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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

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Online publication date: 01 December 2009

To cite this Article Xin, Juanjuan , He, Yihua , Hu, Jing , Duan, Yixiang and Hou, Xiandeng(2009) 'A Compact Spectrophotometer Using Liquid Core Waveguide and Handheld Charge Coupled Device: For Green Method and Ultrasensitive Speciation Analysis of Cr(III) and Cr(VI)', *Spectroscopy Letters*, 42: 6, 351 — 355

To link to this Article: DOI: 10.1080/00387010903185728

URL: <http://dx.doi.org/10.1080/00387010903185728>

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A Compact Spectrophotometer Using Liquid Core Waveguide and Handheld Charge Coupled Device: For Green Method and Ultrasensitive Speciation Analysis of Cr(III) and Cr(VI)

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ABSTRACT In this short letter, we report a compact spectrophotometer consisting of a liquid core waveguide as the optical cell and a handheld charge coupled device spectrometer as the detector. This instrumentation features portability, ultrahigh sensitivity, simultaneous multicomponent detection, and minimal analyte solution. Its ultrahigh sensitivity permits the measurement of Cr(III) without coloration with any reagents. Therefore, a simple, fast, cost-effective, and green analytical method was developed for the ultrasensitive and simultaneous speciation analysis of Cr(III) and Cr(VI) in water samples, with the limits of detection down to the ppb level.

KEYWORDS charge coupled device, Cr(III), Cr(VI), Green Analytical Chemistry, liquid core waveguide, speciation analysis, spectrophotometer

An invited paper submitted to a special issue on Green Spectroscopy and Analytical Techniques, organized by Professor Miguel de la Guardia, of the Department of Chemistry, University of Valencia, Spain, and Professor Arabinda Kumar Das, of the Department of Chemistry, University of Burdwan, West Bengal, India.

Received 1 October 2008;
accepted 25 November 2008.

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INTRODUCTION

Photoluminescence and related spectroscopy are widely used for the analysis or characterization of various materials.^[1] However, their traditional methods suffer from low sensitivity, off-line analysis, or polluted waste. It has become increasingly important to construct ultrasensitive, pollutant-free, cost-effective, and field-portable apparatus for the measurement of trace amount of chemicals, especially those harmful to the environment and human health.

Recently, liquid-core waveguide (LCW) has been increasingly used to enhance the sensitivity of photometric analysis without special optics. LCW can provide long optical path or capture light by constraining light propagation within a liquid medium that has a higher refractive index (R.I.) than the surrounding solid tubing.^[2] In 1989, Dupont introduced a fluoropolymer Teflon AF2400 with a R.I. of ~1.29. As the AF-polymer tubing became commercially available,^[3,4] LCW-based long-path absorption spectrometry

has found a real niche in performing trace analysis in the environment without a preconcentration procedure.^[5–12] On the other hand, using a charge coupled device (CCD) as the spectroscopic detector in spectral analysis has been frequently reported in recent years,^[13,14] with most work focused on the hand-held property of a CCD. The present work utilized a LCW and a compact CCD to build a compact spectrophotometer, which has the advantages of ultrahigh sensitivity, simultaneous multicomponent determination, and green nature due to minimal analyte solution (0.1 mL).

As an example, speciation analysis of inorganic Cr(III) and Cr(VI) was performed with this compact spectrophotometer to demonstrate its advantages.

Chromium is usually present in surface and ground water in either the trivalent or the hexavalent oxidation state. Toxicity, mobility, and bioavailability of chromium depend fundamentally on its chemical form.^[15] Cr(III) is considered to be a trace element essential for the proper functioning of living organisms. On the other hand, Cr(VI) exerts toxic effects on biological systems arising from the possibility of free diffusion across cell membranes and strong oxidative potential.^[16] Therefore, it is increasingly important to accurately define the individual quantity of both valence forms. A large number of methods have been used for the determination of Cr(III) and Cr(VI), most of which need some pretreatment procedures (separation,^[17–19] pre-oxidation,^[20,21] and pre-reduction^[22–24]) and some additional reagents. Pretreatment procedures are considered to be time- and labor-consuming and not suitable for field analytical chemistry. In addition, the reagents used in the procedures may lead to potential pollution. Therefore, it is meaningful to determine ultratrace Cr(III) and Cr(VI) in water samples without any reagents or

pretreatment procedures. In this work, aqueous Cr(III) (green) and aqueous Cr(VI) (yellow) was well differentiated and simultaneously determined by using the developed instrument.

