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Pacific Northwest National Laboratory
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Review of Techniques to Characterize the Distribution of Chromate Contamination in the Vadose Zone of the 100 Areas at the Hanford Site

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Prepared for Fluor Hanford, Inc.
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Summary

The purpose of this report is to identify and evaluate the state-of-the-art techniques for characterization of chromate contamination in the vadose zone of the 100 Areas at the Hanford Site. The techniques include direct techniques for analysis of chromium in the subsurface as well as indirect techniques to identify contamination through geophysical properties, soil moisture, or co-contaminants. Characterization for the distribution of chromium concentration in the vadose zone is needed to assess potential sources for chromate contamination plumes in groundwater at the 100-D, 100-K, and 100-B/C Areas.

No methods for vadose zone chromate characterization have been fully developed and demonstrated. Methods recommended for further evaluation and testing include laser-induced breakdown spectroscopy, Raman spectroscopy, laser-induced fluorescence, x-ray fluorescence, in situ specific conductance, high-resolution resistivity, neutron moisture logging, and partitioning tracers.

Acronyms

CPT	cone penetrometer
Cr(III)	trivalent chromium (the most common valence state in natural sediments)
Cr(VI)	hexavalent chromium (the valence state of chromate and dichromate)
DNAPL	dense, nonaqueous phase liquid
EM	electromagnetic induction (geophysical technique)
EPA	Environmental Protection Agency
GPR	ground-penetrating radar
HRR	high-resolution resistivity
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP/OES	inductively coupled plasma-optical emission spectrometry (equivalent to ICP-AES)
LDMM	Leak Detection Mitigation and Monitoring
LIBS	laser-induced breakdown spectroscopy
LIF	laser-induced fluorescence
NAPL	nonaqueous phase liquid
PITT	partitioning inter-well tracer test
PNNL	Pacific Northwest National Laboratory
SAFE	subsurface air flow and extraction
SCAPS	Site Characterization and Analysis Penetrometer System
SERS	surface-enhanced Raman spectroscopy
TXRF	total reflection x-ray fluorescence
UV	ultraviolet
WMA	waste management area
XRF	x-ray fluorescence
WCH	Washington Closure Hanford

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1.0 Introduction

The purpose of this report is to identify and evaluate the state-of-the-art techniques for characterization of chromate (hexavalent chromium; Cr(VI)) contamination in the vadose zone of the 100 Areas at the Hanford Site. The techniques include direct techniques for analysis of chromium in the subsurface as well as indirect techniques to identify contamination through geophysical properties, soil moisture, or co-contaminants. Chromate is the primary contaminant of concern for this study. In some cases, analysis for total chromium (typically hexavalent plus trivalent chromium) may provide suitable data for evaluating contamination. Chromate is considered more toxic, more soluble, and less strongly sorbed to aquifer sediments than trivalent chromium (U.S. Environmental Protection Agency 1998a, 1998b; Rai and Zachara 1986).

Characterization of the distribution of chromium concentration in the vadose zone is needed to assess potential sources for chromate contamination plumes in groundwater at the 100-D, 100-K, and 100-B/C Areas. To meet this need, techniques were evaluated to provide characterization data for the vertical and lateral chromate concentration distribution over approximately 26 m (85 ft) of depth and thousands of square feet in areal extent. Subsurface access in the Hanford 100 Areas is difficult due to the relatively high percentage of gravel and cobble size sediment materials. Therefore, access requirements for the potential characterization techniques were considered in the evaluation. The effectiveness of potential characterization techniques is dependent on the depth of interest, overall expected extent of the contamination, potential contaminant concentrations, and local vadose zone lithology. Preferential flow paths in the vadose zone may reduce the effectiveness of some methods.

1.1 Source Characteristics

Chromate contamination in the 100 Areas may have resulted from several source types. Chromate was primarily used as a corrosion inhibitor in reactor cooling water. Reactor cooling water contained approximately 700 μg/L of chromate (Peterson et al. 1996). The chromate solution was mixed from dry sodium dichromate at the reactor areas or brought in as a concentrated liquid solution. Liquid sodium dichromate solution was transferred by pipeline to water treatment facilities for addition to the cooling water. The concentrated sodium dichromate solution contained much higher hexavalent chromium concentration (up to 25 wt.% Cr(VI)) and thus is a potential source of much higher vadose contamination concentrations than the cooling water. Cooling water was discharged from the reactors to retention basins for cooling and then released to the Columbia River. In the event of a fuel element failure, the reactor cooling water was discharged to trenches and allowed to infiltrate into the soil. Thus, potential sources of chromate contamination include: releases to trench systems, cooling water basin leaks, pipeline leaks of either cooling water or concentrated chromate solutions, and surface spills of liquid or solid dichromate.

