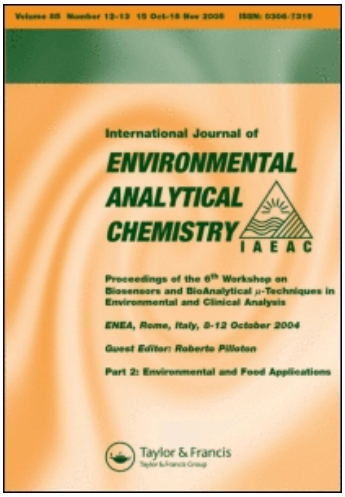


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# A simple optical sensor for chromium(VI) based on a cationic ion exchange film coupled with attenuated total reflectance spectroscopy

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# A simple optical sensor for chromium(VI) based on a cationic ion exchange film coupled with attenuated total reflectance spectroscopy

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A new optical sensor for Cr(VI) in environmental water samples has been developed. The device is based on uptake of Cr(VI) as $HCrO_4^{1-}$ at acidic pH into a quaternized poly(4-vinylpyridine) (QPVP) film followed by direct optical detection using attenuated total reflectance (ATR) spectroscopy in a thin-layer flow cell. Cr(VI) uptake is demonstrated to be reversible such that the film can be regenerated for multiple uses over extended periods of time. The sensor was investigated over a pH range of 3–7 and gave a linear response over a Cr(VI) concentration range of 5 μM to 1 mM at pH 4. Analysis of potential interferences demonstrates that the sensor provides excellent discrimination against cationic species, including Cr(III). We also demonstrate a prototype 'field ready' version of the sensor utilizing a 410-nm light-emitting diode source, fixed angles, and prismless construction that is used in conjunction with a rugged miniature spectrometer.

*Keywords:* Chromium; Sensor; Attenuated total reflectance; Thin film; Ion exchange

## 1. Introduction

Chromium(VI) in the form of dichromate $\left(Cr2O_7^{2-}\right)$, hydrogen chromate $\left(HCrO_4^{1-}\right)$, or chromate $\left(CrO_4^{2-}\right)$ has long been recognized as an environmental toxin that can lead to cancer in humans and animals [1, 2]. While some Cr(VI) occurs naturally in water due to its presence in various minerals, there has been considerable concern about dangerous levels of Cr(VI) in drinking water from man-made sources. Such sources include leather tanneries [3], electroplating baths, steel manufacturing plants, and water-cooling towers [1]. In each of the aforementioned applications, Cr(VI) is prized as a strong oxidizing agent; this is also the property that makes it harmful to biosystems.

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As a result, there is need for development of effective sensors for environmental Cr(VI) such as that found in wastewater runoff from a tannery or steel mill.

To emphasize this point, it was reported in 2004 that a vast Cr(VI) plume from water-cooling towers of an energy utility was threatening the Colorado River, a source of drinking water for some 18 million people [4]. Here, the analytical focus is not necessarily the need for low limit of detection (LOD), but rather rapid on-site determination of the front of the plume. Given that the concentration of Cr(VI) in the plume is believed to be *ca.* 12 ppm (230 μM), this would represent a perfect application for a simple, field-ready chemical sensor such as that which we report here.

Chemical sensing has recently and rapidly become an important means of environmental testing for a number of reasons [5]. Most importantly, modern sensors are small and robust enough for extended field use; in many cases, they also combine the analytical problems of analyte separation (and/or preconcentration) and detection into a single cost-effective device that offers acceptable accuracy, precision, selectivity, and reusability. Numerous sensing schemes have been reported for detection of Cr(VI). Among these are optical sensors [6–10], a microcantilever sensor [11], and several electrochemical (voltammetric) sensors [12–16]. A common approach in many of these designs has been to sequester Cr(VI) into various polymeric materials for later detection [7, 12, 15, 17]. Potential advantages offered by this approach include some degree of selectivity and preconcentration of the analyte in the film.



It is well known that optical detection of absorbing analytes can be enhanced by employing attenuated total reflectance techniques in conjunction with a waveguiding medium [5, 18]. Here, interaction of the evanescent wave with analyte at each reflection point at the waveguide leads to increased absorbance; therefore, multiple reflections result in increased sensitivity. An example of such an approach is detection of $Pb^{2+}$ after reaction with xylenol orange in a sol-gel membrane coated onto a waveguiding substrate [19]. More recently, spectroelectrochemical sensors have been developed around ATR techniques [20] that employ a number of different thin polymeric films [21–24] coated onto a conductive waveguiding medium; these devices offer three modes of selectivity: optical, electrochemical, and charge [25–28]. Furthermore, a compact ATR spectroelectrochemical cell has been reported that makes remote field sensing highly promising [28, 29]. In a somewhat related vein, another Cr sensor has been recently reported that employs detection via diffuse reflectance spectroscopy after Cr has been extracted onto a resin-loaded disk through which water is forced via a syringe [30]. This approach is especially attractive due to its cost-effectiveness and simplicity, thus making it useful for field sampling.

