

Selective measurement of chromium(VI) by fluorescence quenching of ruthenium

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Abstract

A flow injection method is described for the selective measurement of chromium(VI) in aqueous solutions. This method is based on the dynamic quenching of ruthenium(II) fluorescence. The detection limit is 0.43 ppm and 40 samples can be analyzed per hour. Selectivity is demonstrated over ferrous, nickel, cupric and zinc cations and no effect is observed from sulfate, chloride, borate and phosphate. Some interference quenching was measured for cyanide and nitrate, but the method is more responsive to chromium(VI) by factors of 10.2 and 82, respectively. The effects of solution pH, carrier stream flow rate and ruthenium concentration are demonstrated. Results indicate the method is suitable for measuring chromium(VI) in effluents from electroplating baths. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chromium is an important element in environmental science and water pollution control. Natural levels of chromium in unpolluted water are below 2 ppb and its toxicity effects demand a maximum permissible chromium level of 50 ppb in drinking water [1]. Of its various oxidation states, chromium(VI) poses the greatest risk to

human health because of its known actions of toxicity, its high solubility in aqueous solutions and its relatively rapid mobility in soil and solid wastes. Chromium(VI) is known to damage exposed skin, irritate mucous membranes, produce pulmonary sensitivity, create dental erosion, cause loss of weight, induce renal damage, and target the respiratory tract and skin [2–4]. In addition, experimental evidence links chromium(VI) with various types of cancer [5].

Environmental chromium(VI) is generated largely by metal cleaning processes, surface finishing and metal coating processes, ink pigments, dye manufacture and chromate water treatment

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[6]. Effluents from these processes must be monitored to ensure proper chromium removal prior to releasing these effluents into the environment.

Many analytical methods are available for measuring chromium in water samples. General methods include gravimetry, titrimetry [7], colorimetry [8], potentiometry [9], spectrophotometry [10–14], fluorometry [15–17], chemiluminescence spectrometry [18,19], chromatography [20], and solid-phase spectrophotometry coupled with anion exchange membrane for pre-concentration [21]. Although, the lowest detection limits are provided by graphite-furnace atomic absorption spectrometry [22], this technique is not well suited for field applications. Flow injection methods coupled with ion exchange [23], co-precipitation or extraction pre-concentration steps have been proposed for field applications.

This work evaluates the use of dynamic quenching of a ruthenium dye for chromium(VI) measurements. Ruthenium dyes are well known reagents for measuring oxygen in gaseous and aqueous media [24–27]. These measurements are based on dynamic quenching of ruthenium fluorescence by oxygen. In the presence of ambient oxygen ruthenium fluorescence quenching can be detected in the presence of chromium(VI) and this quenching can be used to measure chromium(VI) at sub-ppm concentrations.

2. Experimental work

2.1. Apparatus

All fluorescence measurements were made with an SLM-Aminco SPF 500 C spectrofluorometer equipped with a 250 watt xenon arc lamp for excitation. Ruthenium fluorescence was measured by setting the excitation monochromator to 450 nm with a 1.0 nm slit width and the emission monochromator to 610 nm with a 7.5 nm slit width.

2.2. Chemicals and reagents

Hypophosphorous acid 50% was purchased from Aldrich (Mikwaukee, WI). Methanol (GR grade) was obtained from EM Science (Gibbstown,

NJ). Ethanol (dehydrated, 200 proof) was obtained from Pharmco (Brookfield, CT). 4,7 Diphenyl 1,10 phenanthroline (dpp) was used as received from Lancaster (Windham, NH). Potassium petachlororuthenate monohydrate III ($K_2(RuCl_5 \cdot H_2O)$) was purchased from Alpha (Ward Hill, MA). Phosphoric Acid 85%, KH_2PO_4 , and Na_2HPO_4 were purchased from Fisher Scientific (Fairlawn, NJ).

All standard solutions were prepared with analytical grade materials used as received. Buffer solutions were prepared according to Christian and Purdy [28]. Ruthenium II tris 4,7-diphenyl 1,10 phenanthroline was made according to the published procedure by Lin et al. [29]. All ruthenium standard solutions were prepared by dissolving the dried ruthenium II tris 4,7-diphenyl 1,10 phenanthroline powder in a minimum amount of ethanol and then diluting to mark with distilled-deionized water. Chromium standard solutions were made by dissolving dried potassium dichromate in distilled-deionized water.