Natural background chromium in the sediments is dominantly trivalent chromium. The Hanford formation sediments are heterogeneous mixtures of rock types and thus, background chromium levels are variable. Techniques that perform analyses on small samples may be subject to a large sampling bias for total chromium. Hanford Site soil background chromium has been calculated as 18.5 mg/kg, based on the 90th percentile of a lognormal fit to a suite of background samples (U.S. Department of Energy 2001). The upper limit of expected background chromium can be estimated from the composition of Columbia River basalts since basalt clasts will tend to have higher chromium concentrations than more granitic particles. The Columbia River basalts range up to nearly 300 mg/kg total chromium with most flows having levels below 150 mg/kg (Reidel et al. 2002).

1.2 Baseline Characterization Technology

The baseline method for characterizing vadose zone chromium contamination is soil sampling by excavation or drilling followed by chemical analysis. Typically, drilling at the Hanford Site is performed with cable-tool techniques or less frequently with Becker hammer, sonic, or hollow stem auger. Chemical analysis for chromate is usually performed on aqueous samples or water extracts of sediments by the colorimetric diphenylcarbazide method (EPA SW-846 7196A or a similar field laboratory technique (U.S. Environmental Protection Agency 1997). An alkaline extraction method (U.S. Environmental Protection Agency 1997) is occasionally used to extract hexavalent chromium prior to laboratory analysis. Total chromium analysis is performed by an inductively coupled plasma-atomic emission spectrometry (ICP-AES) method (EPA SW-846 6010) or, less frequently, by inductively coupled plasma-mass spectrometry (ICP-MS) (EPA SW-846 6020). These laboratory analysis methods use the EPA SW846-3010A acid digestion for sample preparation. Total chromium in soil samples can also be analyzed in the field with a portable x-ray fluorescence (XRF) instrument. The XRF measurements provide a surface measurement and may not be representative of the bulk concentration.

Experience on the Hanford Site indicates that drilling can produce reducing conditions in the vicinity of the borehole and that hexavalent chromium may be reduced to trivalent chromium. Development of reducing conditions and production of hydrogen gas as a result of drilling was demonstrated in a Hanford saturated zone borehole (Bjornstad et al. 1994). Drilling near Waste Management Area T (WMA T) in the 200 West Area has shown localized reduction of chromium and technetium-99 in the saturated zone (Hartman et al. 2006, 2007). Reduction of hexavalent chromium during drilling in the vadose zone has not been demonstrated but may need to be evaluated.

1.3 Approach

Technologies were identified through literature research of published applications and through internet web-search methods. The following existing technology review reports and journal review articles were used to screen technologies.

- An extensive review of recent advances in atomic spectroscopy for environmental analysis was valuable in assessing technology advances for further evaluation (Butler et al. 2007).

- Aldstadt and Martin (1997) reviewed analytical methods that may be deployed using cone penetrometer (CPT). The review is useful, but somewhat out of date.

- An intercomparison of XRF methods was reported by Vanhoof et al. (2004). They found limits of detection for the laboratory systems were 10-20 times lower than for a hand-held field system or a "transportable" field laboratory system.

- A recent review of electrochemical analytical methods provided information on several methods, including biosensors (Bakker and Qin 2006).

- A review of geophysical techniques for application to characterization activities at the Hanford Site was reported by Murray et al. (2005). Petersen (2007) presents a review of geophysical and geochemical characterization technologies for application at Hanford. Because of these reviews, only select geophysical methods were investigated for this report.

- Rucker and Sweeney (2004) compared three geophysical methods for subsurface characterization at the BC Cribs.

The ability of a measurement to represent the chromate concentration over the volume of interest is an important consideration. Geophysical techniques and partitioning tracer tests have the advantage of interrogating a large volume. Individual samples are only representative of the area in the immediate vicinity of the borehole. Instrumental measurements such as direct spectroscopic methods typically represent only a small volume of material and may only show the surficial concentration. The small sample size of some methods may be partially offset by collecting multiple measurements

An additional complication is that mineralogical inhomogeneities may affect instrument response or produce other interferences. These factors should be considered in the interpretation of results of any of the proposed methods and ground truth with additional methods or samples is desirable.

2.0 Technology Review

A number of characterization techniques were identified (Table 2.1) based on a review of literature and vendor sources. Appendix A contains brief descriptions of these techniques. Other innovative technologies have been reported but were judged too esoteric to include. The technologies in Table 2.1 were screened to determine which were most appropriate for more detailed review. The criterion used to screen technologies was based primarily on consideration of the type of information provided and the maturity of development.

Technology information is organized into the following categories of application.