In light of these reports, we have developed an ATR-based optical sensor for the direct determination of Cr(VI) in water under acidic to neutral conditions. Central to the success of this design is a quaternized poly(4-vinylpyridine) (QPVP) ion-exchange polymer recently reported by Heineman and co-workers [23]. This material is quickly and easily prepared in a single pot synthesis, is stable over a wide range of pHs, lends itself well to spin coating, and has demonstrated excellent uptake of anionic species such as ferrocyanide [23]. We have found that when coated onto a multiple internal reflectance medium, the QPVP film rapidly and efficiently takes up Cr(VI) as $HCrO_4^{1-}$, which is then optically determined using ATR spectroscopy. We show that the sensor gives a linear response over nearly three orders of magnitude with a limit of detection (LOD) of 5 μM Cr(VI), and effectively discriminates against cationic species, most notably $Cr^{3+}$.

We further present here a highly simplified, field-ready version of the sensor that employs a light-emitting diode (LED) as a source, fixed angles of incidence and collection, and prismless design. This sensor design could easily be powered by the battery pack of a laptop computer and used in conjunction with rugged, inexpensive, commercially available miniature spectrophotometers, thus making it ideal for remote-sensing applications.

## 2. Experimental

### 2.1 *Reagents*

All reagents were purchased from commercially available vendors and used without further purification. Potassium nitrate was sourced from Baker (Phillipsburg, NJ). Potassium dichromate (Fisher, Pittsburg, PA) was the source of Cr(VI). Nitric acid (Fisher, Pittsburg, PA) was used to acidify the chromium solutions. Tris-(2,2′-bipyridine)ruthenium(II) chloride hexahydrate (ICN Pharmaceu-ticals, Plainview, NY), chromium(III) nitrate, and sodium molybdate (both from Fisher) were used as test interferences.

Methyl iodide, from Fisher; poly(4-vinylpyridine) (160,000 average molecular weight) and diiododecane, both from Aldrich (Milwaukee, WI), were used in the preparation of the QPVP films.

Since our initial studies involved evaluating the sensor as a spectroelectrochemical device, potassium nitrate was present as a supporting electrolyte; this protocol was kept, even though the sensor as reported here was ultimately evaluated only as an optical device. Doubly distilled water was used for preparation of all aqueous solutions.



### 2.2 *Preparation of glass/ITO substrates*

ITO surfaces on 1737F glass, obtained from Thin Film Devices (Anaheim, CA), cut to $10 \times 45$ mm sections, were used as conductive substrates. These ITO surfaces were prepared using the following process. They were first sonicated in a VWR Scientific Model 75HT Aquasonic sonicator in a soapy water bath for 30 min at room temperature. The slides were then dried and soaked in a saturated NaOH/ethanol (Pharmco, Brookfield, CT) bath for 1 h, followed by extensive rinsing with distilled water. The slides were stored in a covered beaker of distilled water until ready for use. Just prior to use, each glass/ITO slide was rinsed with absolute ethanol and wiped dry with a Kimwipe. ITO-coated glass was used so that potentials could be applied to the sensor surface for concurrent electrochemical experiments that were carried out but are not discussed here.

### 2.3 *Preparation of QPVP films*

QPVP films were prepared on ITO surfaces using a previously reported procedure [23]. First, quaternized sites were incorporated into the polymer blend by adding 200 μL of methyl iodide to a solution of 0.2 g of PVP and 0.02 g of diiododecane cross-linker in 4 mL of 1-butanol. This mixture was stirred for 1 h and took on a slightly cloudy, light

yellow colouration due to formation of solid particles. The polymer mixture was filtered through a 0.45 μm-pore-size syringe filter, and 250 μL of the filtered solution was evenly dispersed onto the glass/ITO surface (prepared as described in section 2.2) and spun at 3000 rpm for 30 s to prepare uniform films of *ca.* 20% quaternized pyridine. QPVP films prepared in this manner are reported to be *ca.* 320 nm thick. Films were allowed to cure for at least 12 h before use and were equilibrated at least overnight in aqueous 0.1 M $KNO_3$ prior to adjustment to the target pH; this equilibration was accomplished in the ATR flow cell.

### 2.4 *Benchtop ATR flow cell*

For absorbance measurements, a compact, four reflection attenuated total reflectance (ATR) thin-layer flow cell was employed. The cell was originally designed as a spectroelectrochemical cell modified from an electrochemical liquid chromatography detector available from Bioanalytical Systems; detailed diagrams showing its design and geometry have been published previously [31, 32]. Solutions were introduced into the cell using a syringe pump (Sage Instruments, model 341 B) operated at a constant flow rate of 0.15 mL $min^{-1}$.