2.3. Procedures

Dynamic quenching of ruthenium by chromium(VI) was initially characterized by adding the appropriate materials to a disposable polymethylmethacrylate cuvette and measuring the resulting solution fluorescence in the SLM-Aminco fluorimeter. In general, batch measurements of this type were carried out in aqueous solutions of the ruthenium reagent with different amounts of Cr(VI).

The flow injection manifold was constructed according to the schematic diagram presented in Fig. 1. A Harvard model 44/1 syringe pump was used to flow equal volumes of the buffered ruthenium reagent and the carrier buffer through the system. The sample was carried from a six-port injector loop (Upchurch, model V 450) to a mixing-tee where it was mixed with the ruthenium reagent. These two solutions were allowed to mix for 60–100 s as they proceed to the fluorometer for detection. A micro-flow through quartz fluorescence cell was used for detection. The sample loop of the injection port was made to hold 1.0 ml of solution.

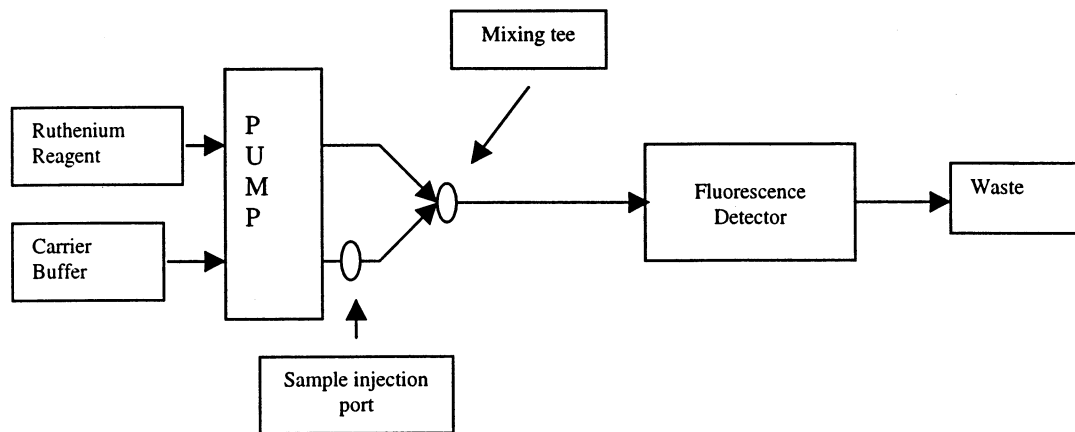


Fig. 1. Flow injection manifold for the determination of chromium(VI) by ruthenium fluorescence quenching.

The response to chromium(VI) was measured as the decrease in luminescence according to the well known Stern–Volmer relationship ($I_0/I = 1 + K_{SV} [Q]$). In this expression, I_0 and I correspond to the fluorescence intensity in the absence and presence of the quenching agent, K_{SV} corresponds to the Stern–Volmer constant and $[Q]$ denotes the concentration of the quenching agent. In the FIA experiments, I_0 was taken as the mean intensity measured for the carrier buffer just before the sample was injected and I was taken as the peak fluorescence signal following sample injection.

3. Results and discussions

Chromium(VI) quenches the fluorescence of ruthenium in a linear Stern–Volmer manner. A plot of $(I_0/I - 1)$ versus chromium(VI) concentration is linear over a chromium concentration range from 3 to 28 ppm. Least squares regression analysis of these data gives a slope of $3.6 (\pm 0.1)$ ppm⁻¹, y -intercept of $-3.7 (\pm 2.0)$ and r -square of 0.9956.

The effect of ruthenium concentration on the extent of fluorescence quenching was established by using the FIA system and comparing responses observed for a series of chromium(VI) solutions ranging in concentration from 0.25 to 5.0 ppm. At all chromium concentrations tested, the extent of

fluorescence quenching increased as the ruthenium concentration increased from 5 to 50 μ M. These findings indicate greater sensitivity can be obtained with higher levels of ruthenium. Unless indicated otherwise, the ruthenium concentration was set at 15 μ M in order to conserve reagent.

