CORRECTION FOR TURBIDITY AND pH INTERFERENCE FOR *IN SITU* HEXAVALENT CHROMIUM MONITORING –16297

Janine Carter* and Stephen Hall*
*Freestone Environmental Services, Inc.

ABSTRACT

Hexavalent chromium is of increasing concern worldwide because of its toxicity, mobility in aqueous media, and relative abundance in waste effluent from a variety of industrial processes. Some of that waste has reached groundwater aquifers. Because of these factors, the fate and transport of hexavalent chromium in aquifers is of great importance for evaluating risk to fresh water sources and to the biosphere, and for designing means for abatement or remediation.

Conventional sampling and analysis of groundwater samples from wells is labor intensive and therefore budget limited. The result is inadequate temporal and spatial characterization of contaminant plumes with respect to rate of movement, concentrations, and contaminant flux.

A submersible hexavalent chromium sensor designed for extended-term deployment and based on ultraviolet colorimetry has been developed and tested at the Hanford Site, Washington. Adaptation of the method for *in situ* measurements requires automatic correction for sample turbidity and pH for every measurement. Turbidity is compensated nephelometrically. A method for estimating sample pH based on absorbance measurements made using two different wavelengths is presented.

INTRODUCTION

Hexavalent chromium, Cr(VI), is of increasing concern worldwide because of its environmental and human health effects, as well as its mobility in aquifers and water bodies. Sources of Cr(VI) include waste effluent originating from the electroplating, galvanizing, leather, and paint industries, as well as from U.S. Department of Energy (DOE) energy and weapons production facilities.[1] As knowledge of the toxicity of Cr(VI) increases, its apparent degree of hazard to human health and the environment also increases.[2,3] The scale and potential severity of the hazard has prompted various governmental agencies to mandate regular testing of water sources either currently exposed or potentially exposed to Cr(VI).[4]

Collecting and analyzing environmental water samples for Cr(VI) are labor intensive tasks. Therefore, costs are high and sampling is commonly performed with minimum required frequency. The most common analytical method used to measure Cr(VI) in water samples is visible range colorimetry based on the Beer-Lambert law.[5] While sensitive and accurate, the visible range method uses chemical reagents and often requires filtered water samples. Freestone

Environmental Services, Inc. (Freestone), of Richland, WA, has developed a direct-reading Cr(VI) sensor that requires neither chemical additives nor filtration. The new sensor provides real-time measurements and is submersible for use in groundwater monitoring wells.

STUDY SITE

Field testing of Freestone's prototype Cr(VI) sensors has occurred at the Department of Energy's 1,518-km^2 Hanford Site (Hanford), located in south-central Washington State. Hanford produced plutonium for the Federal weapons programs between 1944 and 1989. Nine nuclear reactors operated in the "100 Areas" located along the Columbia River in the northern and eastern part of the site. The reactors used single-pass cooling water consisting of Columbia River water treated with sodium dichromate as a corrosion inhibitor. The treated water was passed through cooling tubes that surrounded the fuel rods. After cooling the fuel rods, the water was typically retained in retention basins for thermal cooling and to allow short-lived radionuclides to decay prior to discharge back to the Columbia River. Cooling water leaked from the piping and retention basins, as well as leaks and spills of the concentrated stock sodium dichromate solids and liquids, released Cr(VI) to the environment and ultimately to groundwater.[6,7]

In the 100-D Area, chromium occurs in the groundwater in two distinct plumes with concentrations up to 4,000 µg/L. The plumes are monitored and are under investigation to identify possible continued sources of residual Cr(VI) in the vadose zone. Understanding the nature of the vadose contamination in the area is important for evaluating remediation options.[7] The nearby Hanford Reach is of particular concern because it is the only remaining area on the Columbia River where significant mainstream spawning of fall Chinook salmon occurs.[8,9]

At Hanford, extensive groundwater monitoring programs are underway to monitor the effects of remediation activities and for regulatory compliance. Seasonal and even daily variations in the Columbia River stage, as well as influences from groundwater pump-and-treat systems designed to remove Cr(VI) from groundwater, affect the hydraulic gradients in the Hanford groundwater system. Resulting changes in groundwater flow direction complicate the understanding of rate and direction of contaminant transport in the aquifer.

Many of the hundreds of Hanford monitoring wells are fitted with pressure transducers to allow for real-time assessment of the groundwater system. In addition, wells are sampled regularly to further characterize the groundwater system and access remediation efforts. However, sample collection events and chemical analysis of samples is costly, therefore wells are commonly sampled only quarterly or annually. The results of this are that pump-and-treat operations are not optimized for varying plume conditions, and that contaminant flux from the source to the biosphere cannot be quantitatively addressed.

TECHNICAL APPROACH

The instrument is designed as an alternative to the common colorimetric method for measuring Cr(VI), where 1,5-diphenylcarbohydrazide in acid solution is used to develop a red-violet color measured at 540 nm.[5] This colorimetric method generally requires filtration to compensate for turbidity. The direct measuring instrument under development by Freestone requires neither the use of chemical treatments nor filtration.

At the neutral or near-neutral pH of environmental water samples, the chromate ion (CrO_4^{-2}) is the predominant form of Cr(VI). The chromate ion in aqueous solution exhibits a very strong absorption band in the near-UV range of 365 to 375 nm, with a peak near 371 nm.[10,11] Thus, direct colorimetric measurement within the 365 to 375 nm wavelength range is possible without chemical treatment of samples. The new sensor's operating principle combines near-ultraviolet (UV) colorimetric measurement of the chromate ion, based on the Beer-Lambert law, and simultaneous correction for sample turbidity, which is a common interference in colorimetric measurements. Light scattered by turbidity, reducing the intensity of light reaching the main sensor, leads to an overestimation of absorbance and apparent Cr(VI) concentration.