For spectral measurements, polychromatic light from a Xe arc lamp (CVI Spectral Products Cermax Xe fibre optic light source) was used. The light was directed by a multimode optical fibre (Romack, 400μ core step index, NA = 0.22) through a neutral density optical filter (CVI) into a collimating objective (Newport, 10×, NA 0.25). This collimated light was introduced into the ATR cell by a Schott SF6 coupling prism (Karl Lambrecht) mounted on the reverse side of the ITO slide by a mounting compound with a high refractive index (Cargille Meltmount, $n = 1.702$). Exiting light was decoupled by a second prism and focused on an optical fibre by a focusing objective (Newport, 10×, NA = 0.25). Light leaving the cell was transmitted by optical fibre to an Acton SpectraPro 2150i imaging monochromator (150-cm focal length) and detected by a PMT (Acton). Data collection was accomplished using Acton Spectrasense software (version 4.3.3). Aqueous solutions consisting of 0.1 M $KNO_3$ and $HNO_3$ (varied to control pH between 3 and 7) were used as the blank solutions for determination of absorbance. Unless otherwise specified, all data shown were acquired using the benchtop ATR flow cell.

### 2.5 *Portable ATR flow cell*

As an alternative to the benchtop cell described above, we have constructed a highly simplified 'field ready' ATR flow cell. Figure 1 shows a cartoon of the upper part of the cell assembly. The same stainless steel flow assembly and gasket used in the benchtop cell were reused, but in this case the reverse side (i.e. the side without the sensing film) of the ITO-glass sensing surface rested in a notched assembly constructed of Delrin plastic, as shown in figure 1. Into this assembly were drilled cavities, at fixed 35° angles, to accommodate a violet LED light source on one side and a 0.25-inch ferrule housing a 400-μm optical fibre on the other. We note that this design uses no coupling prisms, which greatly simplifies the cell assembly and alignment procedure. Rather, light is launched directly into one edge of the sensing surface and likewise collected from the opposite edge using an optical fibre. The collected light was directed into the same

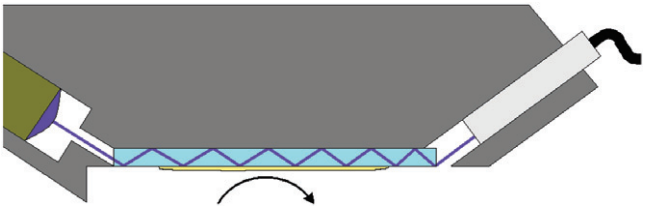

Figure 1. Illustrations of the prismless, portable ATR flow cell showing a side-on view of the upper Delrin unit showing the LED light source (left), glass/ITO sensing platform and QPVP film (centre), and 0.25-inch fibre-optic ferrule (right). Note the four reflections in the region of the sensing film.

monochromator/detector assembly described in section 2.4. The LED was powered using a GW Laboratory DC power supply (model GPS-1850) operated at 3.5 V and 100 mA. The Delrin assembly was machined using a Roland MDX-20 Modela Desktop Rapid Prototyper mill under PC control.



## 3. Results and discussion

### 3.1 *Uptake of Cr(VI) into QPVP films*

One consideration for environmental chromium sensing is that the chemical form in which Cr(VI) is found depends strongly on both pH and concentration. For example, at concentrations $< 0.01$ M between pH 0.75 and pH 6.45, the primary form is $HCrO_4^{1-}$, but as the pH approaches 7, $CrO_4^{2-}$ dominates. These different forms and the conditions in which they exist are illustrated using a Pourbaix diagram such as that found in [14]. Therefore, the sensor response may vary with pH, depending on how the device responds to each form of Cr(VI). Another common problem is that $Cr^{3+}$ is often present in real samples, so differentiation of the two oxidation states is required [9]. We attempt to address both of these situations with our sensor design.

Figure 2 is a conceptual diagram of the ATR sensor. Onto a glass/ITO substrate a thin QPVP film is spin-coated, which means that this serves as the sensing region. Since the pyridine groups in the QPVP film are about 20% quaternized, numerous positively charged ion exchange sites exist throughout the film. As a result, any of the negatively charged forms of Cr(VI) should readily partition into the film. Light is then coupled into the substrate such that four reflections on the ITO/film side are obtained. At each ITO reflection point, the evanescent wave penetrates to a depth of *ca.* one wavelength into the sensing film and is attenuated depending on the concentration of absorbing Cr(VI) sequestered in the film. Finally, light leaving the substrate is collected, and a total absorbance is calculated via comparison of the incident intensity, $I_0$, and the transmitted intensity, $I$. It is noteworthy that the film should allow for effective detection of Cr(VI) in the presence of excess Cr(III), since, in their native states, these species have opposite charges (e.g. $HCrO_4^{1-}$ *vs.* $Cr^{3+}$).

