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# Rapid *In-situ* Determination of Chromium (VI) in Water Using Modified Diphenylcarbazine with Citrate

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**Abstract:** Diphenylcarbazine citrate was synthesized and a high-speed color reaction of the new reagent with Cr (VI) was developed and used to determine trace Cr (VI) in electroplating water. In acid medium, diphenylcarbazine citrate reacted with Cr (VI) to form a magenta-colored complex. The molar absorptivity of the complex is $3.32 \times 10^4$ L · $mol^{-1}$ · $cm^{-1}$ at 540 nm. Beer's law is obeyed for Cr (VI) in the range of 0.03~2.00 mg/L. Contents of Cr (VI) in electroplating waste water was determined *in-situ* and satisfactory results were obtained.

**Keywords:** Portable photometer, Cr (VI), diphenylcarbazine citrate, *in-situ* determination.

In recent years, the determination of Cr (VI) has attracted great attention because of its toxicity to human, plants and animals[1-5]. Usually, in the industrial waste water, the concentration of Cr (VI) is relatively high and should be determined frequently. So, an accurate, quick, and convenient method for the measurement of Cr (VI) in environmental water, as well as in river, lake, sea and tap water, is of great importance. The method for determination of Cr (VI) by diphenylcarbazine (DPCI) spectrophotometry provides the advantage of high sensitivity[6-8], and has been widely used as a standard method in China. However, DPCI is unsatisfactory in water solubility and long term stability even dissolved in acetone. Therefore, it is not suitable to be used in rapid determination of Cr (VI).

In this study, a portable photometer of high sensitivity and a new solid reagent package were developed. With the portable photometer and the reagent package, Cr (VI) in water can be determined within 3 min. It possesses a significant potential in rapid determination.

A portable photometer which had been developed in our lab and sold by Jilin University--Little Swan Instrument Company was used throughout the work[9].

The new reagent is synthesized with DPCI and citric acid. Through FT-IR spectra, it is confirmed that DPCI and citric acid interact by hydrogen bonds. The new

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reagent possesses not only high sensitivity, but also quite good water solubility and an extended linear range. In the reagent package, $KHSO_4$ is added to adjust the acidity.

Diphenylcarbazine citrate dissolves rapidly in water and the hydrogen bonds are then destroyed. In acid medium (pH=1~2), oxidized DPCI chelates Cr (III) with the component ratio of 2:1 and form a magenta complex. The absorption spectrum of the complex shows an absorption maximum at 540 nm. Under the experimental conditions, the completely coloring time is less than 3 min and the complex is found to be stable for 1 h, superior to the solid DPCI whose coloring time is over 30 min. The calibration curve was A=-0.02742+0.63917×C (mg/L), r=0.99952, $\varepsilon=3.32 \times 10^4$ L/mol/cm, the linear range is 0.03~2.00 mg/L. Results of determination of Cr (VI) in industrial waste water by the method show a good agreement with the certified Cr (VI) value, and the RSD is 0.8% (n=5) for the concentration of about 0.80 mg/L. The recovery obtained by standard addition method was in the range of 103.5~105.5%.

In the determination of 10 mL 1.0 mg/L Cr (VI) sample, the presence of $Fe^{3+}$, $Cu^{2+}$, Mo (VI) (2 mg), $Mg^{2+}$, $Ca^{2+}$ (3 mg), $Cs^{+}$, $Ag^{+}$ (100 mg), $Zn^{2+}$, $V^{5+}$, $Pd^{2+}$ (30 mg) is allowed. The noninterferent ions are $Ba^{2+}$, $K^{+}$, $Na^{+}$, $F^{-}$, $Cl^{-}$, $Br^{-}$, $I^{-}$, $SO_4^{2-}$, $NO_3^{-}$, EDTA and so on. KF (50 mg) and EDTA (2 mg) are used to mask the interference of $Fe^{3+}$, $Cu^{2+}$, Mo (VI), $Mg^{2+}$, $Ca^{2+}$, $Cs^{+}$, $Zn^{2+}$, $V^{5+}$, and the amount allowed of interfering ions are increased.

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