



Determination of Trace Chromium(VI) with 3-Methoxy-Azomethine H in Surface-Active Agents

WEN-BIN CHEN^{1,*}, HAI WANG² and YU-LING DU²

¹Jiangsu Institute of Marine Resources, Huaihai Institute of Technology, Lianyungang 222005, P.R. China

²Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P.R. China

*Corresponding author: Tel: +86 13912168711; E-mail: lygcwb11@163.com

Received: 4 May 2013;

Accepted: 11 October 2013;

Published online: 26 December 2013;

AJC-14510

In the presence of microemulsion cetyltrimethyl ammonium bromide and CH₃COOH-CH₃COONa buffer at pH 6.2, the condition of colour reaction of chromium(VI) with 3-methoxy-azomethine H was studied and a new spectrophotometric method for the determination of micro chromium(VI) has been established. Results showed that in the presence of CH₃COOH-CH₃COONa, the maximum absorption wavelength and apparent molar absorptivity are 480 nm and $8.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. Beer's law is obeyed in the range of 0.08-15.0 μg for chromium(VI) in 10 mL solution. The detection limit is 0.02 $\mu\text{g}/10 \text{ mL}$. The recovery was 102.3-103.8 %. The method has been applied to the determination of trace chromium(VI) in natural water and the result was in accordance with that of the standard spectrometry method.

Keywords: 3-Methoxy-azomethine H, Spectrophotometry, Chromium(VI).

INTRODUCTION

Chromium(III) is an essential nutrient for maintaining normal physiological function¹, whereas, chromium(VI) is toxic². The contrasting biological effects of its two common oxidation states, the hexavalent chromium concentration of US drinking water has been reported to vary between 3 and 40 mg/L with a mean of 3.2 mg/L. Chromium salts are used extensively in industrial processes and may enter water supply through the discharge of wastes. Chromate compounds frequently are added to cooling water for corrosion control. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water³. Steel works, chrome-plating, leather tanning industries produce high chromium wastes. Understanding the behaviour of chromium in natural aquatic system is, therefore, of major concern⁴. The presence of chromium in air is mostly due to burning of fossil fuels, which contributes about 1480 metric tons of chromium every year. Soil contamination by chromium results from the land disposal of sewage sludge, land disposal of by-products from ferro-chrome and chrome-steel industries and from the use of phosphatic fertilizers. In view of these facts, the separation and determination of trace amounts of chromium is important in studies of biological processes and for industrial purposes. so chromium determination at trace levels is of significant importance. A wide variety of reagents have been proposed for its spectrophotometric

determination⁵. Some spectrophotometric methods for the determination of chromium as chromium(VI), based on azo reagents^{6,8}. The reactions with these reagents require a heating step for colour development. In this paper, the determination of Cr(VI) with 3-methoxy-azomethine H in CH₃COOH-CH₃COONa buffer solution of pH 6.2 is studied. After the formation of 3-methoxy-azomethine H, Cr(VI) and cetyltrimethyl ammonium bromide microemulsion with a mole ratio of 1:1:1, the molar absorption coefficient is $8.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and common coexistent ions including many precious metal ions in the same quantity do not interfere in the determination of Cr(VI). The method is used for the determination of Cr(VI) in water sample with satisfactory results.

EXPERIMENTAL

UNICO WFJ 7200 spectrophotometer (Shanghai Unico Equipment Co., Ltd.), pH-3C acidimeter (Shanghai Rex Equipment Factory); Chromium(VI) standard solution (1 mg/mL): Prepared by dissolving 0.2829 g K₂Cr₂O₇ in 50 mL of water, adding 1 mL of saturated sodium sulphite solution, acidifying with 1 mL 2.5 mol/L sulphuric acid and then boiling for 2 min to remove excess SO₂ and diluting with water to 100 mL. A suitable volume of this solution was diluted to obtain the working standard. 3-Methoxy-azomethine H (Shanghai Changke Reagent Factory): $5 \times 10^{-3} \text{ mol/L}$, weigh 0.1125 g 3-methoxy-azomethine H and 0.1 g ascorbic acid and dissolve them with water in a 50 mL brown flask up to the defined volume. Note:

prepared solution should be used up, or stored in refrigerator for maximal 4 to 5 days and preserved in darkness; CH₃COOH-CH₃COONa buffer solution: pH 6.2, mix 1 mL of 0.1 mol/L acetic acid and 16 mL of 0.1 mol/L sodium acetate together, calibrate it with pH meter; cetyltrimethyl ammonium bromide (CTMAB): according to quality ratio of components in microemulsion, CTMAB: *n*-butanol:heptane:water = 1.0:1.0:1.0:97, uniformly mix the each component to get the required microemulsion.

All reagents are analytical reagents and the water is secondary distilled water.

Experimental method: Add 1 mL of 10 µg/mL Cr(VI) operating solution in a 10 mL colourimetric cuvette and then add 1.2 mL CH₃COOH-CH₃COONa buffer solution of pH 6.2, 1.5 mL of microemulsion CTMAB, 1.2 mL of 5 × 10⁻³ mol/L 3-methoxy-azomethine H solution in turn, until reaching the defined volume and then shake. After 10 min, measure the absorbance of the solution by using 1 cm colourimetric cuvette at 480 nm with reagent blank as reference.

RESULTS AND DISCUSSION

Absorption spectra: According to the experimental method, the complexes are measured at different wavelengths with corresponding reagent blank as reference without changing other conditions to obtain absorption spectra. The results are shown in the presence of microemulsion CTMAB, maximal absorption peaks of complexes and reagent blank are located at the wavelength of 480 nm and 370 nm respectively and the peak of complex shifts to red side 110 nm compared with reagent blank.

Influence of system acidity: According to the experimental method, the influence of different media on the system is observed. The results show that the absorbance of CH₃COOH-CH₃COONa solution system reaches the maximal value and remains stable when pH value is between 5.6 and 6.5. CH₃COOH-CH₃COONa solution at pH 6.2 is selected to control acidity. When its amount is in the range of 0.8 to 1.4 mL, the purpose of acidity controlling is realized. Therefore, 1.2 mL CH₃COOH-CH₃COONa buffer solution with pH value of 6.2 is selected in the experiment.

Influence of type and quantity of surfactant: A comparative test is carried out with surfactants such as OP solution, Tween-80, Tween-20, β-cyclodextrin solution, CTMAB solution, CPC solution, CPB solution, CTMAB microemulsion, Trion X-100, OP microemulsion, CPB microemulsion, CTMAB-OP mixed microemulsion and so on. The results show that CTMAB microemulsion has relative better stability and sensitivity. In this paper, CTMAB microemulsion is selected to improve stability and sensitivity. The system absorbance reaches the maximum and remains stable when the amount of CTMAB microemulsion is in the range of 1.2-1.8 mL. Therefore, the volume of 1.5 mL is selected.

Influence of amount of chromogenic reagent: According to the experimental method, when the amount of chromogenic reagent is in the range of 0.8 to 1.4 mL, the system absorbance reach maximum and remains stable. Therefore, the volume of 1.2 mL is selected.

Influence of addition sequence of reagents and chromogenic time and stability of complex: The absorbance of test solution is measured by changing the addition sequence of reagents. It is found that the addition sequence of reagents has a great influence on the absorbance and the sequent of this experiment is optimal. Chromogenic reaction takes place completely in the system at room-temperature. And the reaction generally reaches maximal after 10 min. and remains stable for 8 h.

Composition of complex: Molar ratio method and continuous change method are used to determine the ratio of complex Cr(VI) and 3-methoxy-azomethine H. The molar ratio method and continuous change method are used to determine the ratio of complex Cr(VI) and the CTMAB. The results show that Cr(VI): CTMAB = 1:1, Cr(VI): 3-methoxy-azomethine H = 1:1. Therefore, the composition of ternary complex Cr(VI): 3-methoxy-azomethine H: CTMAB = 1:1:1.