Since much environmental sensing of Cr(VI) will likely be done in mildly acidic solutions, we assume that the dominant form of Cr(VI) is $HCrO_4^{1-}$. Figure 3 illustrates the uptake of $HCrO_4^{1-}$ and sensor response after exposure to a 10 mM solution

of Cr(VI) in 0.1 M $KNO_3$ at pH 3. Here, several important points become apparent. First, curve (A) represents the sensor response to the analyte solution with no QPVP film present; a bare ITO/glass substrate was used. It is noteworthy that without the film, there is no measurable absorbance across the visible spectral region. Curves (B), (C), and (D) are spectral scans acquired as a function of time when a film is present and clearly show the rapid uptake of $HCrO_4^{1-}$ into the film. The time that elapsed between acquisition of scan B (fifth scan) and scan D (fifteenth scan) was no more than 5 min, and the uptake had reached equilibrium by scan D. Therefore, the QPVP film plays a pivotal role in the preconcentration and effective optical detection of Cr(VI). Furthermore, rinsing the film with 0.1 M $KNO_3$ at pH 3 results in equally rapid leaching of the $HCrO_4^{1-}$ from the film, thus demonstrating the ability to regenerate the film for subsequent uptake experiments (data not shown). A complete rinse requires roughly the same amount of time as an uptake; in some cases, the original baseline was

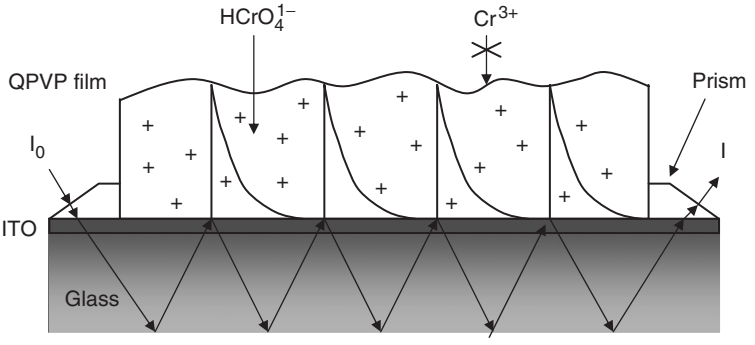


Figure 2. Cartoon illustrating the concept of the film-based ATR sensor employing four internal reflections. The evanescent wave and its decay are represented at each ITO reflection point; (+) symbols represent positively charged ion-exchange sites in the QPVP film. Also demonstrated is the charge selectivity of the film via partitioning of $HCrO_4^{1-}$ but not $Cr^{3+}$.

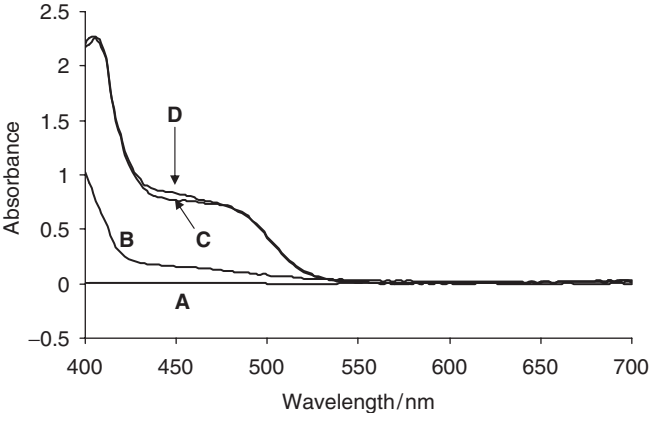


Figure 3. Spectra showing uptake of Cr(VI) into a QPVP film: (A) spectrum obtained at bare ITO in the presence of 10 mM Cr(VI); (B) 5th scan after exposure of a QPVP film to 10 mM Cr(VI); (C) 12th scan; and (D) 15th scan. All data were taken at pH 3 in 0.1 M $KNO_3$.

not achieved. However, the absorbance magnitude of the subsequent uptake remains reproducible with the first uptake.

### 3.2 *pH dependence of Cr(VI) uptake in QPVP films*

As discussed previously, the form of Cr(VI) varies with pH, so the sensor response at a given Cr(VI) concentration is also expected to vary due to differing partition coefficients with respect to the film. Figure 4 shows the sensor response to differing pH values ranging from 3 to 7. Here, the measured absorbance of $HCrO_4^{1-}$ was acquired as a function of time at a single wavelength of 400 nm. Initially, the cell was bathed in 0.1 M $KNO_3$ at the target pH, and solution at that pH containing 50 μM Cr(VI) was switched in at $t = 0$ s. In each case, Cr(VI) uptake is noted a short time later. Uptake is rapid at first, but slows as equilibrium is neared. At 1500 s, the rinse solution was introduced and is followed by rapid leaching of analyte from the film. Comparison of the different sensor response curves [e.g. curve (A) represents pH 3 while curve (E) represents pH 7] clearly indicates that Cr(VI) uptake is favoured at a lower pH where $HCrO_4^{1-}$ is the dominant form. Presumably, $CrO_4^{2-}$, the favoured form at pH 7, has a lower affinity for the film and is hence not as easily detected. This trend is borne out in terms of both the decreased total uptake and the decreased rate of uptake. Uptakes at pH < 3 were not investigated because the QPVP films were reported to delaminate from the substrate due to long-term exposure (e.g. overnight) to excessively acidic conditions [23]. However, numerous uptakes and rinses were carried out using a single film over the pH range of 3–7 over the course of days with no adverse consequences, thus attesting to the durability of these films.