The effect of carrier buffer flow rate was examined over a range of flow rates from 2 to 7 ml min⁻¹. The degree of fluorescence quenching was recorded for a series of chromium concentrations with a fixed ruthenium level of 15 μ M. The results are shown in Fig. 2 where the magnitude of fluorescence quenching is plotted versus solution flow rate. The measurement is relatively independent of flow rate at values below 3.0 ml min⁻¹. The magnitude of the signal drops significantly at faster flow rates corresponding to insufficient mixing times before detection. The flow rate was set at 2.0 ml min⁻¹ unless specified otherwise.

In an attempt to identify the ideal pH for the measurement, the effect of solution pH on the excitation and emission spectra of ruthenium was established. Fig. 3 shows the results of this experiment where the excitation and emission spectra are superimposed for the different pHs tested. The greatest excitation and emission intensities were observed when the solution pH was 2.9 and 3.6. Luminescence falls sharply at pH values below 2.9 and above 9.9. The emission intensity is relatively insensitive to pH over the broad range from 6.5 to 9.0.

The observations described above, motivated an experiment to establish the degree of chromium based fluorescence quenching of ruthenium at pHs between 6.5 and 9.0. This experiment was carried out with the FIA configuration where the magnitude of response was recorded for a series of chromium concentrations with different pHs for the sample and carrier buffer. The results are summarized in Fig. 4 where pH 8.0 is optimal over this tested pH range.

A Stern–Volmer plot and typical time trace are provided in Fig. 5 for the FIA system operating at pH 8.0. In this experiment, the carrier flow rate was 2.0 ml min^{-1} and the ruthenium concentration was $15 \text{ }\mu\text{M}$. The Stern–Volmer plot is linear over the tested concentration from 5 to 60 ppm. This line is characterized by a slope of $0.049 (\pm 0.001) \text{ ppm}^{-1}$, a y -intercept of $0.02 (\pm 0.02)$ and an r -square of 0.9991 . The corresponding estimated limit of detection ($S/N = 3$) is $1.22 (\pm 0.02) \text{ ppm}$.

We also examined the Stern–Volmer plot for data collected with the FIA system operating at pH 3.0. Again, the flow rate was 2 ml min^{-1} , but

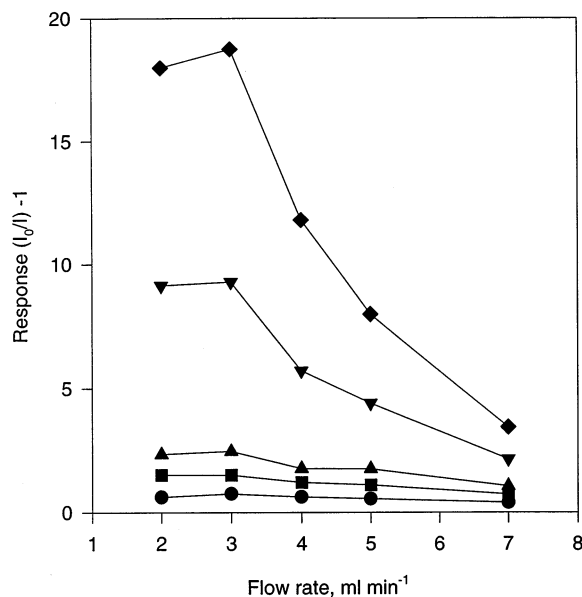


Fig. 2. Effect of carrier stream flow rate on the magnitude of fluorescence quenching measured for chromium concentrations of 20 (circle), 25 (square), 30 (up-triangle), 40 (down-triangle), and 50 (diamond) ppm.

