A Highly Sensitive Spectrophotometric Method for the Determination of Cr(VI) Concentration

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A highly sensitive spectrophotometric method, which is based on the oxidation of leuco methylene blue (colorless) to methylene blue (colored) by Cr(VI), was developed for the determination of the dissolved hexavalent chromium concentrations in water.

Chromium ions exist mostly as Cr(III) or Cr(VI) in natural water.[1] Cr(III) ion is relatively nontoxic and an essential trace nutrient for the human.[2] However, Cr(VI) ion is known to be toxic for animals and humans, highly mobile in aquatic environments, and not easily removed by simple adsorption.[3] Therefore, the quantitative analysis and removal of Cr(VI) ion in the drinking water are very important.

The spectrophotometric determination of Cr(VI) concentration is possible without an additional indicator because Cr(VI) has yellow color itself. This method is very precise, but not very sensitive because Cr(VI) has a low molar absorption coefficient ($\lambda_{max} = 373$ nm; $\varepsilon = 1.4 \times 10^3$ M^{-1} cm^{-1}). Diphenylcarbazide ($\lambda_{max} = 545$ nm; $\varepsilon = 4.3 \times 10^4$ M^{-1} cm^{-1}) is the most popular reagent for the colorimetric determination of Cr(VI).[4,5] However, it has some disadvantages such as interferences from Fe(III), Mo(VI), Cu(II), and Hg(II),[6] and the formed complex is stable for only a limited time in phosphate buffer.[7] Therefore, the development of the more stable, sensitive, reliable, and inexpensive reagent for the determination of Cr(VI) is needed.

Methylene blue (MB^+) is a member of thiazine dye group and it has been used as a redox indicator in several chemical analyses. For example, commercial oxygen indicator, Ageless Eye™, employed MB^+ as a key indicator for the detection of oxygen in modified food packaging.[8] MB^+ is also used in the quantitative analysis of reducing agents, such as ascorbic acid and glucose. The principle behind such redox indicating systems is that the reduced (leuco) form of MB is colorless but the oxidized form of MB is bright blue ($\lambda_{max} = 664$ nm; $\varepsilon = 1 \times 10^5$ M^{-1} cm^{-1}).

Leuco methylene blue (LMB) solution can be easily prepared from a MB^+ solution either by the addition of reducing agent such as sodium dithionite or Zn amalgam (reaction 1) or by visible light illumination in the presence of ascorbic acid (AA) (reaction 2).[9] LMB is very easily reoxidized back to MB^+ by atmospheric oxygen (reaction 3).

$$MB^+ + H^+ + 2e^- \rightarrow LMB \quad (1)$$

$$MB^+ \xrightarrow{h\nu} MB^{+*} + AA \rightarrow LMB + AA_{ox} \quad (2)$$

$$2LMB + O_2 \rightarrow 2MB^+ + 2OH^- \quad (3)$$

However, this reaction is very pH sensitive, with the rate of reaction 3 increasing with pH.[10] Thus, LMB is moderately stable in acidic solutions (pH ≈2). It has been recently reported that LMB solution (prepared by the above method) is stable over 20 min of period in ambient atmospheric condition at pH 2.[11] Therefore, LMB can be used as a colorimetric reagent at least for 20 min. Standard reduction potentials of Cr(VI)/Cr(III)[12] and MB^+/LMB[13] couples are 1.33 and 0.532 V (vs NHE) at pH 0, respectively. Thus, LMB can react with Cr(VI) and reduce it to Cr(III). The overall reaction can be summarized as:

$$3LMB + 2Cr(VI) \rightarrow 3MB^+ + 2Cr(III) \quad (4)$$

$K_2Cr_2O_7$ (Aldrich) and $Cr(NO_3)_3$ (Aldrich) were used for the preparation of Cr(VI) and Cr(III) standard solutions, respectively. LMB solution was prepared by the reduction of MB^+ (Aldrich) by adding Zn amalgam as a reducing agent at pH 2. Detailed preparation method is described elsewhere.[14] A double beam UV–vis spectrophotometer (Shimadzu, UV2401PC) was used for absorbance measurements. The pH of the solution was adjusted with a standard HCl solution and measured with a pH meter (Orion).

An aliquot of the 10 μM LMB solution was transferred into a quartz cell (1 cm pathlength, 4 mL volume), which was located within the spectrophotometer, and then Cr(VI) solutions of various concentrations were added. The subsequent change in absorbance was monitored at 664 nm as a function of time. Throughout the measurement, the solution was stirred magnetically. Cr(VI) quantitatively oxidized LMB into its blue-colored MB^+ in water solution at pH 2, and the resulting colored dye showed a maximum absorbance at 664 nm. The reagent blank had negligible absorbance at this wavelength.

Figure 1 shows the measured absorbance change (at 664 nm) vs time profiles for LMB solution with the addition of Cr(VI) in

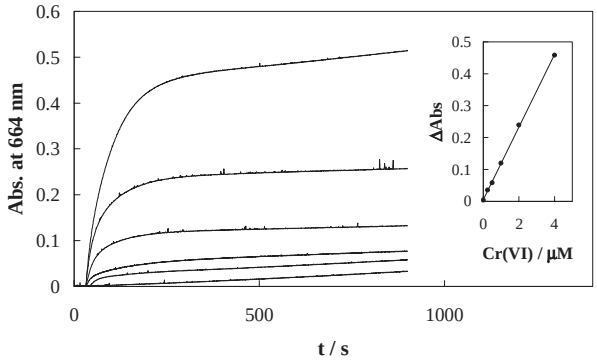

Figure 1. Measured absorbance (at 664 nm) vs time profiles for a LMB solution (10 μM, pH 2) added with Cr(VI) solutions of various concentrations (bottom to top: 0, 0.25, 0.5, 1, 2, and 4 μM). The inset is a standard calibration curve in this condition (data obtained at 300 s).

