

**Hexavalent Chromium Sensor for Real-Time *In Situ* Measurement of Ground Water Contamination - 15433**

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**ABSTRACT**

Hexavalent chromium ( $\text{Cr}^{6+}$ ) is a contaminant of concern at multiple Department of Energy (DOE) and industrial sites across the United States. It is used in stainless steel production, textile dyes, tanning, wood preservation, and in conversion coatings. It was used at DOE sites, such as the Hanford Nuclear Reservation in Washington state, in the form sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) to inhibit corrosion. This has resulted in the release of chromate ( $\text{CrO}_4^{2-}$ ) to groundwater. Chromate is anionic and is readily transported with ground water through the subsurface to receptors such as river biota at Hanford, and in some regions to potable water wells.

To improve  $\text{Cr}^{6+}$  groundwater plume monitoring while reducing monitoring cost, a cable-deployed, submersible sensor was developed for direct measurements of  $\text{Cr}^{6+}$  in natural groundwater. With a diameter of 3.8 cm (1.5 inch) the sensor could be deployed in 5 cm (2 inch) diameter screened wells. The sensor uses ultra violet (UV) photospectroscopy to measure  $\text{Cr}^{6+}$  at concentrations as low as 5 to 10  $\mu\text{g L}^{-1}$  (as hexavalent chromium,  $\text{Cr}^{+6}$ ) in natural water. Turbidity, caused by colloidal material suspended in natural water, can interfere with the chromate measurement but was automatically compensated within the instrument. Because the instrument had some temperature sensitivity, a correction was also applied based on *in situ* temperature measurements in the sensor. The sensor has been tested in the laboratory and was deployed to the field with encouraging results. Laboratory calibrations consistently yielded concentration measurements that correlate well with standard analytical methods ( $r^2 = 0.99$ ).

**INTRODUCTION**

Hexavalent chromium, a known carcinogen, is a groundwater contaminant of concern at multiple industrial and Department of Energy (DOE) sites across the United States. Freestone Environmental Services, Inc. (Freestone) has developed a cable-deployed hexavalent chromium sensor designed for extended service in wells or water bodies. The sensor is intended to serve as an alternative to manual sampling, particularly for remote locations.

Hexavalent chromium compounds are used in stainless steel production, textile dyes, tanning, wood preservation, conversion coatings, and as a corrosion inhibitor. For example, it was used at the Hanford Nuclear Reservation in Washington State to inhibit corrosion in reactor cooling water systems. Leaks and spills have resulted in hexavalent chromium releases to groundwater, with local concentrations above the Environmental Protection Agency (EPA) standard of 100  $\mu\text{g L}^{-1}$  as total chromium (Dresel et al. 2008).

Hexavalent chromium in groundwater with near neutral pH exists as chromate ( $\text{CrO}_4^{2-}$ ; Brito et al, 1997) which is an oxyanion that reacts only weakly with geologic media (Zachara, 1987). The ion is readily transported via ground water to receptors such as biota at groundwater discharge sites, or in some regions to potable water wells.

Field sampling of wells for the purpose of monitoring chromate plume movement is costly and time consuming. Freestone's sensor alleviates the high cost of manual sampling while permitting a far greater sampling frequency at virtually zero incremental cost and without the waste stream associated with conventional sampling and chemical analysis. Such purgeless groundwater monitoring technologies have been identified as a favorable for data collection, though there has been a lag in the availability of such sensors (Hall, 1998; Schalla, 1998).

Objectives for this project were to develop a chromate sensor which could be deployed into groundwater wells for continuous real-time measurement. With the current prototype, objectives were to test the reliability and reproducibility of the sensor measurements.

## **METHODS**

### **Sensor**

The Cr<sup>6+</sup> sensor has a diameter of 3.8 cm (1.5 in) so that it can be deployed in 5-cm (2-in) or larger diameter wells. It's based on near-ultraviolet (UVA) absorption spectrophotometry, measurements are made in real-time, and no chemical additives are needed. The sensor specifically uses IR phototransistors, which measure the intensity of a UV light source transmitted through quartz glass and the solution sample. The light source must emit within the 365 to 375 nm wavelength band where chromate ion in near neutral aqueous solution exhibits strong absorption (Bitro et al. 1997). Measured light intensities (transmitted light sensor voltage) can then be translated to absorbance using the Beer-Lambert law (Equation 1), and this absorbance can then be used to calculate chromate concentration.