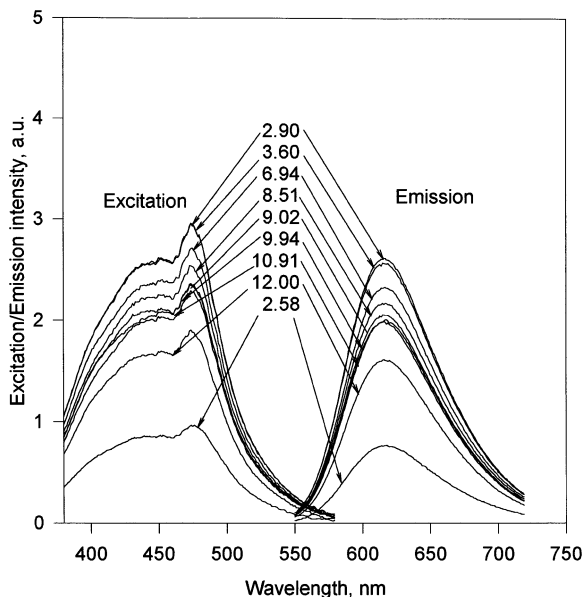


Fig. 3. Excitation and emission spectra for ruthenium II tris 4,7-diphenyl 1,10 phenanthroline at the indicated pH values.

the ruthenium concentration was increased to $50 \text{ }\mu\text{M}$ in this experiment in order to enhance the measurement sensitivity. The resulting Stern–Volmer plot and a typical time trace are presented in Fig. 6. The response to chromium is more

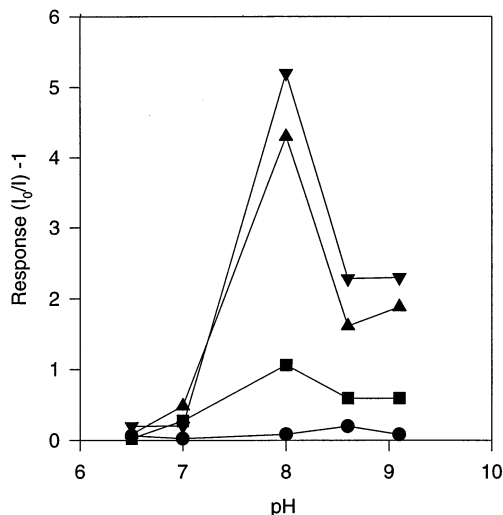


Fig. 4. Effect of carrier buffer pH on the magnitude of response to 10 (circles), 30 (square), 50 (up-triangle) and 60 (down-triangle) ppm of chromium.