### 3.3 *Dependence of sensor response on Cr(VI) concentration*

For a sensor to be effective as a device for quantitative analysis, its response must be sensitive to differing concentrations of analyte in solution. Figure 5 illustrates the

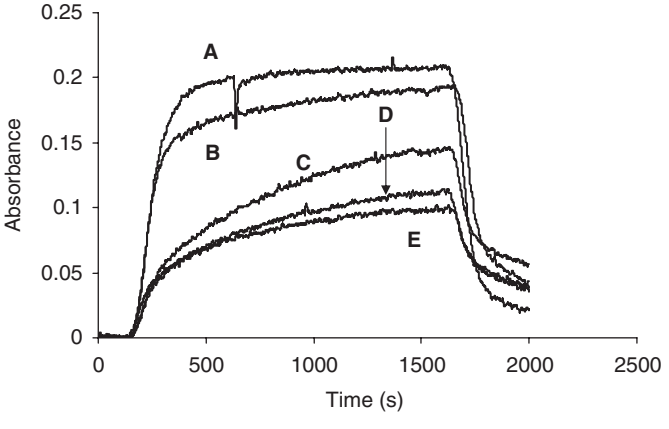


Figure 4. Absorbance *vs.* time profiles showing uptake and release of 100 μM Cr(VI) at the following pH values: (A) pH 3; (B) pH 4; (C) pH 5; (D) pH 6; and (E) pH 7. All data were acquired at 400 nm. In each case, the Cr(VI) solution was switched out for 0.1 M $KNO_3$ at the appropriate pH at 1500 s.

response of the ATR sensor to Cr(VI) concentrations ranging from 5 to 200 μM at pH 4 in 0.1 M $KNO_3$. As is apparent from the figure, the measured absorbance at 400 nm steadily increases with concentration during uptake; also, the rate of initial uptake increases with concentration. The inset of figure 5 is a plot of the measured absorbance taken at 1500 s *versus*. Cr(VI) concentration. The result is linear ($y = 0.0021x + 0.0008$) with a correlation coefficient of 0.99. Indeed, adding data from further trials of 500 and 1000 μM Cr(VI) also led to a linear result (not shown), but with a slightly lower correlation coefficient of 0.97. These data indicate that the sensor has an unoptimized LOD of 5 μM and a linear range of nearly three orders of magnitude.

Also of analytical concern is precision. Since the film is easily regenerated, all of the data in figure 5 were taken using a single film. In order to test the reproducibility of measurement, three successive uptake/rinse cycles were attempted at a single concentration (50 μM) using that film. The sensor absorbances (not shown) nearly overlay one another; the calculated standard deviation at 1500 s for the three trials is 0.0032 absorbance units (AU). As a further test, when a fourth uptake at the same concentration taken two days previously was added, the standard deviation decreased to 0.0031 AU. These results correspond to relative standard deviation values of 3.0 and 2.9%, respectively. Similarly reproducible data were also achieved at other Cr concentrations as evidenced in repeated uptakes using a prismless sensor design (vide supra).