- In situ analysis methods for chromate, chromium, or co-contaminants
- In situ detection and geophysical surveys of physical properties potentially associated with contamination
- Ex situ/field analytical methods

Table 2.1. Listing of Technologies Identified

Technology	Potential Deployment
Chromate	
Raman Spectroscopy	Laboratory/Field/In Situ
Ion Chromatography	Laboratory
Stripping Voltammetry	Laboratory/Field?
Capillary Ion Electrophoresis	Laboratory
Microcantilever Sensors	Laboratory/Field?
Biosensors	Laboratory/Field?/In Situ?
Ultraviolet Absorption	Laboratory/Field
Chromium	
X-Ray Fluorescence	Laboratory/Field/In Situ
Laser-Induced Fluorescence	Laboratory/Field/In Situ
Laser-Induced Breakdown Spectroscopy	Laboratory/Field/In Situ
Neutron Activation Analysis	In Situ
Ion chromatography	Laboratory
Capillary Ion Electrophoresis	Laboratory
Ionic Contaminants	
Conductivity Probe	Laboratory/Field/In Situ
Electromagnetic Survey	Surface Geophysics
High-Resolution Resistivity	Surface Geophysics
Soil Moisture	
Neutron Logging	Borehole Geophysics
Electromagnetic Survey	Surface Geophysics
Partitioning Tracers	In Situ

Some technologies can be used for multiple applications and fall into more than one of the above categories. Technologies are identified and reviewed in this report based on their functionality, not necessarily based on a specific instrument or vendor. Specific cost estimates have not been made because of the varying degree of development and the unknowns regarding specific applications. Qualitative relative costs are based on author judgment.

Two rapidly expanding areas of analytical chemistry are notable but were considered too new for a reliable evaluation of their applicability to vadose zone chromate issues. Still, they are worth watching as the technologies develop. The first is the area of biosensors. Briefly, biosensors use enzymes, antibodies, DNA, other bio-molecules, or even living microbial "bioreporters" to sense and provide a readable signal from analytes of interest. Reviews that discuss biosensors include Wolfbeis (2006) and Bakker and Qin (2006). The second area is that of microcantilever sensors. These sensors are designed with a microscopic tip attached to a cantilever arm that interacts with the analyte. The force of interaction is sensed by the deflection of the cantilever. The microcantilever systems are more suited to aqueous analysis. Two recent papers have investigated microcantilevers for chromate detection (Pinnaduwage et al. 2004; Boiadjiev et al. 2005). Technology descriptions are not included in Appendix A for biosensors or microcantilever sensors.

A number of innovative technologies for detection of chromate or other contaminants in groundwater have been reported recently. However, these technologies are not readily transferable to application in the vadose zone. Soil samples brought to the surface for analysis may have the chromate easily extracted with water for analysis. This may provide a role for new water analysis techniques if they are faster, more sensitive, or produce less waste than the baseline technology. Brief descriptions of these techniques are included in Appendix A but they are not considered further in this report since the baseline colorimetric method is well established and a major benefit was not seen at this time. One exception is surface-enhanced Raman spectroscopy (SERS), which is discussed because of its close tie to other Raman techniques that were evaluated and its potential for rapid, non-destructive screening analysis.

Table 2.2 contains a listing of technologies, including the aqueous analytical methods, which were not considered further in this report but may be of use for other types of application at Hanford or in the future as they develop.

The following three sub-sections contain technology information for the categories of application described above. In each section, the overall characteristics of each technology retained through the screening are compiled in the first table in each section (e.g., Table 2.3). The technology information under each category is either from the identified data source or, for state of development and cost categories, is based on an assessment by the authors. The state of development was assessed based on whether a technology has been widely applied (commercial – widely available), has had limited application (commercial – limited), is still in the development stage (emerging – research), or where field applications have been primarily for testing purposes (emerging – deployed).

Additional detail about the technology functionality is presented in the second table in each section (e.g., Table 2.4). Again, information is either directly from the data source or based on an assessment by the authors. The data interpretation category is assessed based on whether a unique or non-unique interpretation can be obtained and whether the interpretation is simple or complex. The relative data quality category is assessed based on whether the data is quantitative (concentration results are comparable to baseline analysis), semi-quantitative (results show relative concentrations but may not be comparable to baseline analysis or may have significant uncertainties), or are qualitative (show the presence or absence of the parameter of interest but give only limited indications of concentration or are not clearly related to the chromate concentration).

Table 2.2. Technologies from Table 2.1 Not Considered Further in the Report

Technology	Reason Not Considered
Ion Chromatography	Aqueous method. Laboratory/field laboratory technology that does not appear to offer significant advantages over baseline. Does not offer a path to portable or in situ measurements.
Stripping Voltammetry	Aqueous method. Laboratory technology excellent for low-level determination of chromate and may be possible to deploy for field measurements. Does not appear to offer significant advantages for levels of interest.
Capillary Ion Electrophoresis	Aqueous method. Laboratory technology that does not appear to offer significant advantages over baseline. Research in microfluidic and microchemical techniques may provide advantages of miniaturized sensors in the future.
Microcantilever Sensors	Aqueous method. Early development stage.
Biosensors	Generally aqueous methods. Early development stage.
Ultraviolet Absorption	Current research on analysis for aqueous solutions is promising and offers a path to in situ groundwater monitoring but currently does not appear to offer significant advantages for field studies of soils.
In Situ Neutron Activation Analysis	Early testing does not show promise for successful in situ deployment.