The prototype instruments are constructed with a UV light-emitting diode (LED) having a peak wavelength of 375 nm. Each instrument also includes at least two light sensors. One sensor is used to measure the intensity of the UV beam transmitted through a water sample, which is held in a transparent sample chamber, where the presence of the analyte Cr(VI) reduces beam intensity, per the principles of Beer-Lambert absorption colorimetry.

A secondary sensor, positioned normal to the axis of the transmitted UV light beam, provides an innovative means to circumvent the need for filtration.[12] The secondary sensor measures the intensity of light scattered, from the light path of the transmitted beam, by suspended particulates in the sample (i.e., a nephelometric estimate of turbidity).

By measuring both the transmitted light and the scattered light at the 375 nm wavelength, the analytical measurement can be corrected for light loss caused by turbidity. Specifically, the intensity of light reaching the secondary sensor is increased by turbidity, but partially decreased by absorption, while the transmitted light intensity is decreased by both absorption and suspended particulate (turbidity) scattering. Given these two distinctly different relationships, a simultaneous solution has been developed that distinguishes the effect of turbidity from absorption by Cr(VI).

The culmination of the development research is a stainless steel and polymer instrument with an outside diameter of 1.5 inches and length of 18 inches. These dimensions allow the sensor to be deployed in monitoring wells constructed using 2-inch diameter (or larger) casing. Two-inch diameter casing and screen is

commonly used for monitoring well construction. Each sensor is pressure tested to the equivalent of at least 90 feet of fresh water submergence.

ANALYTICAL INTERFERENCES

Freestone's instrument corrects for turbidity, but correction for other interferences is not similarly inherent in the sensor design. Specifically, any substance in the water being tested that absorbs UV light at the analytical wavelength, or is excited to fluoresce at some longer wavelength that is within the range detectable by the instrument's phototransistors, will be an analytical interference if it is present in sufficient concentration.

Fortunately, the inorganic anions and cations that make up most natural waters are inert to the near-UV analytical wavelength (370 to 375) nm. Further, at the Hanford Site, where the submersible instrument is being field-tested, the groundwater in the unconfined aquifer has been extensively characterized with respect to naturally occurring major and trace substances, as well as to contaminants.[13] Direct laboratory comparison of the sensor's analytical method with conventional methods, as well as a search of a comprehensive UV/visible photochemistry database, have established that there are no direct chemical interferences observed to date at Freestone's Hanford test wells.[14]

Sample pH, on the other hand, represents an indirect interference that must be addressed for every site where the Cr(VI) sensor is used. This arises because the fundamental sensitivity of the method is significantly affected by the effect of pH on Cr(VI) speciation.[11]

The research described here is focused principally on correcting the effect of pH on the sensor's Cr(VI) measurements. The correction for turbidity is described briefly because the first field data validating the method have been recently obtained and because, like pH, it is always a concern for *in situ* measurements made using the submersible sensor. That is, correction for turbidity must be viewed as the first step to be taken before pH can be addressed.

Investigation of pH effects has suggested that the current instrument's novel optical train [15] could be modified for direct correction, as has been accomplished for turbidity correction.

METHODS AND MATERIALS

The method for compensating for the effect of turbidity for *in situ* measurement of Cr(VI) has been described previously.[16] The data used to initially develop the correction algorithm were gathered solely in the laboratory. New data presented herein demonstrating the turbidity correction method were collected during the extended-term deployment of a fully functional submersible hexavalent chromium sensor in Hanford monitoring well 199-D5-125. The well is completed in the water table aquifer in the vicinity of Hanford's 100-D Area reactor site. The local aquifer is the current subject of pump-and-treat remediation to remove hexavalent

chromium contamination. The groundwater intercepted by the test well has a burden of 59 to 86 µg/L as Cr(VI) based on samples collected and analyzed in the laboratory.

The field test installation is solar powered, with real-time telemetry to an offsite server. Signals from the optoelectronic sensing circuit are digitized within the submersed sensing module before being transmitted to the surface control module that contains the telemetry instrumentation.

The analytical method used in the Freestone laboratory to measure Cr(VI) in water samples is the EPA accepted 1,5-diphenylcarbohydrazide spectrophotometric method adapted from Standard Methods for the Examination of Water and Wastewater.[5]

Near-UV spectrophotometric measurements at various wavelengths were made for development of the pH correction method. Buffer solutions were prepared according to Bates and Bower. [17] Hexavalent chromium solutions of known concentration were prepared using a commercial 50 mg/L [as Cr(VI)] standard solution.

TURBIDITY CORRECTION

Sample turbidity, caused by suspended particulate matter, mimics absorption by scattering light from the transmitted beam. Unless compensated, the reduced transmission (expressed as %T) is interpreted as increased analyte concentration. The submersible sensor compensates for the turbidity by nephelometrically sampling the intensity of the scattered light and using the result to correct the %T.[12]

The basis for the correction is the empirical observation that for an analyte concentration *C1*, a plot of %T *versus* scattered light intensity as turbidity increases will be parallel to similar plots for concentrations *C2, C3,* and so on. Figure 1 illustrates this pattern for six Cr(VI) concentrations ranging from 83 to 1000 µg/L.