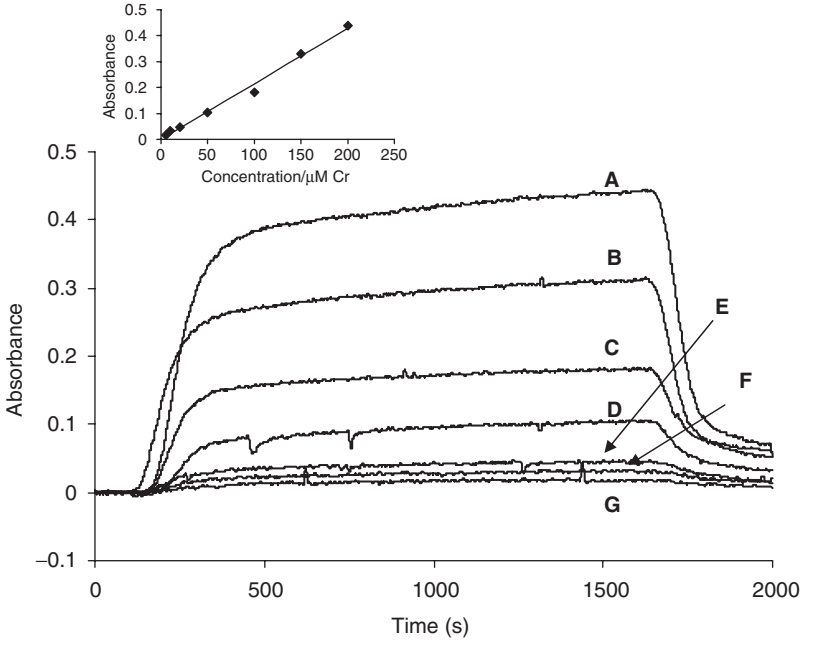


Figure 5. Calibration data for different concentrations of Cr(VI) in 0.1 M $KNO_3$ at pH 4 acquired at 400 nm. Individual curves represent uptake profiles for the following Cr(VI) concentrations: (A) 200 μM, (B) 150 μM, (C) 100 μM, (D) 50 μM, (E) 25 μM, (F) 10 μM, and (G) 5 μM. For each concentration, film rinsing with 0.1 M $KNO_3$ at pH = 4 was initiated at 1500 s. The inset is the linear sensor response over the same concentration range.

### 3.4 *Evaluation of a miniaturized, prismless field-ready sensor*

The most likely application for a sensor device such as that described here will be rapid field detection of environmental toxins in real water samples. Therefore, such sensor designs must be small, portable, inexpensive, and rugged. To this end, we have developed a field-ready prototype Cr(VI) sensor employing a simple violet LED source emitting at 410 nm that can be coupled to an inexpensive miniature spectrometer employing fixed optics and a CCD array detector. As shown earlier in figure 1, the sensor assembly itself has fixed angles of incidence and collection, and uses no coupling prisms, thus making it extremely user-friendly and rugged.

An initial set of experiments using this sensor employed a single 300-nm QPVP film. Triplicate sets of uptake profiles were acquired at 409 nm for Cr(VI) concentrations of 10, 50, and 150 μM at pH 4. The resulting uptakes are shown in figure 6; each uptake curve is the average of three independent trials. An obvious concentration dependence exists, with larger bulk Cr concentrations yielding larger equilibrium absorbances. The inset of figure 6 illustrates the linear relationship between absorbance, measured at 1000 s, and bulk Cr concentration in solution ($R^2 = 0.98$). Also included on the curve are error bars representing one standard deviation on either side of the mean



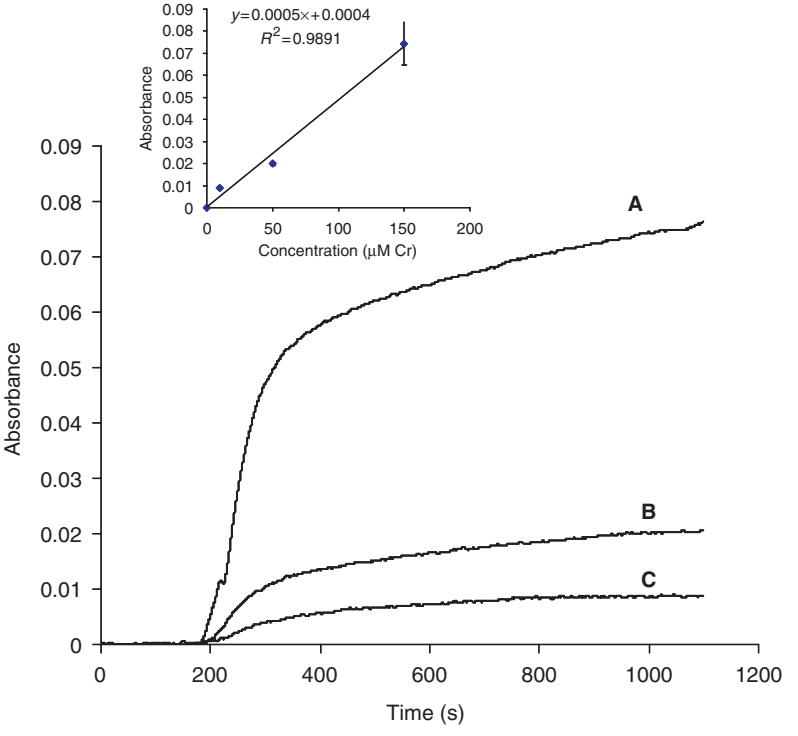


Figure 6. Absorbance uptake profiles taken at different Cr(VI) concentrations in 0.1 M $KNO_3$ at pH 4 using the prismless sensor in conjunction with a 410-nm LED source. The profiles correspond to the following concentrations: (A) 150 μM, (B) 50 μM, and (C) 10 μM Cr(VI). In all cases, optical data were acquired at 410 nm using a sample flow rate of 0.15 mL $min^{-1}$. The inset represents a preliminary calibration curve using data taken 1000 s into each experimental trial. Error bars represent one standard deviation on either side of the absorbance mean for each concentration based on three trials.

absorbance; resulting relative standard deviation values range from 4.6% (50 μM) to 13.2% (150 μM).