Table 2.3. Characteristics of In Situ Analytical Technologies

Technology	Characterization Target	Use Platform	State of Development	Relative Cost	Data Source
Laser-Induced Breakdown Spectroscopy	Chromium and many other elements	CPT. Possible to adapt to other penetration techniques.	Emerging – deployed Prototype subsurface fiber optic system has been tested	Moderate equipment cost; inexpensive analytical cost	Mosier-Boss and Lieberman (2005) Ciucci et al. (1996) U.S. Department of Energy (2000a) Theriault et al. (1995, 1998)
Raman Spectroscopy	Chromate and possible co-contaminants	CPT. Possible to adapt to other penetration techniques.	Emerging – deployed A CPT based Raman system has been tested for DNAPL characterization SERS Raman has been evaluated for in situ groundwater monitoring	Moderate equipment cost; inexpensive analytical cost	Rossabi et al. (2000) Farquharson (2002) Space and Naval Warfare Systems Center (2003)
Laser-Induced Fluorescence	Chromium and other elements.	CPT or possibly other penetration techniques	Emerging – research CPT based system has been deployed for characterization of organic compounds	Moderate equipment cost; inexpensive analytical cost	Bujewski and Rutherford (1997) Hilbk-Kortenbruck et al. (2001) Sdorra et al. (1989) Telle et al. (2001)
X-Ray Fluorescence	Chromium and other elements	CPT or other penetration techniques	Emerging – deployed CPT based systems have been demonstrated for lead, uranium and other contaminants (chromium was not reported in the studies evaluated)	Moderate equipment cost; inexpensive analytical cost	U.S. Department of Energy (2000b) Elam et al. (2000)

2.1 In Situ Contaminant Analysis

In situ measurements of chromate distribution in the deep vadose zone would be highly desirable but no technology is commercially available at present. However, a number of technologies show promise for development of in situ analytical capabilities for chromium or for providing secondary indications of chromate contamination. Several in situ methods have been developed for other environmental contaminants and some system components may transfer to application for chromate contamination. In addition, ex-situ field and laboratory techniques could be modified for in situ application. Technology information for in situ analysis is compiled in Tables 3 and 4.

In situ analytical methods are dependent on drilling or penetration technology to provide access for the analysis system. Most development work has been performed using CPT methods. Although CPT has had limited success at accessing the deep vadose zone at Hanford, in situ analytical instrumentation may be adaptable to other access methods. Evaluations of access technologies for application at Hanford are ongoing, thus no formal screening will be included here. Plans to use a hydraulic hammer rig in the 100-D Area are being developed and this should be evaluated as a potential platform for in situ analytical systems.

Table 2.4. Functionality of In Situ Analytical Technologies

Technology	Capabilities	Requirements for Use	Interferences	Other Considerations	Data Interpretation	Relative Data Quality
Laser-Induced Breakdown Spectroscopy	Provides simultaneous optical emission spectra of multiple elements	Specially adapted CPT with sapphire window and optics are needed	Natural Cr(III) may interfere with contaminant chromate determination; spectral overlap; variations in moisture and soil type	Currently not designed for saturated sediments or groundwater	Data analysis is automatable. Relationship between measurements and bulk analysis needs to be verified.	Semi-quantitative
Raman Spectroscopy	Can distinguish chromate ions and chromate minerals	Specially adapted CPT with sapphire window and optics are needed	Fluorescence of organics and other species; background color	Relatively high detection limits unless enhanced techniques are used. Possible to combine with LIBS	Data analysis may be automated if the appropriate spectral libraries are developed.	Semi-quantitative or qualitative
Laser-Induced Fluorescence	High sensitivity/selectivity analysis of multiple elements	Specially adapted CPT required. For metals analysis an excitation source is needed	Fewer spectral interferences than LIBS	May be combined with LIBS for improved measurement.		Semi-quantitative. Better sensitivity and selectivity than LIBS or XRF for total metal analysis.
X-Ray Fluorescence	Can distinguish chromate ions	Specially adapted CPT with boron carbide window and optics are needed	Fluorescence of other elements/ contaminants may interfere	Relatively high detection limits	Data analysis is automated.	Semi-quantitative

The only chromate-specific analytical method that currently has potential for in situ vadose zone analysis is Raman spectroscopy. The deployment of in situ Raman spectroscopy has been demonstrated for organic contaminants but not for chromate. In situ Raman analysis for groundwater is in the developmental stage. The main potential issues with in situ Raman spectroscopy of chromate are interferences from background color/fluorescence and the relatively high detection limits. Several techniques may enhance the Raman sensitivity. Resonance Raman spectroscopy appears to offer potential enhancement for in situ characterization (See Appendix A). Raman spectroscopy may potentially be able to be deployed in a combined system with laser-induced breakdown spectroscopy (LIBS) although the analysis would presumably have to be performed separately because the LIBS system would break down the chromate ions. Testing of Raman spectroscopy is recommended to understand the capabilities for chromate analysis and to develop a conceptual deployment system.