Individual plots in Figure 1 were prepared by adding turbidity to a known volume of water. The source of the turbidity was the silt and clay from local surface soil. A small amount of soil was mixed with water, allowed to settle to remove the coarse particle fraction, and finally decanted, yielding very turbid water. Aliquots of the turbid water were used to establish various levels of turbidity.

Then, for each level of turbidity, aliquots of a standard solution of Cr(VI) were added stepwise to the sample to establish each of the six concentration levels. Despite some obvious data scatter, the plots in Figure 1 justify the expectation that such plots can be generally taken as parallel to one another.

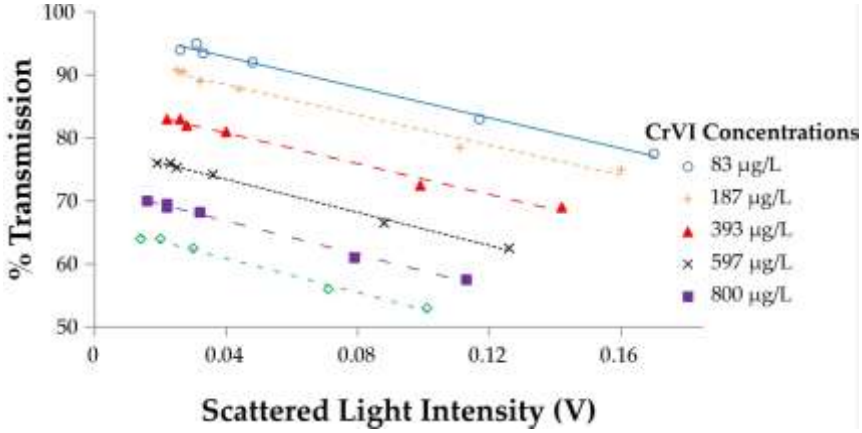

Fig. 1. %Transmission versus scattered light intensity as turbidity increases for six levels of Cr(VI) concentration.

Not more than about 20% of the transmitted light was lost due to turbidity in the plots shown in Figure 1. Within that range, the plots can be for practical purposes treated as linear. Each plot can be described using the formula for a straight line:

$$\%T_{meas.} = mV + \%T_{corr.} \quad \text{(Eq. 1)}$$

Where $\%T_{meas.}$ is the measured main signal strength, m is the mean slope common to all of the plots, V is the scattered light signal in volts, and intercept $\%T_{corr.}$ is the corrected %T. That is, the plot defined by a measured transmitted light signal and a scattered light signal is extrapolated to zero turbidity by rearranging terms:

$$\%T_{corr.} = \%T_{meas.} - mV \quad \text{(Eq. 2)}$$

Because the slope, m, is negative, the corrected %T will be greater than the measured %T.

One additional correction is needed. The zero-chromium plot extrapolates to an intercept slightly greater than 100%T because there is always a small amount of scattering as light passes through a medium and there is also likely to be some reflected "stray" light. Let Δ be the difference between the intercept of the zero-chromium plot and 100%T. The equation for the corrected %T is then:

$$\%T_{corr.} = \%T_{meas.} - mV - \Delta \quad \text{(Eq. 3)}$$

Figure 2 illustrates efficiency of the turbidity correction based on recent field data collected from a sensor deployed on the Hanford Site. Signals, in millivolts (mV), are from the phototransistors monitoring the transmitted light intensity (Plot A) and scattered light intensity (Plot B) located within the prototype sensor deployed in a Hanford 100-D Area well. Three samples were collected, one by pumping and others by using a manual bailer over the course of sensor deployment.

Inspection of Plots A and B in Figure 2 show that sharp reductions in transmitted light intensity (Plot A) correspond to similarly sharp increases in scattered light intensity (Plot B). The spikes in scattered light intensity are a direct result of turbidity caused by fine sediments stirred up during sampling events.

