Determination of Trace Chromium(Ⅵ) in Tanning Wastewater by Flow Injection Spectrophotometry**

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Abstract: In 1.0 mol/L H_2SO_4 solution, a rapid and simple flow—injection spectrophotometric method has been developed for Cr(Ⅵ) determination, based on the violet—red Cr(Ⅵ)—diphenylcarbazide chelates formed by reactions. The results show, under optimum conditions, the maximum absorption of the complex is at 540 nm and the detection limits of the method is 0.0136mg/L for Cr(Ⅵ) and Beer's law is obeyed for Cr(Ⅵ) in the range of 0.03—1.60mg/L. The determination frequency is l00times/h. The relative standard deviation of eleven replicates is less than 4.0%. The method has been applied to the determination of trace Cr(Ⅵ) in tanning wastewater with satisfactory results.

Key words: flow—injection spectrophotometry; Cr(Ⅵ); tanning wastewater; diphenylcarbazide

1 Introduction

There are various techniques for the determination of Cr(Ⅵ) reported at present, such as arsenazoⅢ spectrophotometry[1], diphenylcarbazide (DPC) spectrophotometry[2], flow-injection analysis[3], iodine-starch spectrophotometry[4] and atomic absorption spectrometry[5]. Thus, there has been a great need to develop a simple, rapid, convenient method for the determination of Cr(Ⅵ) in water. In this paper, a method of DPC—FIA spectrophotometric determination of trace Cr(Ⅵ) is described. The method is based on DPC spectrophotometric method which is the GB and ISO method, and the FIA coupled with spectrophotometric method could greatly shorten the time. It features excellent selectivity, high sensitivity, rapidness and accuracy .With this method, satisfactory results can be achieved in determination of trace Cr(Ⅵ) in tanning wastewater.

2 Experimental

2.1 Major Reagents and Apparatus

A model LZ-1000 Combination flow injection Analyzer(PTFE tube 0.5 mm inside diameter) made in Shenyang Zhaofa Analytical Instruments Research Institute was used. A model UV-160A UV/Visible Spectrophotometer made in Shimadzu was used. A Model pHS-3C pH meter made in the second branch of ShangHai Analytical Instrument Company was used for all pH measurements. A Model CS-501 SP digital display super thermostat made in Chongqing Sida Laboratory Instrument Plant was used. A sample valve made in Shandong Yellow Sea Fisheries Research Institute was used. A model XWT automatic balance recorder made in Shanghai Dahua Instrument Factory was used.

Cr(Ⅵ) standard solution: exactly 1.415g $K_2Cr_2O_7$(baked at 140℃ for 2h) was dissolved in 0.10 mol/L H_2SO_4 solution, diluted it to 500mL with 0.10mol/L H_2SO_4 solution for use later, and further diluted it to 0.10mg/mL working solution when it was used; 0.80g/LDPC solution: exactly 0.40g DPC was dissolved in 20ml Acetone, and diluted it to 500mL with water; 1.00mol/L H_2SO_4 solution was used as a carrier.

2.2 Procedure

The flow path comprising the system was made of 0.5mm diameter PTFE tubes. The analytical

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system is schematically illustrated in Fig. 1. Instrument parameters: pump speed 0.8~1.2mL/min, sample loop volume 150μL, sampling time 15s, determination of time 20s, determination of frequency 100 times/h. The absorbance of the solution is red at 540nm using a 10mm flow—through cuvette, while automaticly recording the input signal.

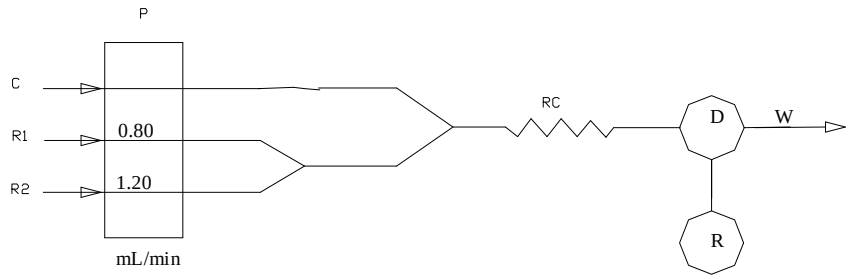

Fig. 1 Flow injection manifold for the determination

P. peristaltic pump; C. Cr(Ⅵ) samples; R_1. 1.00 mol/LH_2SO_4(carrier); R_2. 0.80 g/LDPC solution; RC. reaction coil; D. spectrophotometer; R. recorder; W. waste

3 Results and discussion

3.1 Absorption Spectrum and Determination of Wavelength

According to our research, redox reaction takes place between DPC and Cr (Ⅵ) in acidic solution, and then an chelation reaction could occur. The chemical composition of the reaction product were identified as Cr(Ⅵ)-enol-diphenylcarbazide and Cr(Ⅵ)-keto-diphenylcarbazide. The determination of absorbance is shown in Fig. 2. This paper chooses 540nm as the wavelength for determination.

