samples must be determined accurately. In diluted hydrochloric acid medium, trace Hg (II) plays a significant catalytic role in hydrochloric nile blue (HNB) oxidized by potassium bromate reaction in presence of nitrilotriacetic acid. This paper hereby investigates the catalytic fading reaction of trace Hg (II) to hydrochloric nile blue (HNB) oxidized by potassium bromate, a new method for the determination of trace Hg (II) by catalytic kinetic spectrophotometry is established. The results show that the maximum absorption wavelength of the colored solution is 610nm, the detection limit is 4.5×10^{-9} g/mL, catalytic extent and Hg (II) have a good linearity relationship in the 0 to 0.10 mg / L range. The method is used for the determination of trace mercury in water and sewage samples with satisfactory results.

Keywords: Mercury, Catalytic Spectrophotometry, Water Sample, Sewage Sludge Sample, Monitoring

Mercury is recognized as one of the most toxic elements, its concentration in the environmental water and sewage samples must be accurate determined. In recent years, most of Hg (II) spectrophotometric determination reports are spectrophotometry and catalytic spectrophotometry. [2-5]. But because of the restrictions of these methods, such as sensitivity, selectivity and reproductivity etc., it is difficult to have a common approach. The establishment of a new dynamic analysis methods still have practical significance. Research showed that in diluted hydrochloric acid medium, trace Hg (II) plays a significant catalytic role in hydrochloric nile blue (HNB) oxidized by potassium bromate reaction in presence of nitrilotriacetic acid. Accordingly, method for the determination of trace Hg (II) by dynamics spectrophotometry is established, and the optimum conditions for the determination are decided.

1 Experimental

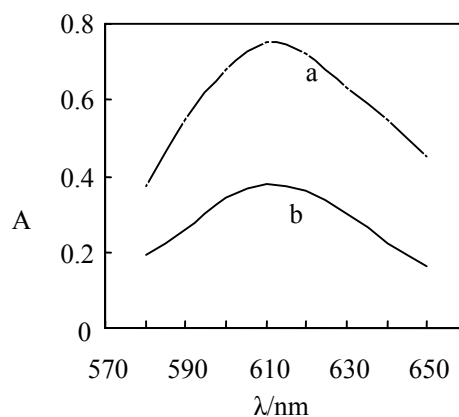
1.1 Main Reagents and Equipment

722 type spectrophotometer, pHs-3C acidimeter, CS-501 SP digital electric- heated thermostatic water bath. Hg (II) standard solution ($10 \mu\text{g} / \text{mL}$), appropriate dilution when use; HNB repertory liquid: 0.05% (1% $\text{C}_2\text{H}_5\text{OH}$); 5.0×10^{-4} mol/L KBrO_3 solution; 6.0×10^{-3} mol / L NTA solution; 0.1 mol / L HCl solution. The reagents used are analytical purity.

1.2 Experimental Method

At first add a certain amount of Hg (II) standard solution to a beaker (25 mL) accurately, then followed by adding 3.0 mL 0.1 mol/L HCl solution, 1.0 mL 0.05% HNB solution, 1.5 mL 6.0×10^{-3} mol/L NTA solution

and 2.5 mL 5.0×10^{-4} mol/L KBrO_3 solution in order, dilute the solution to scale by water, shake well. Place the beaker in boiling water bath for 8 min reaction, then quickly remove and cool 3 min by flowing water. Using water as reference, the reagent absorbance of blank and catalyst system are measured in the 610 nm wavelength with 1cm colorimetric plate, and calculate with $\Delta A = A_0 - A_c$.



a. Non-catalyst system, b. Catalyst system
Figure 1. Adsorption Spectrum

2 Results and Discussion

2.1 Absorption Spectrum

The absorption spectrum of the system is shown in Figure 1, results shows that in the vicinity of 610 nm wavelength, the ΔA of the two solution is maximal and stable, other components absorption in this wavelength could be ignored. In this paper, we select 610 nm wavelength as detecting wavelength.

2.2 Select of Experimental Conditions

2.2.1 The impact of reaction medium and acidity

The results shows that when the pH value is too low, both the catalytic and the non-catalytic system are fading fast; When pH value is high, they are fading slow and the ΔA values are small. Only when the amount of 0.1 mol/L HCl solution is in the range of 2.0~4.0 mL, the high sensitivity could be obtained. The maximum ΔA is got and could be kept constant. This method selects 3.0 mL 0.1 mol/L HCl to control the acidity of the catalytic reaction.