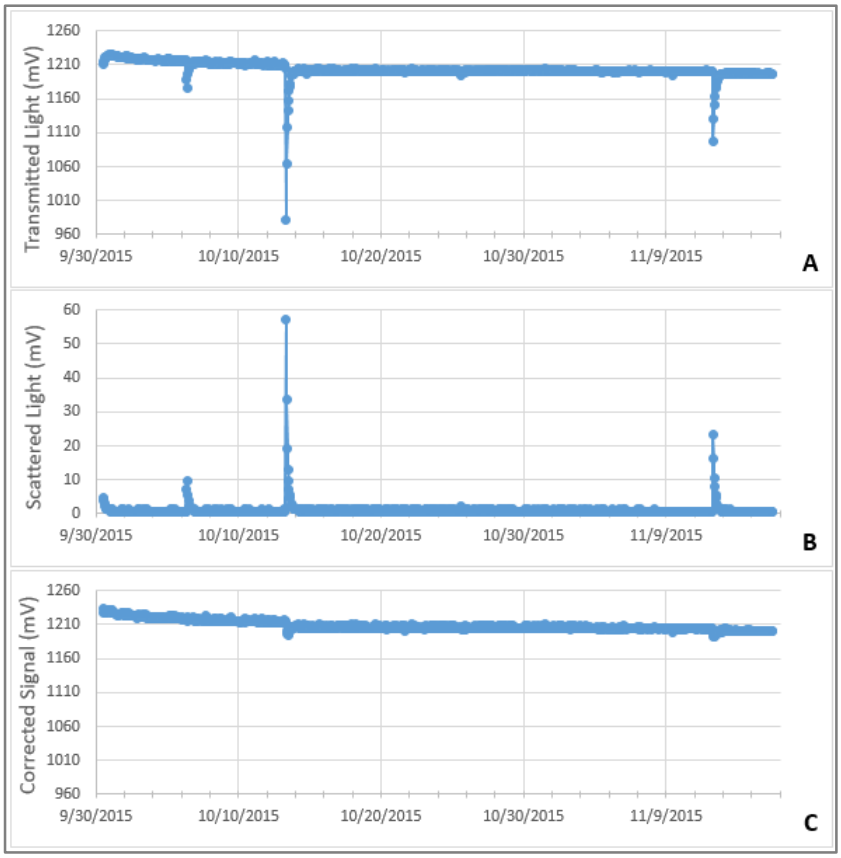

Fig. 3. Transmitted light signal (A), scattered light signal (B), and transmitted signal corrected for turbidity (C).

Plot C in Figure 2 represents the transmitted light intensity corrected for turbidity.[12] Note that the transmitted light signal appears to not have been fully corrected for the turbidity caused by a Hanford scheduled pumped-sample event on October 14. The cause for this is that the Cr(VI) is not evenly distributed vertically within the aquifer, and the procedure of pumping three bore volumes to purge the well before sample collection caused a temporary increase in Cr(VI) concentration in the upper part of the aquifer where the sensor was located. Manual sampling caused similar but much smaller mixing effects.

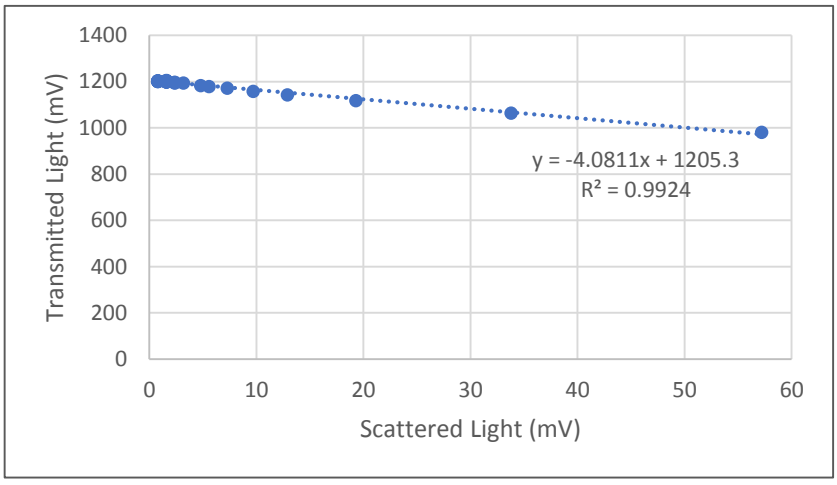

Fig. 2. The linear relationship between transmitted and scattered light permit a simplified correction for sample turbidity.

Figure 3 shows the transmitted light signal versus the scattered light signal for the 12-hour period immediately following the

pumped-sample event. The figure corroborates the assumption of linearity as represented by Figure 1.

CHROMIUM SPECIATION RELATIVE TO pH

When sample pH is less than approximately 7.8 to 8, the ability of Cr(VI) to absorb light at 370 to 375 nm is significantly reduced. Peak absorbance for chromate is at 371 nm.[10] UV LEDs are currently available at nominal 5-nm wavelength increments. Both 370 nm and 375 nm LEDs have performed well in the Freestone sensor. In environmental waters, four species of Cr(VI) can coexist in aqueous solutions, chromate, hydrogen chromate, dichromate, and dihydrogen chromate.[11] Their relative abundance in a given solution is a function of pH and of the total Cr(VI) concentration.

Each of these Cr(VI) species exhibits a unique coefficient of absorptivity at the analytical wavelength currently used in the submersible sensor. Each species contributes to the total measured sample absorbance according to its concentration and coefficient of absorptivity. Therefore, the relative abundance of the species must be known in order to interpret measured total absorbance in terms of the individual contribution of each species to the total.

Fournier-Salaun and Salaun [11] provide a mathematical approach to estimate the concentration of each species based on total Cr(VI) and solution pH. Their analysis is based upon the following equilibrium equations and equilibrium constants (K), expressed at 25°C and with concentration in units of molarity (mol/L).

$$K_1 = \frac{[H^+]\left[HCrO_4{}^{-1}\right]}{[H_2CrO_4]} = 0.20 \qquad \text{(Eq. 4)}$$

$$K_2 = \frac{[H^+]\left[CrO_4{}^{-2}\right]}{\left[HCrO_4{}^{-1}\right]} = 1.87 \times 10^{-6} \qquad \text{(Eq. 5)}$$

$$K_3 = \frac{\left[HCrO_4{}^{-1}\right]^2}{\left[Cr_2O_7{}^{-2}\right]} = 0.031 \qquad \text{(Eq. 6)}$$

It is clear that Eq. 4 through Eq. 6 can be rearranged to express chromate, dihydrogen chromate, and dichromate in terms of hydrogen chromate, and that the total molar concentration of Cr(VI) is equal to the sum of the molar concentrations of chromate, hydrogen chromate, and dihydrogen chromate plus twice the molar concentration of dichromate. Substituting and rearranging yields the following second order equation:

$$[CrVI]_{Total} = \frac{[H^+]\left[HCrO_4{}^{-1}\right]}{K_1} + \left[HCrO_4{}^{-1}\right] + \frac{K_2\left[HCrO_4{}^{-1}\right]}{[H^+]} + \frac{2\left[HCrO_4{}^{-1}\right]^2}{K_3} \qquad \text{(Eq. 7)}$$

A Microsoft Excel®[a] spreadsheet was prepared to calculate total Cr(VI) using Eq. 7 for a wide range of pH and for three Cr(VI) concentrations representing the likely range of concentrations that the Freestone sensor has been designed to address [10 to 1000 µg/L as Cr(VI)].