EXPERIMENTAL

Apparatus

As shown in Fig. 1, the heart of the experimental setup is a Teflon AF-2400 LCW (37.6 cm in length, 560 μm i.d. and 800 μm o.d.). Two quartz windows were agglutinated to one end of the “T” tubes, respectively. The other ends of the “T” tubes were agglutinated to the each end of the Teflon AF 2400 tubing, respectively. Analyte solution was pumped through the fiber. The detector is a hand-held CCD spectrometer (BRC 100E-USB-UV, $8.9 \times 6.0 \times 3.0$ cm in dimension, and 150 g in weight) with a spectral range of 158–408 nm. The overall weight of the experimental setup (including the mercury lamp, the brackets, and the peristaltic pump) is about 7 kg. The light source is a high pressure mercury lamp (GY-11). The lamp and lens were all purchased from Gangdong Scientific Development Inc., Tianjin, China. Sampling is achieved with a peristaltic pump (HL-2D, Huxi Analytical Instrument Co., Shanghai, China) at a flow rate of $\sim 1.7 \text{ mL min}^{-1}$. In order to avoid formation of bubbles in the optical path and to use minimal sample volume, the pump was active only during the period of sample introduction.

Reagents

1 mg mL^{-1} Cr(III) standard stock solution was prepared by dissolving 0.2500 g Cr powder (99.99%, The Second Metallurgy Factory, Shanghai, China) in 15 mL 1:1 hydrochloric acid and diluted to 250 mL

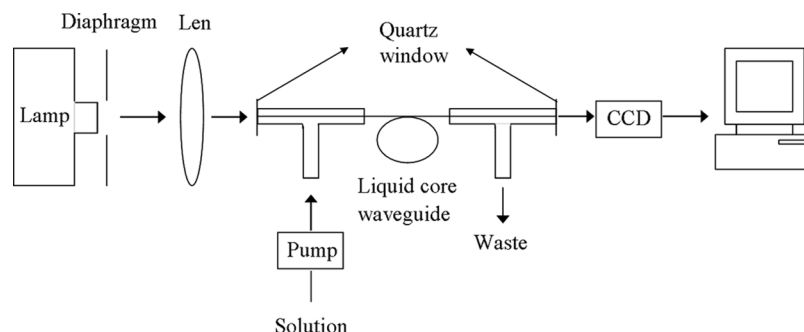


FIGURE 1 Schematic diagram of the experimental setup.

with distilled water. 1 mg mL⁻¹ Cr(VI) was obtained by dissolving 0.2829 g K₂Cr₂O₇ (A.R., Kelong Chemical Factory, Chengdu, China) in 100 mL distilled water.

Procedures: Cr(III) and Cr(VI) Determination

For preparation of individual standard solutions, appropriate amounts of Cr(III) or Cr(VI) standard stock solutions were transferred to 25 mL volumetric flasks and diluted with distilled water. The final concentrations were 10, 20, 30, 40, 50, 60, 80, and 100 mg L⁻¹ for Cr(III) and 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, and 1 mg L⁻¹ for Cr(VI). Synthetic standards containing different concentrations of Cr(III) and Cr(VI) were also prepared from the standard stock solutions and the concentrations were 100, 0.05; 50, 0.1; 20, 0.2; 10, 0.4; and 5, 0.8 mg L⁻¹ for Cr(III) and Cr(VI), respectively. 0.5 mg L⁻¹ solution of Cr(VI) and 50 mg L⁻¹ solution of Cr(III) were used for recording the full absorption spectra of aqueous Cr(III) and Cr(VI), and the absorbance at 241 nm, 321 nm, and 365 nm were simultaneously recorded by the CCD for the dual wavelength spectrophotometric determination. The pH of the Cr(III) analyte solution is about 3.8, and the pH of Cr(VI) analyte solution or the Cr(III) and Cr(VI) mixed solution is about 5.8.

RESULTS AND DISCUSSION

Brief Discussion on the Instrumentation

By use of the LCW as an optical cell, the optical path is prolonged, thus the sensitivity is greatly enhanced compared to traditional spectrophotometry. Furthermore, the capacity of the LCW is only 0.1 mL and the total required sample solution is about 1 mL including the thorough pre-cleaning process. So the waste solution is greatly reduced, thus facilitating green analytical methodologies. The use of the handheld CCD spectrometer as a detector miniaturizes the instrument, and provides multichannel capability for simultaneous multicomponent measurements. The whole system is compact and portable. The whole system is very stable, and a precision of less than 1% relative standard deviation is routinely achievable.