LIBS has been deployed for in situ vadose zone measurements, using a fiber optic system to transmit the excitation laser energy and the spectroscopic signal. Prototype systems have been evaluated for chromium contamination and field-testing has been performed. Although the methodology is not chromate specific, it is attractive where the total chromium contaminant concentration is significantly above background. LIBS is a multi-element technique and thus may provide indications of co-contaminants such as elevated sodium. Testing and demonstration for LIBS deployment at Hanford is recommended, provided that a suitable subsurface access technology can be provided.

XRF is considered a baseline technology for field screening of chromium contamination during surface remediation activities in the Hanford 100 Areas. XRF is not specific for chromate, so chromate contamination levels must be higher than the background total chromium concentration to identify contamination. XRF has been evaluated for in situ chromium analysis. The instrumentation for XRF is not complex; however, analytical interferences with the XRF technique may be more significant than the potential interferences for the LIBS technique. Testing and demonstration for in situ XRF deployment at Hanford is recommended, provided suitable access can be provided.

Laser-induced fluorescence (LIF) shares features with LIBS and XRF. At the present state of development, in situ LIF should be considered an elemental analytical technique that will not distinguish chromate from other chromium species. A powerful application of LIF is to combine it with LIBS. The LIBS system forms a plasma containing the chromium and a secondary laser is used to perform the LIF analysis. This combined application increases overall sensitivity and decreases interferences. However, combined LIBS/LIF systems are not yet available for in situ analysis.

Table 2.3 lists the characteristics of in situ analysis methods. The functionality of the technologies is described in Table 2.4.

2.2 In Situ Detection/Geophysical Surveys of Physical Properties

Chromate contamination in the vadose zone may cause or be associated with changes in soil physical properties. Characterization of these properties can provide indirect indication of the contaminant distribution. Chromate in the soil moisture is an ionic species and the elevated ionic strength increases the specific conductance of the solution (decreases the electrical resistivity). Thus electrical conductance/ resistivitiy can be affected by the presence of inorganic contaminants. Low concentrations of chromate may be masked by solutes in the background soil moisture and it is possible to have releases of low-conductivity water with chromate contamination. However, process knowledge and characterization to date indicates that much of the vadose contamination is associated with concentrated chromate sources that are likely to increase the specific conductance. Geophysical methods have not been demonstrated to be able to detect chromate contamination in the subsurface and any method applied will require verification sampling.

Spills, leaks, and discharges of contaminated water to the surface or near-surface soils at Hanford increase the soil moisture content. This soil moisture increase can persist for extended periods of time, particularly above lithologic changes that produce capillary breaks, impeding the downward migration of water. There is evidence for lateral migration of contamination in these zones (e.g., Serne et al. 2002; DePaolo et al. 2004). It is likely that much of the chromate contamination in the 100 Areas was associated with relatively small volume leaks or surface spills, however the possibility of these producing variation in soil moisture should be evaluated. In addition, chromate appears to be dominantly present in solution in soil moisture so areas of increased moisture will contain greater mass of chromate. Thus careful consideration of soil moisture distribution may indicate areas of possible increased contaminant mass and may help direct more specific sampling.

Electrical conductivity or resistivity can be measured by in situ techniques or by surface geophysical methods. Table 2.5 lists the characteristics of in situ measurement and geophysical techniques identified for characterization of soil moisture and conductance/resistivity. The functionality of the technologies is described in Table 2.6.

Table 2.5. Characteristics of Physical Property Characterization Technologies

Technology	Characterization Target	Use Platform	State of Development	Relative Cost	Data Source
Specific Conductance Probe	Ionic contaminants; not chromate specific	CPT or other technique where the probe can be placed in contact with the soil	Commercial – widely available. Commercially available for CPT	Inexpensive	Beck et al. (2000)
Electromagnetic Geophysical Survey	Soil moisture or ionic contaminants; not chromate specific	Surface geophysical method	Commercial – widely available.	Inexpensive	Rucker and Sweeney (2004)
High-Resolution Resistivity	Ionic contaminants; not chromate specific	Surface geophysical method	Commercial – limited.	Moderate	Barnett et al. (2002) Rucker and Sweeney (2004)
Nuclear Magnetic Resonance	Soil moisture; not chromate specific	Surface geophysical method	Emerging – deployed. Being developed under the SBIR program	Moderate	Yaramanci (2002)
Neutron Logging	Soil moisture; not chromate specific	CPT or other technique where the probe can be lowered through the tubing or push-rod	Commercial – widely available. Commercially available for CPT or conventional vadose boreholes	Inexpensive	Horton and Randall (2000)
Partitioning Tracers	Soil moisture; not chromate specific	Vadose monitoring wells or CPT well points, depending on scale of the test	Emerging – deployed. Has been demonstrated for moisture characterization	Expensive	Cameron et al. (2002)