[a] *Microsoft Excel® is a trademark of Microsoft Corporation in the United States and/or other countries.*

Inspection of TABLE 1 shows that for Cr(VI) concentrations up to 1000 µg/L (1.92×10^{-5}M) there is no significant concentration expected for dichromate or dihydrogen chromate for sample solutions within the range of pH 3.5 to pH 11.5.

TABLE 1. *Relative mole percent of Cr(VI) species for total concentrations up to 1000 µg/L*

pH	% H_2CrO_4	% $HCrO_4^{-1}$	% CrO_4^{-2}	% $Cr_2O_7^{-2}$
3.5	0.16	99.20	0.59	0.03
4	0.05	98.06	1.83	0.03
4.5	0.01	94.35	5.58	0.03
5	0.00	84.21	15.75	0.02
5.5	0.00	62.82	37.15	0.01
6	0.00	34.84	65.15	0.00
6.5	0.00	14.46	85.53	0.00
7	0.00	5.08	94.92	0.00
7.5	0.00	1.66	98.34	0.00
8	0.00	0.53	99.47	0.00
8.5	0.00	0.17	99.83	0.00
9	0.00	0.05	99.95	0.00
9.5	0.00	0.02	99.98	0.00
10	0.00	0.01	100.00	0.00
10.5	0.00	0.00	100.01	0.00
11	0.00	0.00	100.01	0.00
11.5	0.00	0.00	99.87	0.00

Other investigators have reported equilibrium coefficients that differ from those shown for Eq. 4 to Eq. 6. Tong and Li [18] reported results calculated per Eq. 7 for total ionic strengths from ~0 to 3.0, $[Cr(VI)]_{Total}$ ranging from 10^{-6} to 10^{-2} mol/L, and various reported equilibrium constants. For the lower concentrations, the calculated results are in general agreement with the conclusion based on TABLE 1 that chromate and hydrogen chromate predominate.

Figure 4 illustrates the ratio of chromate to hydrogen chromate as a function of pH. The calculated values for chromate and hydrogen chromate can be expressed as a ratio by rearranging Eq. 5:

$$\frac{\left[CrO_4^{-2}\right]}{\left[HCrO_4^{-1}\right]} = \frac{K_2}{[H^+]} = K_2 \times 10^{pH} \qquad \text{(Eq. 8)}$$

From Eq. 8, the molar ratio of chromate to hydrogen chromate (y in Figure 4) can be calculated directly from solution pH. Means to address the accuracy of Figure 4 is discussed below. Fournier-Salaun and Salaun [11] noted that each species will absorb light at 371 nm according to its concentration and effective coefficient of absorptivity at that wavelength. Therefore, if the coefficients of absorptivity are known, and the molar ratio is determined from sample pH, then the measured sample absorbance can be interpreted as total Cr(VI) concentration as follows.

INSTRUMENT CORRECTION FOR pH

From Fig. 4, Cr(VI) solutions at pH = 9.2 and at pH = 3 are seen to represent virtually 100% chromate and 100% hydrogen chromate, respectively. The absorbance of chromate and of hydrogen chromate were measured using a Hach DR2800[b] spectrophotometer adjusted to the ideal 371 nm chromate absorption peak and solutions of known Cr(VI) concentration having pH adjusted to 9.2 and 3.

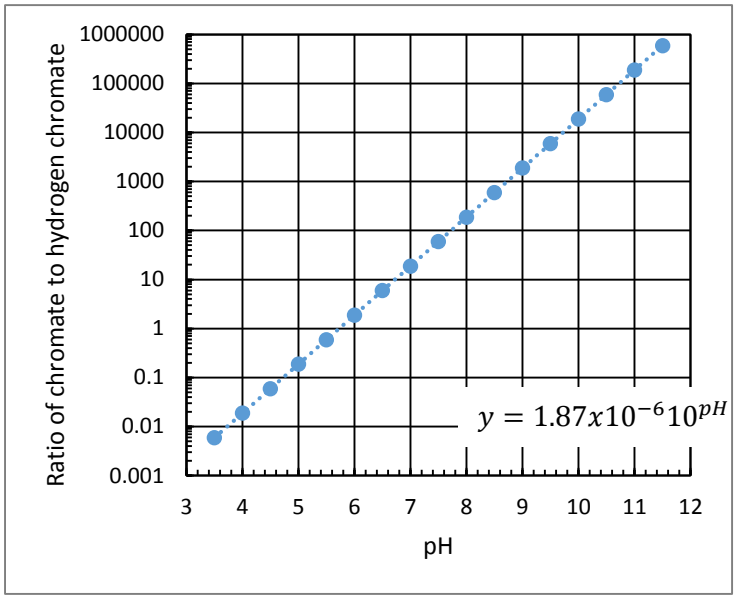

Fig. 4. The ratio of chromate to hydrogen chromate as a function of pH

The Beer-Lambert law was then used to calculate molar absorptivity for each of the species. Therefore, if the coefficients of absorptivity are known, and the molar ratio is determined from sample pH, then the measured sample absorbance can be algebraically interpreted as total Cr(VI) concentration as well as the concentration of each of the species.