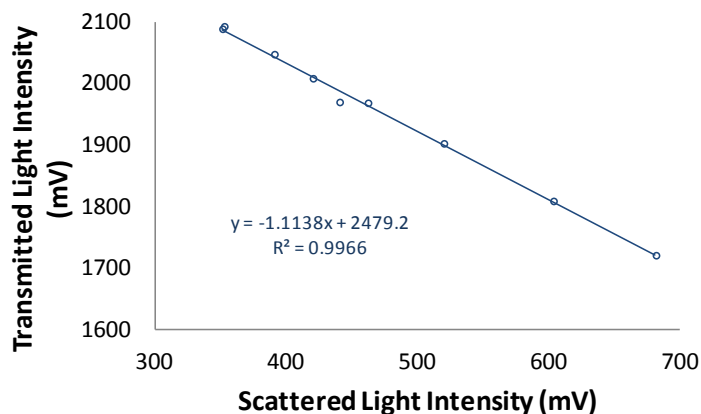
$$Absorbance = \log_{10} \left( \frac{100}{\%T} \right) = \alpha l C \quad (1)$$

Where:

- $\%T$  is percent of light intensity measured ( as voltage) relative to a calibration blank (where %T is equal to 100%)
- $\alpha$  is absorptivity
- $l$  is optical path length through the sample
- $C$  is concentration

Detection limits are comparable to those obtained with the widely used diphenylcarbazide colorimetric method.

Turbidity, caused by colloidal material suspended in natural water, can interfere with the chromate measurement by mimicking absorption (Figure1). It is automatically compensated within the instrument by use of a second phototransistor (scattered light sensor) positioned to measure scattered light orthogonal to the emitted light source (Figure 1). With the measured linear relationship algorithms can be developed to compensate for presence of turbidity.



**Figure 1.** Turbidity calibration voltage signals for transmitted light intensity versus scattered light intensity with multiple turbidity values.

### Laboratory Experiments

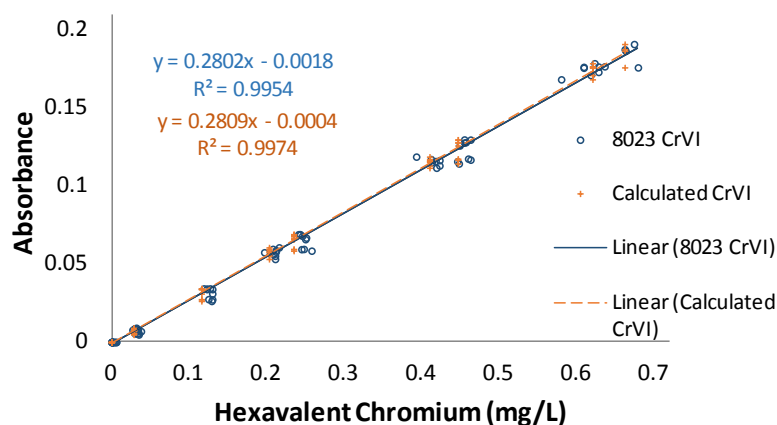
Laboratory experiments, using  $900 \mu\text{g L}^{-1}$   $\text{NaHCO}_3$  water to simulate ionic strength of natural waters, were conducted to test measurement reliability. Chromate was introduced to test samples by pipetting suitable aliquots of a  $50 \text{ mg L}^{-1}$  (as  $\text{Cr}^{6-}$ ) standard solution. The target CrVI concentrations for the tests were  $30\mu\text{g}$ ,  $200\mu\text{g}$ ,  $400\mu\text{g}$ , and  $600\mu\text{g}$ . One series of tests was designed to determine the effect of a large number of repeated measurements on instrument performance in terms of measurement noise and systematic drift. These tests were conducted in triplicate, using multiple chromate concentrations, and three nominally identical sensors. Calculated concentrations of the prepared test solutions were verified by independent measurement using the diphenylcarbazide method (Hach DR 2800 spectrophotometer at 540 nm). Sensor results were analyzed based on a paired Student t-test. Additional tests were designed to investigate temperature influence on chromate measurements. For this, a series of tests were conducted where the ambient temperature was manipulated while the sensor was programmed for continuous monitoring. Step inputs of CrVI were added to the testing reservoir during the using the same target CrVI concentrations of  $30\mu\text{g}$ ,  $200\mu\text{g}$ ,  $400\mu\text{g}$ , and  $600\mu\text{g}$ .

### Field Tests

Three sensors were deployed to three field wells at Hanford 100-D Area. Sensors deployed at field sites were coupled with automated sampling and measurement and subsequent telemetry to a remote server and virtual datalogger.

## RESULTS AND DISCUSSION

Comparing successive calibrations with Student t-test demonstrated that there was no significant difference between paired treatments (Figure 2). This suggests that successive calibration of the probe were not measuring chromate that may have adsorbed to the glass chamber where measurements are taken. Similar tests were conducted to determine if there was significant temperature sensitivity to calibrations due to time the sensor was in contact, and thus thermally equilibrating, with the calibration water. These tests were also conducted in triplicate and there was no significant difference between paired tests.