Table 2.6. Functionality of Physical Property Characterization Technologies

Technology	Capabilities	Requirements for Use	Interferences	Other Considerations	Data Interpretation	Relative Data Quality
Specific Conductance Probe	Measures electrical conductivity of the soil which can be related to the presence of ionic species	Must be in contact with soil	Affected by soil moisture		Straight-forward	Quantitative; indirect indicator
Electromagnetic Survey	Electrically conductive zones distort an induced magnetic field and can be related to the presence of moisture or ionic contamination	Access to surface	Buried metal objects		Moderately complex	Indirect indicator
High-Resolution Resistivity	Measures electrical resistivity in the subsurface	Access to surface soils	Buried metallic objects		Complicated	Indirect indicator
Nuclear Magnetic Resonance	Induces a magnetic field in soil moisture	Relatively shallow	Buried metal objects Power lines		Complicated	Indirect indicator
Neutron Logging	Measures soil moisture content	Measures a zone around the logging tool. Needs access of sufficient diameter	Affected by the soil composition.	Should be calibrated for similar materials. Calibration facilities available on Site	Data interpretation procedures are well established	Quantitative.
Partitioning Tracers	Measures retardation of tracers injected into soil gas and relates the measurements to moisture content and distribution. Provides moderately large-scale results.	Two screened vadose wells or push holes with distance between dependent on scale of the test	Ionic strength of the soil moisture can affect results	Provides understanding of moisture distribution at a scale not easily found in other ways.	Complicated	Quantitative

2.3 Novel Ex-Situ/Field Analytical Methods

Ex-situ, field analytical methods require the retrieval of a sample for analysis at the surface. This complicates and slows the overall characterization process but simplifies the analytical system requirements over in situ systems. In general, the state of development for field portable systems is greater than for in situ systems since field systems have applicability to military, national security, forensic, mineral exploration, and product testing markets. Some development will likely be needed to demonstrate field systems for chromate characterization activities. It will be simpler to develop and test analytical methods on ex-situ analysis and this may provide a practical path towards ultimate in situ deployment. Thus, innovative ex-situ methods may be worth pursuing to evaluate whether the technique could lead to in situ systems as well as for their immediate value.

Field deployable XRF systems are not considered in this section since hand-held field XRF is considered to be a baseline technology for field screening of soil samples. However, it should be noted that a variation on XRF, total reflection x-ray fluorescence (TXRF) may improve detection limits for XRF (Mages et al. 2003; Kunimura and Kawai 2007). However, in field testing of a commercially available bench-top TXRF unit, significant improvement for chromium detection was not seen (Stosnach 2005; U.S. Environmental Protection Agency 2006).

Evidence to date indicates that the chromate in the vadose zone is dissolved in pore water with possible contribution from sorbed or high-solubility mineral phases. Thus, a simple water extraction is a viable method to prepare samples for analysis. Field analysis can then be easily performed on aqueous sample extracts, increasing the options for analytical methods. The baseline colorimetric diphenylcarbazide method is performed on aqueous extracts for field analysis and provides accurate results with suitable detection and quantitation limits. The disadvantages to the colorimetric method are that it produces chemical waste, is somewhat slow, which limits sample throughput, and does not provide information on potential co-contaminants. It is difficult to envision a path toward deploying the colorimetric method in situ.

Raman spectroscopy is capable of distinguishing chromate from background trivalent chromium. In addition to the characteristics discussed in Section 2.1, ex-situ Raman spectroscopy provides the capability of performing analysis on water extracts. The analysis is fast and non-destructive, producing no waste. Surface-enhanced Raman spectroscopy (SERS) is a technique that provides a Raman signal enhanced by several orders of magnitude, decreasing the detection limit. SERS is an option for chromate analysis of aqueous samples or aqueous extracts of soils.

LIBS is applicable for field measurement of chromium in soil samples. LIBS systems are commercially available and may present an attractive alternative to field XRF or colorimetric analysis, although detection limits would need to be determined and the method does not distinguish trivalent chromium from the hexavalent chromium in chromate. LIBS provides a rapid multi-element analytical capability that the baseline methods do not.

LIF is most suited to field deployment as a combined LIBS/LIF system. The advantage of the combined system would be greater sensitivity and fewer interferences than with LIBS alone (Sdorra et al. 1989; Hilbk-Kortenbruck et al. 2001; Telle et al. 2001). The plasma produced by the LIBS system provides an excellent medium for subsequent LIF measurement. The addition of a separate laser and spectrometer system complicates system design and adds to the cost. These systems have been laboratory tested for chromium and other species but have not been field-deployed. The laboratory results are promising; in particular, Hilbk-Kortenbruck et al. (2001) reported a chromium detection limit of 2.1 mg/kg in spiked soil samples.