Recall the Beer-Lambert Law:

$$log_{10}\left(\frac{100}{\%T}\right) = Abs = \alpha l \mathcal{C} \qquad \text{(Eq. 9)}$$

Where: α= coefficient of absorptivity, l= path length, which is 2.54 cm for the sample vials used, and $\mathcal{C}$= concentration. Absorbance measurements were made using solutions containing 500 µg/L ($9.619x10^{-6}$ mol/L) and 1000 µg/L ($1.923x10^{-5}$ mol/L) to determine coefficients of absorptivity for chromate and hydrogen chromate at 371nm as well as at 349 nm, which is the absorbance peak for hydrogen chromate.[11] TABLE 2 lists the results. The values reported by Fournier-Salaun and Salaun [11] were derived from data gathered using a Unicam Helios Alpha©[c] spectrophotometer which has a 2 nm spectral bandwidth, while the

[b] *Hach Company DR2800 Spectrophotometer© is a copyright of Hach Company in the United States and other countries.*

[c] *Unicam Helios Alpha Spectrophotometer© is a copyright of Unicam Limited, Thermos Spectronic in the United States and other countries.*

Hach DR2800 used by Freestone has a bandwidth ≤8 nm. Bandwidth and other instrument characteristics will affect measured absorptivity coefficients.

TABLE 2. Calculated molar absorptivity coefficients compared to values reported by Fournier-Salaun and Salaun [11].

Wavelength (λ)	pH	L/mol-cm (500 ppb)	L/mol-cm (1000 ppb)	L/mol-cm (mean)	L/mol-cm Reported
371 nm	9.2 (CrO_4^{-2})	3930	4238	4084	4730
371 nm	3 ($HCrO_4^{-1}$)	819	839	829	590
349 nm	9.2 (CrO_4^{-2})	2046	2375	2210	
349 nm	3 ($HCrO_4^{-1}$)	1228	1290	1259	

To calculate total Cr(VI) from sample absorbance at 371 nm, let:

$\alpha_{CrO_4^{-2}}$ = chromate absorptivity

$\alpha_{HCrO_4^{-1}}$ = hydrogen chromate absorptivity

And:

$$Abs_{Total} = \alpha_{CrO_4^{-2}}\left(CrO_4^{-2}\right)l + \alpha_{HCrO_4^{-1}}\left(HCrO_4^{-1}\right)l \quad \text{(Eq. 10)}$$

Also, from Figure 4, let:

$$\frac{\left(CrO_4^{-2}\right)}{\left(HCrO_4^{-1}\right)} = y \quad \text{(Eq. 11)}$$

So:

$$\left(HCrO_4^{-1}\right) = \frac{\left(CrO_4^{-2}\right)}{y} \quad \text{(Eq. 12)}$$

Substituting and rearranging:

$$Abs_{Total} = \alpha_{CrO_4^{-2}}\left(CrO_4^{-2}\right)l + \alpha_{HCrO_4^{-1}}\left[\frac{\left(CrO_4^{-2}\right)}{y}\right]l \quad \text{(Eq. 13)}$$

$$Abs_{Total} = \left(CrO_4^{-2}\right)\left(\alpha_{CrO_4^{-2}} + \frac{\alpha_{HCrO_4^{-1}}}{y}\right)l \quad \text{(Eq. 14)}$$

We get:

$$\left(CrO_4^{-2}\right) = \frac{Abs_{Total}}{\left(\alpha_{CrO_4^{-2}} + \frac{\alpha_{HCrO_4^{-1}}}{y}\right)l} \quad \text{(Eq. 15)}$$

Similarly:

$$\left(CrO_4^{-2}\right) = y\left(HCrO_4^{-1}\right) \quad \text{(Eq. 16)}$$

Substituting and rearranging:

$$Abs_{Total} = \alpha_{CrO_4^{-2}} y\left(HCrO_4^{-1}\right)l + \alpha_{HCrO_4^{-1}}\left(HCrO_4^{-1}\right)l \quad \text{(Eq. 17)}$$

$$Abs_{Total} = \left(HCrO_4^{-1}\right)\left(\alpha_{CrO_4^{-2}} y + \alpha_{HCrO_4^{-1}}\right)l \quad \text{(Eq. 18)}$$

We get:

$$\left(HCrO_4^{-1}\right) = \frac{Abs_{Total}}{\left(y\alpha_{CrO_4^{-2}} + \alpha_{HCrO_4^{-1}}\right)l} \quad \text{(Eq. 19)}$$

Substituting $1.87x10^{pH-6}$ for *y* and 2.54 cm for path length *l* permits direct calculation of chromate and hydrogen chromate concentration

Combine results from Eq. 15 and 19 and we get total molar concentration of Cr(VI):

$$\left(Cr^{6+}\right)_{Total} = \left(CrO_4^{-2}\right) + \left(HCrO_4^{-1}\right) \quad \text{(Eq. 20)}$$

Figure 4 was derived ultimately from Eq. 4 through Eq. 6 and the accuracy of ratio y depends on the accuracy of equilibrium coefficient K_2. The accuracy of K_2 can be tested by using Eq. 10 to calculate total absorbance using the experimentally derived coefficients of absorptivity, the value for y from Figure 4 for the known pH, and the known concentration, where:

$$\left(CrO_4^{-2}\right) = \frac{\left(Cr^{6+}\right)_{Total}}{1 + \frac{1}{y}} \quad \text{(Eq. 21)}$$

Eq. 12 then yields ($HCrO_4^{-1}$) and Eq. 10 is applied. If there is a poor match between the calculated and observed absorbance, *y* can be varied. A plot of *y* against calculated absorbance will quickly reveal the best value. Eq. 8 will then yield a corrected K_2.