Table 1. Sensitivity of three different Cr(VI) determination methods

	LMB	DPC	Cr(VI) itself
sensitivity[a]	0.1139[b]	0.0415	0.0015

[a]Slope of the calibration curve (unit: abs./μM). [b]taken from Figure 1.

various concentrations. The blue coloration of the mixed solution rapidly proceeded in the initial stage and then reached a plateau region. The absorbance changes (ΔA) at either the initial or saturated period can be used for plotting the calibration curve (i.e., ΔA vs [Cr(VI)]) and either of the two methods showed a good linear relationship as shown in the inset of Figure 1. The slow rise of absorbance observed in the absence of Cr(VI) is due to the slow oxidation of LMB by atmospheric oxygen (reaction 3). For the test of Cr(III) reactivity, an aliquot of Cr(III) was added into LMB solution. As we expected, there was no marked change in the overall absorbance of the sample solution. Thus, this analytical system utilizing LMB showed good selectivity to Cr(VI) in the mixture of Cr(VI) and Cr(III) solution.

For the comparison of the sensitivity of different analytical methods, Cr(VI) solutions were also analyzed by the direct absorbance measurement of Cr(VI) itself and the diphenylcarbazide (DPC) complexation method, respectively. As shown in Table 1, LMB method showed the highest sensitivity among the three different determination methods. LMB method has almost three times higher sensitivity compared to the conventional DPC method.

Another advantage of the LMB method is that the reagent can be repeatedly used in successive analyses when LMB is prepared from the ascorbic acid (AA)–visible light system (reaction 2). Whenever we need LMB, it can be regenerated from MB simply by irradiating visible light (500-W tungsten lamp) in the presence of AA. Five successive measurements of Cr(VI) could be achieved in the same spectrophotometric cell without depleting initially added MB as shown in Figure 2.

Upon spiking Cr(VI) to the initial LMB solution prepared by reaction 2, the absorbance at 664 nm rapidly increased to reach a saturation within a few minutes as Cr(VI) was depleted as a result of reaction 4. After the first analysis, LMB was regenerated (i.e., bleached) under visible light irradiation and then the second spike of Cr(VI) was followed with the subsequent rise of the absorbance. This process could be repeated over and over.

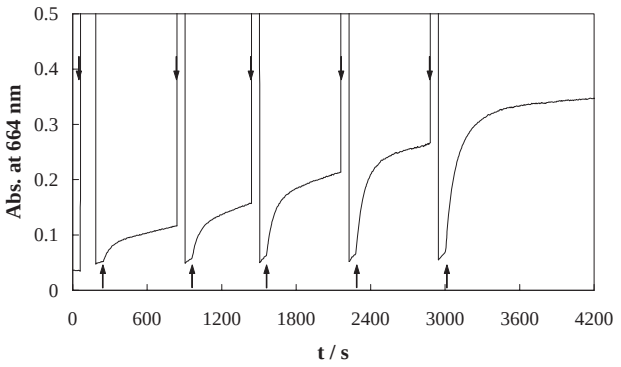

Figure 2. Successively measured absorbance (at 664 nm) vs time profile for a LMB solution (10 μM, pH 2) added (↑) with various concentrations of Cr(VI) (left to right; 1, 1.96, 3.77, 7.02, and 12.3 μM) in the presence of AA (120 ppm). The abrupt rise of the absorbance was caused by an instrumental perturbation when visible light was irradiated (↓) from an external lamp to regenerate LMB. The absorbance dropped back to a normal level when the light was off.

Possible interferences from other aquatic species should be considered. For example, the effect of ferric ions, which can oxidize LMB like Cr(VI) and hence interfere in the determination of [Cr(VI)], was investigated. Their presence did influence the LMB analysis of Cr(VI): 10 μM Fe(III) in a sample water containing 1 μM Cr(VI) induced about 30% error. In the case of DPC method, 2% error has been reported at the above conditions.[15] Therefore, the problem of interferences should be resolved for the real sample applications. The interference of Fe(III) might be masked by the addition of complexing reagents such as EDTA. Other redox and adsorbing species found in various water samples may also interfere. Their potential effects on this new analytical method and the method for eliminating or correcting the interference errors are being investigated.

The reproducibility of the LMB method was established by the analysis of standard solutions of 1.25, 2.5, and 5 μM of Cr(VI). Three replicate determination of each concentration gave the standard deviation of 0.05, 0.15, and 0.33%, respectively. To check out how much unknown impurities in tap water influence the LMB analysis of Cr(VI), the known concentration of Cr(VI) samples which were prepared using ultrapure water and tap water were measured and they were compared. The calibration curve obtained using tap water was essentially identical to the one obtained using ultrapure water, which indicates that impurities in tap water little influence the LMB determination of Cr(VI). Therefore, this simple and highly sensitive spectrophotometric determination can be proposed as a new analytical method for Cr(VI) concentration in drinking water and can be further applied to wastewater and natural water samples when any interfering components are removed or masked prior to the analysis.

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