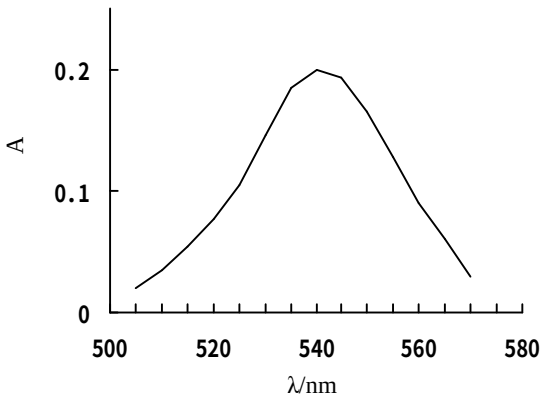

Fig. 2 Absorption spectrum

3.2 Impact of Reaction Medium and Acidity

According to the experimental method, sulfuric acid, nitric acid and phosphoric acid solution were used. The best results were obtained with the use of sulfuric acid solution. The impacts of different sulfuric acid concentrations were also investigated in this experiment. A sulfuric acid medium of 1.00mol/L is selected for this experiment.

3.3 Determination of the Optimum Conditions of Flow Path

Impact of H_2SO_4 solution (R_1) volume flow: The absorbance reaches a maximum at a flow rate of 0.80mL/min. A flow rate of 0.80mL/min was selected.

Impact of DPC solution (R_2) volume flow: The absorbance reaches a maximum at a flow rate of 1.20mL/min. A flow rate of 1.20mL/min was selected.

Impact of reaction tube length: The absorbance reaches a maximum, when the reaction tube(RC) length was 90cm. A length of 90cm was selected.

Impact of sample injection volume(V): The absorbance reaches a maximum and remains constant for injection volumes greater than 150μL.

3.4 Determination of the Optimum Conditions of the Color Reaction

Impact of DPC solution mass concentration: The absorbance reaches a maximum and remains constant at a mass concentration of 0.60~1.00g/L. A mass concentration of 0.80g/L was selected.

Impact of the H_2SO_4 solution molarity: The absorbance reaches a maximum and remains constant at a molarity of 0.80~1.20mol/L. A molarity of 1.00mol/L was selected.

3.5 Impact of Coexisting Ions

As we all know, strong reducing ions and Cr(Ⅵ) ions are not stable under very strong acid conditions. According to the experimental method and with the relative error of ≤±5%, an interference experiment was made for the common elements. The coexisting ions that don't interfere with Cr(Ⅵ) determination with the allowable amount (mg) include: Na^+, K^+, SO_4^{2-}, Cl^-(>500); Ca^{2+}, Mg^{2+}(400); NH_4^+, CO_3^{2-}, NO_3^-, HCO_3^-(300); Hg^{2+}(150); Zn^{2+}(100); Mn^{2+}(80); Fe^{3+}(70); Ni^{2+}, Cr^{3+} and Mo(Ⅵ)(20). As can be seen, Cr(Ⅵ) have a high selectivity for DPC in acidic solution. Most common ions do not interfere.

3.6 Precision and Working Curve

The curves were drawn according to the experimental method. The linear regression equation is: $A=0.238C_{Cr(VI)}$(mg/L) +0.0051. Its correlation coefficient was 0.9994(n=10) and the sensitivity was 0.238L/mg. Beer's law is obeyed for Cr(Ⅵ) in the range of 0.03~1.60mg/L. According to IUPAC recommendations, the limit of detection was 0.0136mg/L.

4 Samples analysis

Decant the tap water into a beaker, into which Cr(Ⅵ) was added, and then 1.0mL of Cr(Ⅵ) standard solution was added. The said experimental method was used to determine the content of total chromium in the solution, and repeat the experiment 11 times. The recovery rate of adding standard solution was in the range of 97.8~104.5 (RSD=3.7 %).

The wastewater discharged out of the general wastewater outlet of Qiqihar Tannery, which contained chromium, was put still and filtered first for removal of suspended substances. H_2SO_4 and HNO_3 were added to the wastewater for removal of organic substances. The wastewater was diluted to 50mL with deionized water. The adding standard recovery experiment was done according to the following experimental method. Tab. 1 gives the results.

Tab. 1 Analytical results of tanning wastewater samples

Samples	Found(mg/L, n=6)	Found by DPC method(mg/L)	Added(mg/L)	Recovery(%)
A1	6.585	6.438	1.0	97.8
A2	7.132	7.006	1.0	102.4
A3	6.056	6.203	1.0	99.8
B1	5.518	5.510	0.5	102.2
B2	4.205	4.125	0.5	98.5
B3	5.876	5.786	0.5	104.3

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