ESTIMATING pH BY DUAL WAVELENGTH MEASUREMENTS

Recent laboratory work has suggested an approach for estimating pH that, if suitably precise, may eliminate the need for a conventional pH sensor.

As described above, knowing pH allows us to easily calculate the ratio of chromate to hydrogen chromate. Therefore, if chromate and hydrogen chromate were to be independently measured, the results would logically be interpretable as pH. This was tested in the laboratory as follows.

The chromate and hydrogen chromate species have absorption peaks at 371 nm and 349 nm, respectively. In the laboratory, the 100, 500, and 1000 µg/L Cr(VI) solutions measured at 371 nm for pH values ranging from pH 3 to pH 9.2 were also measured at 349 nm using the DR2800 spectrophotometer. Buffer solutions were prepared based on Bates and Bowes [17] and verified using a pH electrode meter. The difference in measured absorbance for the two peaks, *Abs(371 nm)-Abs(349*

nm), was plotted as a function of pH for the three concentration levels. Figure 5 illustrates the results. From Figure 5 it is clear that if the measured absorbances are equal, the pH is very near to 5.6. The more general approach for estimating pH from absorbance measured at both 371 nm and 349 nm is based on simultaneous equations.

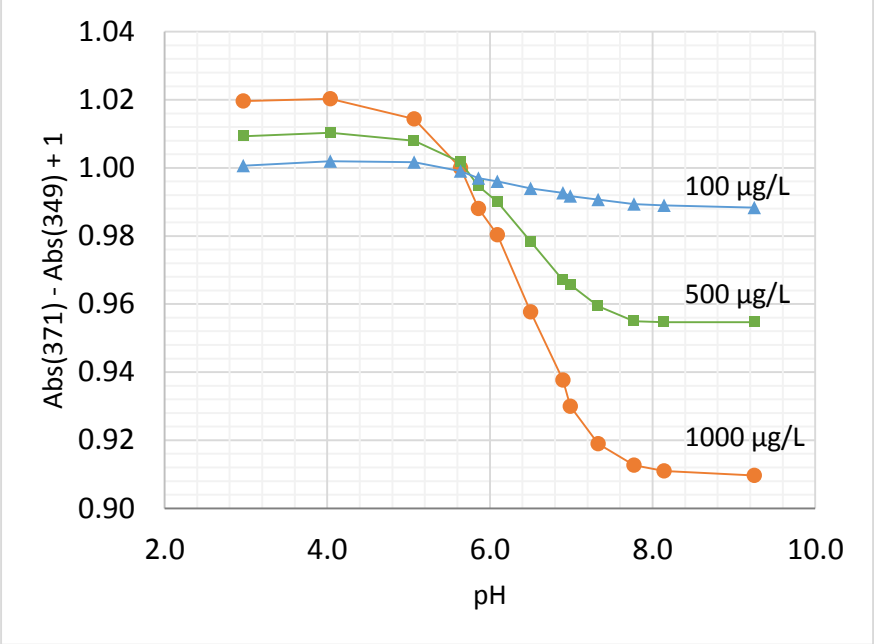

Fig. 5. Absorbance at 371 nm minus absorbance at 349 nm as a function of pH for three levels of Cr(VI) concentration, 100, 500, and 1000 µg/L.

By rearranging Eq. 5 and substituting into Eq. 10, the result is:

$$Abs_{371\,nm} = \alpha_{CrO_4^{-2}} \frac{K_2}{[H^+]}\left(HCrO_4^{-1}\right)l + \alpha_{HCrO_4^{-1}}\left(HCrO_4^{-1}\right)l \qquad \text{(Eq. 22)}$$

Letting the symbol β represent absorptivities derived for the 349 nm wavelength, Eq. 23 is the result:

$$Abs_{349\,nm} = \beta_{CrO_4^{-2}} \frac{K_2}{[H^+]}\left(HCrO_4^{-1}\right)l + \beta_{HCrO_4^{-1}}\left(HCrO_4^{-1}\right)l \qquad \text{(Eq. 23)}$$

Eq. 22 and Eq. 23 are simultaneous equations that can be solved to directly yield $[H^+]$ from the ratio, *R*, of the measured absorbances, Abs_{371}/Abs_{349}, and application of Eq. 24:

$$[H^+] = K_2(\alpha_{CrO_4^{-2}} - R\beta_{CrO_4^{-2}})/(R\beta_{HCrO_4^{-1}} - \alpha_{HCrO_4^{-1}}) \qquad \text{(Eq. 24)}$$

And pH is of course defined as $-\log_{10}[H^+]$. Initial tests using the data represented by Figure 5 were favorable. Initial mechanical and optical design for incorporating the second wavelength into the submersible sensor has been completed.

CONCLUSIONS

The submersible hexavalent chromium sensor was conceived as an economical alternative to conventional sampling and analysis at sites such as the Hanford Site, WA, where Cr(VI) contamination in the ground water is widespread, and many of the monitoring wells are in remote locations. Budgets limit conventional sampling and laboratory analysis, both of which are labor intensive. Paucity of data necessarily limits the ability to assess the fate and transport of Cr(VI) contaminant plumes.