### 3.5 *Assessment of potential interferences*

For any real-world sensor design, interfering species must be evaluated. This is especially true for sensing of analytes in natural water samples that can harbour myriad chemical components. Most commonly encountered are ionic species such as metal cations. A distinct advantage of the QPVP film is that it should easily discriminate against such species due to charge repulsion. Theoretically, this should eliminate common aqueous cations as Fe(II), Fe(III), Cu(II), and Ni(II). Nonetheless, we decided to examine the effectiveness of the film for shielding such interferences. In order to optically evaluate the film's blocking ability, we first examined $Ru(bpy)_3^{2+}$, a brightly coloured complex ion that absorbs at 520 nm. A QPVP film mounted in the flow cell was exposed to a 1 mM solution of $Ru(bpy)_3^{2+}$ in 0.1 M $KNO_3$ at pH 4 for 15 min with no optical evidence of uptake, thus providing good initial evidence that the film effectively discriminates against cationic species.

Discussed earlier was the importance of evaluation of Cr(VI) in the presence of the much less harmful Cr(III), both of which may be found in runoff samples. Again, the QPVP film should be highly effective at discerning Cr(VI) (e.g. as $HCrO_4^{1-}$) from Cr(III) due to their opposing charges. To test this assumption, equilibrium uptake spectra of two solutions were compared. The first solution consisted of only 100 μM Cr(VI) at pH 4 in 0.1 M $KNO_3$, while the second solution contained 100 μM Cr(VI) along with 10 mM Cr(III). The two spectra perfectly overlaid one another across the entire scanned wavelength range of 400–700 nm, thus demonstrating that Cr(III), even in 100-fold excess concentration, does not interfere with the Cr(VI) measurement.

Interferences posing a far greater challenge to the sensor are those carrying a negative charge, as they will likely partition into the QPVP film to interfere spectrally and/or compete for ion-exchange sites. Fortunately, there are fewer of this type of interference in real water samples. However, to test the effect of such species on the sensor response, molybdate ion $(MoO_4^{2-})$ was assessed as a model interference. While $MoO_4^{2-}$ is transparent across the visible spectrum, it is expected to compete with $HCrO_4^{1-}$ for ion exchange sites in the film. First, a 2-mM solution of Cr(VI) at pH 4 in 0.1 M $KNO_3$ was introduced into the ATR flow cell and allowed to uptake to equilibrium. This sample resulted in a measured absorbance at 400 nm of 2.359 AU. Next, a solution containing 2 mM Cr(VI) and 2 mM $MoO_4^{2-}$ at pH 4 in 0.1 M $KNO_3$ was tested in an identical manner; in this case, the measured absorbance at 400 nm was 0.569 AU. These data correspond to a 76% decrease in signal attributed to Cr(VI), thus indicating the favoured partitioning of $MoO_4^{2-}$ into the film. In fact, a solution containing a 100-fold excess of $MoO_4^{2-}$ showed no measurable uptake of Cr(VI). It is therefore expected that other anionic interferences will affect the magnitude of the analyte signal to varying degrees depending upon their film partition coefficients relative to that of the favoured Cr(VI) form at a given pH. It is recommended that analyses attempted in samples known to have appreciable concentrations of such interferences be done using the method of standard addition with an understanding that there may well be compromised LOD.

## 4. Conclusions

A new thin film-based ATR sensor for Cr(VI) has been reported. Based on the reversible uptake and leaching of Cr(VI) as $HCrO_4^{1-}$, the sensor was found to have an unoptimized LOD of 5 μM Cr(VI) at pH 4 and provide a linear response out to 1 mM Cr(VI). The measured absorbance of Cr(VI) was most favourable at a low pH (e.g. 3–4) with decreasing absorbance as the pH increased to a value of 7. While cationic species do not interfere, anions partitioning into the film can compete for ion-exchange sites, thus decreasing the Cr(VI) response. We have also successfully demonstrated under laboratory conditions the applicability of a field-ready prototype sensor that should be well suited to remote-sensing applications. In field situations where a faster analysis time is required, thinner QPVP films could be used but with a possible decrease in sensitivity.

Perhaps the greatest advantage of this sensing approach for Cr(VI) is its intrinsic simplicity. Rather than relying on a ligand-exchange process either prior to sensing or within the film as other optical methods do, we take advantage of the native visible absorbance of $HCrO_4^{1-}$. A reasonably low LOD is achieved by preconcentration of the analyte in the QPVP film coupled with multiple internal reflections in the ATR cell. In fact, our LOD is competitive with other Cr(VI) sensors recently reported in the literature and is certainly low enough for many field applications [8, 14].