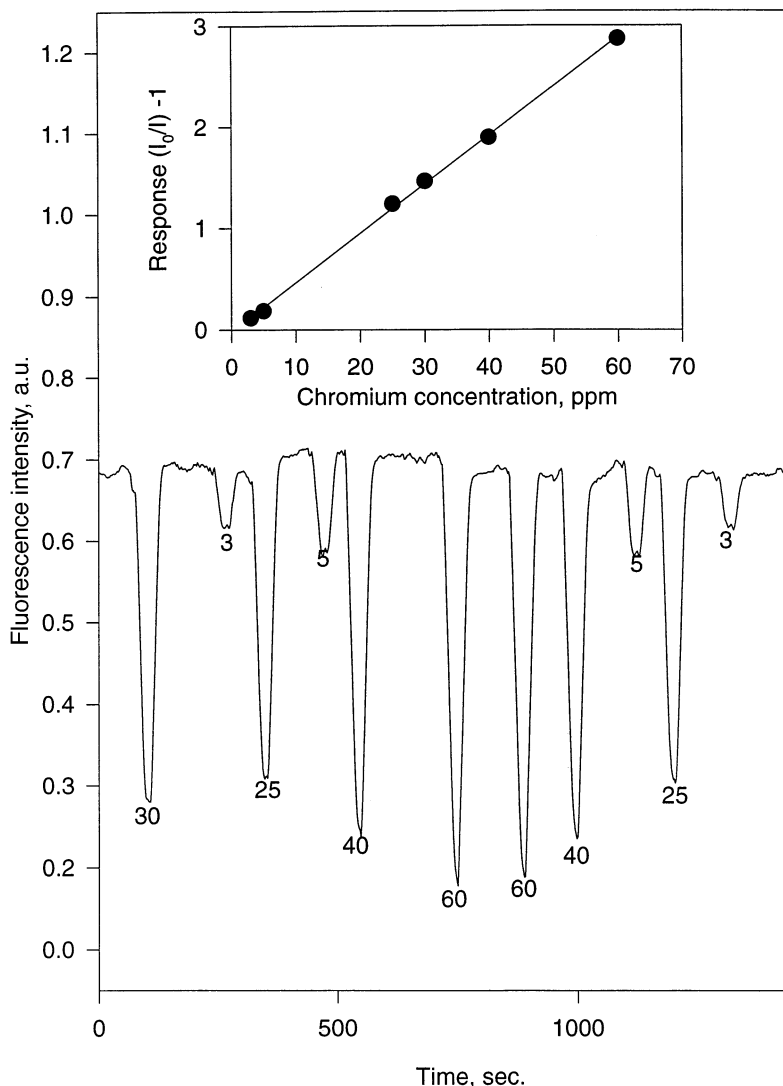


Fig. 5. Fluorescence intensity time trace for the indicated concentrations of chromium when the FIA system operates at pH 8.0. Inset shows the corresponding Stern–Volmer plot.

sensitive under these conditions. Linear regression analysis indicates a slope of $0.29 (\pm 0.02) \text{ ppm}^{-1}$, a y -intercept of $0.21 (\pm 0.04)$, and an r -square of 0.9795 over the tested chromium concentration range (0.1–5 ppm). The computed limit of detection is $0.43 (\pm 0.027) \text{ ppm}$ under these conditions.

Selectivity for chromium(VI) was investigated by monitoring the response observed after injecting samples with high concentrations of potential interfering cations and anions. The list of tested

cations includes nickel(II), copper(II), zinc(II), and iron(II). These cations represent the most likely interferences in effluents from common electroplating baths. Each cation was tested by injecting a 1000 ppm solution of the cation prepared with the chloride salt. No fluorescence quenching was observed from any of these cations. The tested anions include cyanide, sulfate, nitrate, chloride, borate, and phosphate. Again, these anions were tested at 1000 ppm concentrations from

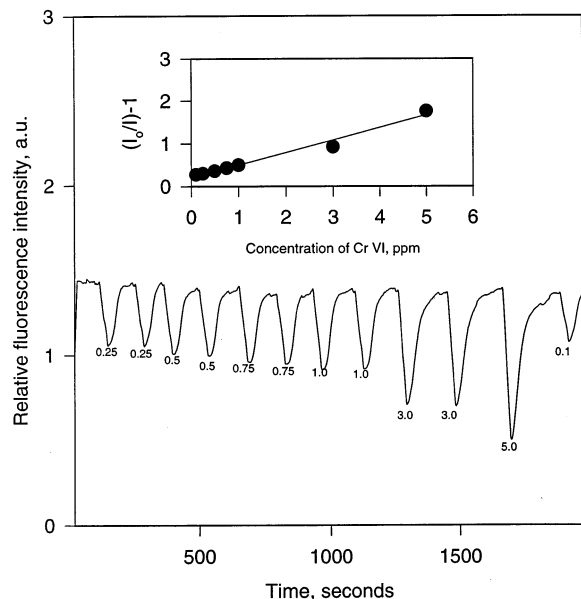


Fig. 6. Fluorescence intensity time trace for FIA system operating at pH 3.0 and 50 μ M ruthenium. The corresponding Stern–Volmer plot is provided at the inset.

solution prepared with the sodium salt. No response was observed for sulfate, chloride, borate and phosphate. Significant quenching was observed, however, for both cyanide and nitrate. The relative magnitude of these interfering responses compared to chromium(VI) was established by interpolating from the corresponding chromium Stern–Volmer plot. This analysis shows that 1000 ppm nitrate gives the same response as 98 ppm chromium and 1000 ppm cyanide gives the same response as 12.2 ppm chromium. These values correspond to selectivity ratios of 10.2 and 82, respectively, relative to chromium(VI). Finally, no response was observed from a single solution composed of a mixture of nickel, copper, zinc, iron, sulfate, chloride, borate, and phosphate.

4. Conclusion

Chromium(VI) can be measured selectively by the proposed FIA system based on ruthenium fluorescence quenching. This method is suitable

for on-site measurements of environmental samples. The method provides sufficient selectivity over interferences prevalent in the metal finishing industry e.g. electroplating. Finally, the method does not require a sample pretreatment step to remove iron and copper which are the primary interferences of in the 1,5 dipheylcarbazine method [30].

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