2.2.2 The impact of KBrO₃ amount

When the amount of KBrO₃ solution is in the range of 1.5~3.5 mL, maximum ΔA is got and can be kept constant. The amount of 2.5ml is selected.

2.2.3 The impact of HNB amount

When the amount of HNB solution is in the range of 0.5~1.5 mL, ΔA slow increased with the increasing amount of reagent. We select 1.0ml considering the absorbance reading scope.

2.2.4 The impact of NTA amount

When the NTA solution amount is in the range of 1.0~2.0 mL, maximum ΔA is got and can be kept constant. The amount of 1.5ml is selected.

2.2.5 The Impact of Reaction Temperature and Heating Time

The ΔA values are measured after reacting 6 min at different temperatures according to the experimental method. The results shows that, at room temperature, the catalytic reactions are slow, when $T > 65^\circ\text{C}$, ΔA values increased with increasing temperature, when $t > 90^\circ\text{C}$, maximum invariable ΔA is got. This method selects water bath heating because it is convenient for controlling temperature.

Heat different time in selected boiling water bath, measured the ΔA value. The results shows that ΔA and time have a linear relationship when it is between 3~8 minutes. Maximum and invariable ΔA is got which illuminated the fading reaction is dynamics first order reaction. The reaction rate is constant. This method selects 8min boiling water bath heating. The absorbance of the solution which is faded completely can maintain at least 3h at room temperature.

2.3 Working Curve

Select different amount of standard Hg (II) solution to draw working curves according to the experimental method. Results shows that the amount of Hg (II) has a linear relationship with ΔA when the amount of Hg (II)

is between 0~0.10mg/L. The correlation coefficient is 0.9985 measured in the 610nm wavelength. According to the standard deviation and the working curve slope of the 11 times blank experiments, the detection limit of this method is 4.5×10^{-9} g / mL by three times method.

2.4 The Impact of Coexist Ions

The interference experiments of common elements shows that in this paper's conditions, the relative error is no more than $\pm 5\%$ according to experimental methods. Took 1.0 μg Hg (II) from 25 mL for experiments, the multiple of the coexistence ions are as follows: Na^+ , K^+ , Ca^{2+} , NH_4^+ and NO_3^- , SO_4^{2-} (1500 times of Hg); AsO_3^{3-} , PO_4^{3-} (1000 times of Hg); Mg^{2+} , Bi^{3+} (500 times of Hg); Ba^{2+} , Al^{3+} , Zn^{2+} (200 times of Hg); Fe^{3+} , Sn^{4+} , Co^{2+} , Ni^{2+} (150 times of Hg); Cd^{2+} , Cu^{2+} (10 times of Hg); Mn^{2+} , Cr^{3+} (5 times of Hg). It shows that this method has good selectivity.

3 Sample Analysis

1) Determination of sewage Hg: After filtering and digesting the mine water of Jiangxi Pingxiang Mines Bureau, mensurate the content of Hg according to the above method. Results are shown in Table 1.

Table 1 Analysis results of hg in mine water samples

Samples	Testing results/(mg/L)	Adding amounts of Hg (II) /(mg/L)	Recovery rate /%	Variation coefficient /%
Sewage 1	0.052	0.050	99.4	3.5
Sewage 2	0.060	0.050	98.9	2.4
Sewage 3	0.080	0.050	104.1	2.8

Table 2 Analysis of Hg in sewage sludge

Samples	Testing results/(mg/L)	Adding amounts of Hg (II) /(mg/L)	Recovery rate /%	Variation coefficient /%
Sewage Sludge 1	1.05	1.00	98.8	2.7
Sewage Sludge 2	0.86	1.00	103.9	4.4
Sewage Sludge 3	1.38	1.00	97.3	3.0

2) Determining the amount of Hg in sewage sludge: The sewage sludge is took from Changsha No. 1 Sewage Treatment Plant, weigh 2- 5g dry sewage sludge samples from 250 mL conical bottle, wet it by water, volatilized silicon by adding H_2SO_4 -HF. After the SO_3 are run out,

add 10 mL mixed acid of vitriol and nitric acid. Add 10 mL water and 5 mL KMnO_4 solution (2%) after violent reacting, then do the tepefaction decomposition on electric-board. After cooling, drop 100g /L hydroxyl ammonium chloride until MnO_2 and KMnO_4 are fade. Filtrate the solution and make its constant volume to 50 mL, take appropriate solution respectively, mensurate according to the following method. The results are shown in table 2.

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