Future goals will include refinement of the design with a focus toward further miniaturization along with assessment using actual environmental water samples.



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## References

[1] A. Townshend. In *Encyclopedia of Analytical Science*, A. Townshend (Ed.), Vol. 2, pp. 729–743, Academic Press, New York (1995).
[2] S.A. Katz. In *Environmental Analysis and Remediation*, R.A. Meyers (Ed.), Vol. 2, pp. 1128–1158, Wiley-Interscience, New York (1998).
[3] B. Rivela, M.T. Moreira, C. Bornhardt, R. Mendez, G. Feijoo. *Environ. Sci. Technol.*, **38**, 1901 (2004).
[4] R. Renner. *Environ. Sci. Technol.*, **38** (2004).
[5] B.R. Eggins. *Chemical Sensors and Biosensors*, Wiley, Chichester, UK (2002).
[6] D. Xiao, K. Wang, W. Xiao. *Analyst*, **126**, 1387 (2001).
[7] Y.M. Scindia, A.K. Pandey, A.V.R. Reddy, S.B. Manohar. *Anal. Chem.*, **74**, 4204 (2002).
[8] Q. Li, K.J. Morris, P.K. Dasgupta, I.M. Raimundo Jr, H. Temkin. *Anal. Chim. Acta*, **479**, 151 (2003).
[9] L. Wang, L. Wang, T. Xia, L. Dong, G. Bian, H. Chen. *Anal. Sci.*, **20**, 1013 (2004).
[10] G. Samanta, C.B. Boring, P.K. Dasgupta. *Anal. Chem.*, **73**, 2034 (2001).
[11] V.I. Bioiadjiev, G.M. Brown, L.A. Pinnaduwage, G. Goretzki, P.V. Bonnesen, T. Thundat. *Langmuir*, **21**, 1139 (2005).
[12] J.A. Cox, P.J. Kulesza. *Anal. Chim. Acta*, **154**, 71 (1983).
[13] I. Turyan, D. Mandler. *Anal. Chem.*, **69**, 894 (1997).

[14] C.M. Welch, O. Nekrasova, R.G. Compton. *Talanta*, **65**, 74 (2005).
[15] Y.J. Yang, H.J. Huang. *Anal. Chem.*, **73**, 1377 (2001).
[16] N.A. Malakhova, A.V. Chernysheva, K.Z. Brainina. *Electroanalysis*, **3**, 803 (1991).
[17] S.T. Farrell, C.B. Breslin. *Environ. Sci. Technol.*, **38**, 4671 (2004).
[18] D.C. Harris. *Quantitative Chemical Analysis*, 7th Edn, pp. 439–440, W.H. Freeman, New York (2007).
[19] L. Yang, S.S. Saavedra. *Anal. Chem.*, **67**, 1307 (1995).
[20] W.R. Heineman, C.J. Seliskar, J.N. Richardson. *Aust. J. Chem.*, **56**, 93 (2003).
[21] Z. Hu, A.F. Slaterbeck, C.J. Seliskar, T.H. Ridgway, W.R. Heineman. *Langmuir*, **15**, 767 (1999).
[22] L. Gao, C.J. Seliskar, W.R. Heineman. *Anal. Chem.*, **71**, 4061 (1999).
[23] S.D. Conklin, C.J. Seliskar, W.R. Heineman. *Electroanalysis*, **17**, 1433 (2005).
[24] Y. Shi, C.J. Seliskar. *Chem. Mater.*, **9**, 821 (1997).
[25] J.N. Richardson, A.L. Dyer. *Anal. Chem.*, **74**, 3330 (2002).
[26] T. Shtoyko, J.N. Richardson, C.J. Seliskar, W.R. Heineman. *Electrochim. Acta*, **50**, 3191 (2005).
[27] J. DiVirgilio-Thomas, W.R. Heineman, C.J. Seliskar. *Anal. Chem.*, **72**, 3461 (2000).
[28] M.L. Stegemiller, W.R. Heineman, C.J. Seliskar, T.H. Ridgway, S.A. Bryan, T. Hubler, R.L. Sell. *Environ. Sci. Technol.*, **37**, 123 (2003).
[29] T. Shtoyko, I. Zudans, C.J. Seliskar, W.R. Heineman, J.N. Richardson. *J. Chem. Educ.*, **81**, 1617 (2004).
[30] S.A. Steiner, M.D. Porter, J.S. Fritz. *J. Chromatogr. A*, **1118**, 62 (2006).
[31] N. Kaval, C.J. Seliskar, W.R. Heineman. *Anal. Chem.*, **75**, 6334 (2003).
[32] J.N. Richardson, Z. Aguilar, N. Kaval, S.E. Andria, T. Shtoyko, C.J. Seliskar, W.R. Heineman. *Electrochim. Acta*, **48**, 4291 (2003).