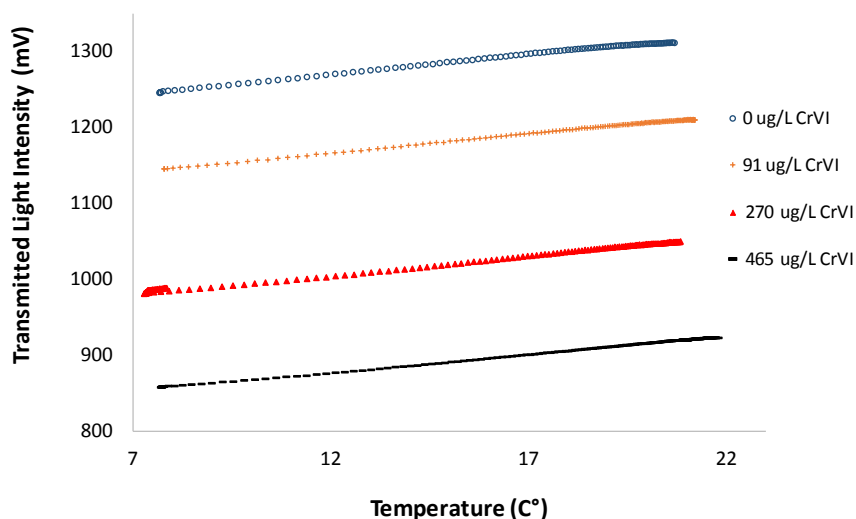


**Figure 2.** Combined measured absorbance from repeated measurements on five sensors. Absorbance is plotted for all data against the known spike CrVI concentrations (Calculated) and against the standard EPA 8023 diphenylcarbazide method using a Hach DR2800 spectrophotometer (8023 Cr VI), using aliquots from the same sensor tests.

The summation of the calibration sensor measurements consistently yielded concentrations that correlate well with known concentrations ( $r^2 = 0.99$ ), for samples with 0 - 660  $\mu\text{g L}^{-1}$  as  $\text{Cr}^{6-}$  (Figure 2). The coefficient of variation is 4% to 8% for sample concentrations over 200  $\mu\text{g L}^{-1}$ . The coefficient of variation was 18% at a concentration of 30  $\mu\text{g L}^{-1}$ .

Turbidity (Figure 1) and temperature (Figure 3) can influence the voltage signal measured by the transmitted light sensor, and as a result would give incorrect absorbance and CrVI concentration. Because of this algorithms can be written to adjust for these parameters based on measurements taken in parallel with the transmitted light sensor. It was hypothesized that at increased CrVI concentrations the slope of the line for transmitted light sensor versus temperature would change in a predictably manner. However, no significant pattern emerged based on a triplicate temperature tests (Figure 3).

In addition to laboratory testing sensors were deployed to wells in the field. Initial field measurements are also encouraging, with sensors measuring within 15% of well CrVI concentrations. Engineering improvements are being implemented to produce field measurements as precise as laboratory measurements.



**Figure 3.** Temperature dependence test of transmitted light intensity voltage signal for one blank and three CrVI concentrations. Plot is of one of three probes used in experiment, the other probes yielded similar results. Temperature is a direct measurement from the internal thermistor.

## CONCLUSION

Based on these findings the hexavalent chromium sensor is robust and precise with measurements, and interference variables, such as temperature and turbidity, can be compensated for with linear algorithms. Initial field tests demonstrated that the can be deployed for extended periods and collect real time data remotely.

## REFERENCES

1. Brito, F., J. Ascanioa, S. Mateoa, C. Hernandeza, L. Araujoa, P. Gili, P. Martin-Zarab, S. Dominguez, 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.
2. Dresel, P.E., C.C. Ainsworth, N.P. Qafoku, C. Liu, J.P. McKinley, E.S. Ilton, J.S. Fruchter, J.L. Philips. 2008. Geochemical characterization of chromate contamination in the 100 area vadose zone at the Hanford site. PNNL-17674, Pacific Northwest National Laboratory, Richland, Washington.
3. Hall, S. H. 1998. Today's sensor technology. In: Workshop to Help Improve Your Groundwater Monitoring with Continuous Water Quality Sensing, G. Gustafson, Ed., Harry Reid Center for Environmental Studies, U. Nevada Las Vegas, Jun 11-12, pp. 53-74.
4. Schalla, R. 1998. State of the art in groundwater sampling and sensing technology. In: Workshop to Help Improve Your Groundwater Monitoring with Continuous Water Quality Sensing, G. Gustafson, Ed., Harry Reid Center for Environmental Studies, U. Nevada Las Vegas, Jun 11-12, pp. 8-52.
5. Zachara JM, DC Girvin, RL Schmidt, and CT Resch. 1987. "Chromate Adsorption on

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Amorphous Iron Oxyhydroxide in the Presence of Major Groundwater Ions.” *Environ. Sci. Technol.* 21:589-594.