Cr(III) and Cr(VI) Analysis

Individual Calibrations

The maximal absorption for aqueous Cr(III) and Cr(VI) were at 404 nm and 365 nm, respectively. At 404 nm, a linear dynamic range of absorbance *versus* Cr(III) concentration is 0.09–100 mg L⁻¹, with a limit of detection (LOD) of 0.09 mg L⁻¹; and at 365 nm, for Cr(VI), a linear dynamic range is 0.0007–1 mg L⁻¹, with a limit of detection of 0.0007 mg L⁻¹. The LOD is defined as 3 SD divided by slope of the calibration curve, and here SD is the standard deviation of 11 measurements of a blank. The linear regression equation is described by $y = 0.011x + 0.011$ ($r = 0.998$, and $n = 8$) for Cr(III), and $y = 1.15x + 0.04$ ($r = 0.999$, and $n = 7$) for Cr(VI), where y is absorbance, x is the concentration of analyte, and r is the linear correlation coefficient. The relative standard deviations (RSDs) for five measurements of 0.3 mg L⁻¹ Cr(VI) and 40 mg L⁻¹ Cr(III) were 0.6% and 1.0%, respectively.

Compared with the LODs of Cr(VI) and Cr(III) of only 0.05 mg L⁻¹ and 1 mg L⁻¹, respectively, by using a traditional UV-Vis spectrophotometer, the present method shows much higher detectability. It is attributed to the effective increase of the optical path length for higher absorbance.

Dual Wavelength Spectrophotometric Determination of Cr(III) and Cr(VI)

For the dual wavelength spectrophotometry (DWS), it is necessary to find two wavelengths where the analytical signals for one of the species is equivalent, while for the other one the signals should be as different as possible. In this work, the absorbance signals for Cr(III) at 241 nm and 365 nm were equivalent, while the absorbance signals for Cr(VI) at the two wavelengths were different enough for the quantitative analysis of Cr(VI). Although the maximal absorption signal of Cr(III) appeared at 404 nm, there was no appropriate wavelength where Cr(III) had no absorption while the absorbance of Cr(VI) was equivalent to the absorbance at 404 nm. However, at 321 nm, the sensitivity was high enough for the quantitative analysis of Cr(III) and there was an absorbance of only 0.009 even for 1 mg L⁻¹ Cr(VI) solution, which was the upper linear range for Cr(VI) analysis. Therefore, the absorbance at 241 nm,

321 nm, and 365 nm were recorded by the CCD spectrometer for the simultaneous quantitative determination of Cr(III) and Cr(VI).

Calibration Curves of the Mixture of Cr(III) and Cr(VI)

The calibration graph of Cr(III) in the synthetic standards was constructed as the absorbance at 321 nm (A_{321}) versus the concentrations of Cr(III) in the range of 5–100 mg L⁻¹ with the linear regression equation described by $y = 0.009x + 0.04$ ($r = 0.999$, and $N = 5$). The calibration curve of Cr(VI) in the synthetic standards was constructed as the difference of the absorbance at 365 nm and 241 nm ($A_{365} - A_{241}$) versus Cr(VI) concentrations in the range of 0.05–0.8 mg L⁻¹ with the linear regression equation described by $y = 1.02x + 0.03$ ($r = 0.999$, and $N = 5$). The LOD and linear dynamic range (LDR) for Cr(III) in the synthetic standards were the same as its individual standards, while that of Cr(VI) would be limited by the concentration of Cr(III).

CONCLUSIONS

Green Analytical Chemistry has been one of the important trends for analytical chemistry in recent years, and spectroscopic methods can be the best ways toward green purpose.^[25] There are several advantages of the proposed LCW–CCD-based spectrophotometer, most of which are of green nature: (1) it can be made portable for field analytical chemistry; (2) the sensitivity is remarkably enhanced with the LCW; (3) the volume of the LCW is only 0.1 mL, therefore the required amount of analyte solution/the waste is minimal; (4) the use of CCD enhanced the capability for simultaneous multicomponent determination; and (5) the proposed method can be a fast (90 s/per sample), ultrasensitive, reagent-free, and green analytical method for the speciation analysis of Cr(III) and Cr(VI) in water samples. However, the applicability of the proposed scheme for the speciation analysis awaits further validation in real sample analysis.

ACKNOWLEDGMENT

We acknowledge the financial support from the Ministry of Education of China for the research on green analytical chemistry (NCET-04-0869).

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