To be an economical alternative, simplicity of design and construction of the sensor continues to be of foremost concern. For example, if it ultimately proves practical to estimate pH using the above dual-wavelength method, the expense and complexity of separate instrumentation to monitor pH is obviated.

At Hanford, remediation of hexavalent chromium plumes is currently conducted using pump-and-treat plants. At each plant, contaminated water from several extraction wells serves as plant feedstock, with the treated effluent returned to the aquifer via injection wells. Sensors to monitor the Cr(VI) content of the several influent streams could be effective in maximizing plant efficiency.

REFERENCES

1. Darrie, G., 2001. *Commercial extraction technology and process waste disposal in the manufacture of chromium chemicals from ore*. Environmental Geochemistry and Health, 23, 187- 193. Doi: 10.1023/A:1012295927081.
2. Eisler, R., 1986. *Chromium hazards to fish, wildlife, and invertebrates: a synoptic review*. U.S. Fish and Wildlife Service Biological Report, 85 (1.6), 60 pp.
3. U.S. Environmental Protection Agency (EPA), 2012. *Table 1: Prioritized Chronic Dose-Response Values.* Office of Air Quality Planning and Standards. Retrieved from website: http://www.epa.gov/ttn/atw/toxsource/table1.pdf
4. *Safe Drinking Water Act*, 1974. Public Law 93-523, as amended, 88 Stat. 1660, 42 USC 300f et seq.
5. Rice, E.W., R.B. Baird, A.D. Eaton, and L. S. Clesceri, (Eds.), 2012. *Standard Methods for the Examination of Water and Wastewater*, 22nd Edition. American Public Health Association, American Water Works Association, and Water Environment Federation.
6. U.S. Department of Energy (DOE), 2010. *Report on Investigation of Hexavalent Chromium Source in the Northern 100-D Area.* DOE/RL-2010-40. U.S. Department of Energy, Assistant Secretary for Environmental Management, Richland, Washington.
7. Dresel, P.E., C.C. Ainsworth, N.P. Qafoku, C. Liu, J.P. McKinley, E.S. Ilton, J.S. Fruchter, J.L Phillips, 2008. *Geochemical Characterization of Chromate Contamination in the 100 Area Vadose Zone at the Hanford Site.* PNNL-17674. Pacific Northwest National Laboratory, Richland, Washington.
8. Patton, G.W., Dauble, D.D., Chamness, M.A., Abernethy, C.S., and McKinstry, C.A., 2001. *Chromium Toxicity Test for Fall Chinook Salmon (Oncorhynchus tshawytscha) Using Hanford Site Groundwater: Onsite Early Life-Stage Toxicity Evaluation.* PNNL-13471. Pacific Northwest National Laboratory, Richland, Washington.
9. Woodward, D.F., Farag, A.M., DeLonay, A.J., Cleveland, L., Brumbaugh, W.G., and Little, E.E., 1999. *The Potential for Contaminated Ground Water to Adversely Affect Chinook Salmon (Oncorhynchus tshawystcha) under Exposure Conditions Simulating the Hanford Reach of the Columbia River, Washington, USA.* Biological Resources Division, U.S. Geological Survey, Washington, D.C.

10. Brito, F., J. Ascanioa, S. Mateoa, C. Hernandeza, L. Araujoa, P. Gili, P. Martin-Zarab, S. Dominguez, and A. Mederos, 1997. *Equilibria of chromate (VI) species in acid medium and ab initio studies of these species.* Polyhedron, vol. 16, no. 21, pp. 3835-3846.
11. Fournier-Salaun, M. C., and P. Salaun, 2007. *Quantitative determination of hexavalent chromium in aqueous solutions by UV-Vis spectrophotometer*. Central European Journal of Chemistry, vol. 5, no. 4, pp. 1084-1093.
12. Hall, S. H., 2014. U.S. PATENT 8,699,025, *Method and apparatus for measuring hexavalent chromium in water*.
13. Hartman, M. J., L. F. Morasch, and W. D. Webber, (Eds.), 2004. *Summary of Hanford Site groundwater monitoring for fiscal year 2004*. PNNL-15070-SUM, Pacific Northwest National Laboratory, Richland, Washington.
14. Noelle, A., G. K. Hartman, A. Fahr, D. Lary, Y-P Lee, P. Limao-Vieira, F. J. Martin-Torres, J. J. Orlando, F. Salama, A. C. Vandaele, R. P. Wayne, and C. Y. R. Wu, (Eds.), 2013. *UV/Vis+ Spectra Data Base*, 9th Edition, science-softCon Publication 1301; ISBN 978-3-00-041177-9.
15. Hall, S. H. and K. A. Schuyler, 2014. *U.S. PATENT (Pending) Improved apparatus for measuring hexavalent chromium in water.*
16. Rod, K., K. A. Schuyler, and S. H. Hall, 2015. *Hexavalent chromium sensor for real-time in situ measurement of groundwater contamination.* Waste Management Symposium, 2015, paper 15433, Phoenix, Arizona, USA.
17. Bates, R. G., and V. E. Bower, 1963. *The measurement of pH*, in: Meites, L. (Eds.), *Handbook of Analytical Chemistry*, McGraw-Hill.
18. Tong Shen-yang and Li Ke-an, 1986. *The distribution of chromium (VI) species in solution as a function of pH and concentration*. Talanta, vol. 33, no. 9, pp. 775-777.

ACKNOWLEDGMENT

This work was funded in part by the U. S. Department of Energy Small Business Innovative Research (SBIR) grant number DE-SC 0007674 and Freestone Environmental Services, Inc.