Table 2.7 lists the characteristics of ex-situ/field analytical techniques identified for characterization of chromate, chromium, and co-contaminants or indicator compounds. The functionality of the technologies is described in Table 2.8.

Table 2.7. Characteristics of Ex-Situ/Field Analytical Technologies

Technology	Characterization Target	Use Platform	State of Development	Relative Cost	Data Source
Laser-Induced Breakdown Spectroscopy	Multi-element chemical analysis including chromium	Field portable. Remote detection (several m stand-off) is possible. Primarily applicable to solids but methods for analysis of liquid samples are under development.	Commercial – widely available. Field and laboratory systems available commercially. Remote systems have been designed and tested for specific applications but may not be available commercially.	Moderate	Yueh et al. (2000)
Raman Spectroscopy	Chromate and possible co-contaminants	Field Portable. Remote detection may be possible. Applicable to solids or liquids. May be able to achieve better detection with liquids or water extracts from solids	Commercial- widely available. Field and laboratory systems available commercially. Remote systems have been designed and tested for specific applications but may not be available commercially.	Moderate	See vendor lists in Appendix B
Laser-Induced Fluorescence	Chromium and possibly selected other elements	Field instruments have not been developed but are conceptually practical	Emerging – research. Has been demonstrated for chromium analysis	More expensive than LIBS alone	Sdorra et al. (1989) Telle et al. (2001)

Table 2.8. Functionality of Ex-Situ/Field Analytical Technologies

Technology	Capabilities	Requirements for Use	Interferences	Other Considerations	Data Interpretation	Relative Data Quality
Laser-Induced Breakdown Spectroscopy	Provides simultaneous optical emission spectra of multiple elements	Self-contained systems available	Natural Cr(III) may interfere with contaminant chromate determination.	Currently not designed for saturated sediments or groundwater	Data analysis is automatable. Relationship between measurements and bulk analysis needs to be verified	Quantitative or semi-quantitative
Raman Spectroscopy	Provides chromate-specific analysis. Non-destructive	Self-contained systems available. Additional sample preparation or mounting needed for SERS	Fluorescence and background color may interfere	SERS can significantly enhance detection limits for liquid samples	Data analysis may be automated. May need to develop appropriate spectral library	Qualitative or semi-quantitative
Laser-Induced Fluorescence	High sensitivity/ selectivity analysis of multiple elements	For metals analysis an excitation source is needed	Fewer than LIBS	May be combined with LIBS for improved measurement.	Automated data analysis is available. Calibration needs to be verified.	Quantitative. Better sensitivity and selectivity than LIBS, XRF for total metal analysis.

3.0 Conclusions

Several of the technologies reviewed in this report show promise as useful additions to characterization of chromate contamination in the deep vadose zone at the Hanford Site 100 Areas (Table 3.1). The applicability depends on the particular project objectives and the technological maturity relative to timelines and budgets. Technologies for in situ measurement of contaminants or direct field measurement of soil samples are more restricted than for measurement of water extracts in samples. Most methods will require further development and testing for application at Hanford. It may be productive to first develop and test instrumental methods for field analysis of samples as a stepping-stone to full in situ deployment.

Table 3.1. Summary of Technologies Recommended for Further Evaluation or Testing

Technology	Chromate	Total Chromium	Specific Conductance/ Resistivity	Soil Moisture	Other Constituents	Recommendation
Laser-Induced Breakdown Spectroscopy	No	Yes	No	No	Yes	Pursue field and in situ demonstration testing
Raman Spectroscopy	Yes	No	No	No	Possible	Evaluate Raman and combined LIBS/Raman systems for field testing
Laser-Induced Fluorescence	No	Yes	No	No	Yes	Evaluate conceptual combined LIBS/LIF system for in situ or field testing
X-Ray Fluorescence	No	Yes	No	No	Possible	Pursue in situ demonstration testing
Specific Conductance	No	No	Yes	No	No	Consider deployment if it can be used in conjunction with other techniques
High-Resolution Resistivity	No	No	Yes	No	No	Pursue field demonstration testing
Neutron Log	No	No	No	Yes	No	Consider deployment if it can be used in conjunction with other techniques
Partitioning Tracers	No	No	No	Yes	Not currently	Consider deployment to provide more detailed characterization in areas targeted by other methods

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Appendix A – Brief Descriptions of Technologies Evaluated

Appendix A

Brief Descriptions of Technologies Evaluated

A.1 Laser-Induced Breakdown Spectroscopy (LIBS)

Category: Chemical Analysis

Laboratory/field laboratory: Commercially available
Stand-alone field instrument: Commercially available
In situ/down hole: Has been demonstrated

Target Analyte: Chromium and other elements

Operating Principle: LIBS is an atomic-emission spectroscopy technique where the material is ablated from the surface with a high-energy laser, forming a plasma bubble. The sample is broken down to atomic form by the plasma. Excitation of the atomic electrons to different energy levels and subsequent decay to the ground state releases photons with wavelengths that are characteristic of the atomic makeup. The spectrometer identifies and quantifies the substance by the wavelengths and intensities of the emission.

