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Spectrophotometric Determination of Trace Chromium(VI) in Mass Chromium(III)

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Abstract: The method for the sepration and determination of trace Cr(VI) exiting in mass Cr(III) has been researched. The method is highly sensitive and less interference, but is simple and useful for analysis trace Cr(VI).

Keywords: Spectrophotometric, Cr(VI), Cr(III), diphenyl carbazide(DPC), 4-methyl-benzene sulfonic acid.

There is little conclusive evidence of the toxic effects of Cr(III) so far, but Cr(VI) has carcinogenic activity, so the analysis of the chromine ions is very important in environmental research and the quality control of industry products. Usually Cr(III) and Cr(VI) interfere with each other in the species analysis, the measurement of Cr(VI) of numerous previous papers is related to the Cr(VI) samples, which contain a little Cr(III). When the amount of trivalent chromine exceeds ten thousands than that of hexavalent chromium, the results obtained have an unacceptable precision, a few of the good analytical methods are very time-consuming and some of the instruments are complicated. In the present paper, a new method for the determination of hexavalent chromium is reported, based on the liquid-liquid extraction after formation of a red three-complex containing Cr(VI), diphenyl carbazide, 4-methylbenzenesulfonic acid.

The red three-complex has a maximum absorption at 540 nm in UV spectrum, the coloring rate and absorbance are not noticely affected by temperature from 10 to 45°C. An appropriate amount of Cr(VI), 2 mL of 0.08 mol/L DPC, 2 mL of 0.5 mol/L 4-methylbenzenesulfonic acid, were pipetted into a 25 mL comparison tube, respectively. After shaking up the mixture, 5 mL of isopentyl alcohol was added. Then the mixture was diluted to 25 mL with deionized water and shaking up again. After 20 minutes, the absorbance at 540 nm wavelength was measured against the extractive solvent.

The influence of the chemical variables on the system was investigated separately in order to determine the optimal conditions for implementation of the proposed method. In this paper, four kinds of extractive solvent, *i.e.* MIBK, N-235, isopentyl alcohol, CCl_4 were tested. However, when isopentyl alcohol was introduced in the system, the complex has the strongest and stablest absorption, so isopentyl alcohol was selected in further experiments.

The effects of concentration of DPC and 4-methylbenzenesulfonic acid on the absorption intensity were investigated. When the concentration of DPC was controlled in 0.5 mol/L, and the concentration of 4-methylbenzenesulfonic acid was 0.08 mol/L, the system showed the strongest absorption intensity. So, they were selected as optimum concentration in further experiments. At the same time, the absorption intensity remained constant in the pH range of 3.5~4.5, the working pH was thus adjusted to 3.8 because it was only controlled by the 4-methylbenzenesulfonic acid.

The effect of time on the absorption intensity was investigated with 0.4 µg/mL Cr(VI) and 20 mg/mL Cr(III) in the optimum system. The absorption intensity can remain constant at least 3 h. The solution after standing for 12 h become orange color, so it is unfit for determination.

The three-complex system has very high selectivity almost to all ions, such as Na^+, K^+, Ni^+ were of no influence. The tolerance limits (error 5%) of interference ions are: Al^{3+} (3×10^4), Zn^{2+} (2×10^4), Cu^{2+} (1×10^4), Co^{2+} (5×10^4), Cr^{3+} (1×10^5), Ca^{2+} (2×10^4), Mg^{2+} (5×10^4). Fe^{3+} and Hg^{2+} have an influence on the absorption, however, Fe^{3+} can been masked by H_3PO_4, Hg^{2+} have no influence on the absorption because of its discoloration when stayed ten minutes.

The composition of the three-complex system was determinated under the established experimental conditions by Job's continuous variation method. The results indicated that the composition ration of Cr(VI) to DPC is 2:3 and DPC to 4-methyl-benzenesulfonic acid is 3:2; the relative molar absorption coefficient is 5×10^4 $L\cdot mol^{-1}\cdot cm^{-1}$, extraction balance constant is 1.8×10^5.

The calibration graph for the determination of Cr (VI) was constructed under the optimal conditions. Excellent linearity was obtained over the range 0~0.8 µg/mL of Cr (VI). The linear equation was A=0.1271C+0.091 (A, absorbance; C, Cr concentration) and the correlation coefficient was 0.9991. The limit of detection was 0.002 µg/mL.

The proposed method was used to the determination of trace Cr (VI) in chrome agent and synthetic samples, the relative absorption intensities were measured and the results are shown in **Table 1.**

Table 1 The results of the determination of trace Cr (VI) in chrome agent

Samples	Given value µg/mL	Found value µg/mL	Average value µg/mL	RSD (%)
Chrome agent	1.2	1.21, 1.19, 1.18, 1.18, 1.20	1.190	1.17
Synthetic samples	2.0	2.01, 2.02, 1.97, 2.01, 2.01	2.004	1.74

References and note

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3. The amounts of component ions per 100 g of the synthetic sample are Cr^{3+} (1g), Cr^{6+} (0.01mg), Na^+ (1g), K^+ (1g), Ni^+ (1g), Al^{3+} (0.3g), Zn^{2+} (0.2g), Cu^{2+} (0.1g), Ca^{2+} (0.2g), Mg^{2+} (0.5g), Co^{2+} (0.5g), Fe^{3+} (0.1g), Hg^{2+} (0.1g), the other is water.

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