Influence of Co-existent ions: According to experimental method, 10 mg Cr(VI) is determined, relative error ≤ ± 5 %. The results show that allowable volume of co-existent ions (unit: mg). K⁺(1 5000); Na⁺(1 2000); Ba²⁺(800); Mg²⁺(750); Ca²⁺(600); Al³⁺(700); Fe²⁺(600); Mn²⁺(500); Cd²⁺(400); Pt⁴⁺(200); Mo(VI), Co²⁺(150); Ce(IV), In³⁺(100); As(III)(80); Ru³⁺(50); Sn⁴⁺, V⁵⁺(8), Ti⁴⁺(40); Sb(V)(30); Ag⁺, Ga³⁺(25); Au³⁺, Rh³⁺(20); Pt²⁺(15); Ge²⁺(10); Ir³⁺, Os(IV)(5); Cu²⁺(4); tartaric acid (5000); citric acid (3000), triethanolamine (480). The common ions such as SO₄²⁻, PO₄³⁻, NO₃⁻, NO₂⁻, Cl⁻, do not interfere in the determination, while Fe³⁺, Pb²⁺, Bi³⁺ and so on do interfere. Comparing the effect of masking agents including hydroxylamine hydrochloride, NH₄F, EDTA, it is found that with the masking of NH₄F, Fe³⁺(500), Pb²⁺(350) and Bi³⁺(200) do not interfere in the determination.

Working curve and sensitivity: Add a certain amount of Cr(VI) standard solutions in a series of 10 mL chromogenic cuvette. Chromogenic reaction is measured according to the test method. In the 10 mL solution, the amount of chromium in the range of 0.08-15 mg complies with Beer's law, the determination low limit is 0.02 mg/mL, linear regression equation is $A = 0.1634 \times \rho$ (µg/10 mL) + 0.002 46, the linear correlation coefficient $r = 0.999 9$; apparent molar absorption coefficient $\epsilon = 8.5 \times 10^4$ L mol⁻¹ cm⁻¹.

Analysis sample analysis of natural water: Each filtered environmental water sample (100 mL) was analyzed for chromium. They tested negative. To these samples known amounts of chromium(VI) (200 mg) were spiked and analyzed for chromium by the proposed procedure for chromium(VI) were treated with 5 mL nitric acid and the mixture were evapo-

TABLE-1
DETERMINATION RESULTS OF CHROMIUM(VI) IN THE WATER SAMPLES (n = 6, µg/10 mL)

Sample	Certified*	Average	RSD (%)	Added (µg)	Recovery (%)
River water 1	2.50	2.48	2.15	15	103.8
River water 2	2.27	2.19	1.86	15	102.3

rated to dryness. The residue was leached with 5 mL 0.5 mol/L H₂SO₄. The solution was treated with 5 mL HCl and 10 mL MIBK to extract chromium. The aqueous layer was separated and diluted to a known volume with water, after neutralized with dilute ammonia. Solutions were also analyzed according to the standard diphenylcarbazide method and the results are shown in the Table-1.

The method has been used for the determination of trace chromium(VI) in nature water with satisfactory results and the result was in accordance with The RSD and recovery.

ACKNOWLEDGEMENTS

This article is financially supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

REFERENCES

1. Q.U. Wei, C.-Y. Zhou and L.-L. Cai, *Chem. Anal.*, **852**, 48 (2012) (in Chinese).
2. J.M. Eckert, R.J. Judd, P.A. Lay and A.D. Symons, *Anal. Chim. Acta*, **255**, 31 (1991).
3. Y. Zhang and X.-Y. Chen, *Appl. Chem. Ind.*, **852**, 48 (2012) (in Chinese).
4. Y.-L. Cao and S.-H. Chen, *Physical Testing Chem. Anal.*, **177**, 30 (1994) (in Chinese).
5. Y. Zhang, J. Liu and D.-H. Yu, *Metallurg. Anal.*, **57**, 19 (1999) (in Chinese).
6. S. Subrahmanyam and M.C. Eshwar, *Mikrochim. Acta*, **66**, 579 (1976).
7. G.A. Parker and D.F. Boltz, *Anal. Chem.*, **40**, 420 (1968).
8. S. Fu-Sheng, *Talanta*, **30**, 446 (1983).