The laser energy and the emission light may be transmitted to and from the surface by fiber optics. The laser may also be aimed directly through the air and the emission focused on the detector telescopically for operations at distances up to ten meters or more (e.g., Palanco et al. 2006).

Advantages: LIBS provides multi-element analysis of a variety of materials. It is best suited to solid materials in unsaturated conditions. Some ability to profile into the material is possible if multiple measurements are made at the same spot. The analysis is not affected greatly by chemical or mineralogical form of the material. Light elements that may not be measurable by other methods can be analyzed by LIBS. The sample analysis is rapid and quantitative.

Limitations: LIBS only gives the chemical composition, i.e., total chromium, and does not provide information on oxidation state or mineral/compound present. Measurements in saturated conditions require modified systems. A number of potential interferences must be considered. Some matrix properties can affect the measurements so the results should be calibrated for the sample medium of interest.

Example Applications:

- Remote measurement of trace metals
- In situ determination of lead in paint
- Process control in manufacturing
- In situ analysis of reactor steam generator tubing
- In situ analysis of materials in reactor cooling ponds
- Authentication of art works

- Analysis of geological materials on Mars
- Analysis of wood preservatives (including chromates)

Deployment Platforms:

Laboratory/Field Laboratory: Laboratory instrumentation is commercially available. The instruments could probably be deployed in a field laboratory.

Field Deployable: Battery-powered field deployable fiber optic or hand-held units are commercially available. Transportable telescopic systems for remote detection have also been developed.

Subsurface/In situ: Prototype subsurface fiber optic systems for CPT deployment have been tested. The use of fiber optics-LIBS deployed using a cone penetrometer for detection of buried automotive scrap residue was described by Mosier-Boss and Lieberman (2005).

State of Development: A detection limit of 2.5 μg/kg chromium in soil was reported for a laboratory study by Hilbk-Kortenbruck et al. (2001). That study combined LIBS and laser-induced fluorescence to decrease the detection limits for other analytes but was not investigated for chromium because the LIBS measurements met their objectives. Fichet et al. (2006) compared LIBS to inductively coupled plasma/optical emission spectroscopy for samples in aqueous solution and found that LIBS compared well but more dilutions were needed to cover the analytical range and LIBS had higher detection limits.

A CPT-deployed LIBS system was tested at Sandia National Laboratory for detection of metals in the vadose zone, including chromium (U.S. Department of Energy 2000a). Some issues were identified that required further development work.

LIBS has also been tested for use in identifying the geochemistry of samples from the Yucca Mountain Project (Blacic et al. 1996). Measurement of the chemistry of dust samples from air rotary core drilling was partially successful. This may be an option where CPT cannot be used.

Application at Hanford: LIBS has several promising applications for field investigations at Hanford. The multi-element analysis may provide an added benefit in identifying co-contaminants. Field analysis of samples brought to the surface appears to be practical and would not produce any additional chemical waste aside from the sample. The ability to distinguish chromate contamination from the natural background chromium would have to be based on the total chromium concentration level.

For CPT investigations, the sampling depth would be limited but LIBS could add considerable value by providing a practical way to obtain chromium depth profiles rather than rely on discontinuous sampling. It may be valuable to evaluate LIBS results on existing contaminated samples or spiked soils prior to investing in the deployment of an in situ system.

Although LIBS may be applicable to measurement of aqueous samples, the methodology is somewhat different and some instrument development or testing would likely be needed.

A.2 Laser-Induced Fluorescence Spectroscopy (LIF)

Category: Analytical Method

Laboratory/field laboratory:	Tested
Stand-alone field instrument:	No documentation found
In situ/down hole:	Possible
Target Analyte:	Chromium and other elements

Operating Principle: A laser is used to excite electrons of atoms in the material of interest. The resulting fluorescence produced as the orbitals are repopulated is analyzed. Thus, the method is similar to XRF. Speciation information may be obtained by tuning the laser or other techniques such as time-resolved laser-induced fluorescence (Chang et al. 2006), but currently such techniques require laboratory-grade instrumentation and cryogenic conditions. In many applications, the sample is atomized first by an alternate means such as a graphite furnace or a separate laser-induced plasma (Sdorra et al. 1989; Axner and Rubinsztein-Dunlop 1993). Thus, LIF may be combined with LIBS to achieve greater sensitivity or selectivity than provided by LIBS alone (Hilbk-Kortenbruck et al. 2001; Telle et al. 2001). LIF is also used for analyzing organic compounds.

Advantages: LIF may provide high sensitivity and reduce interferences when compared to other techniques such as LIBS and XRF.

Limitations: LIF for trace metal analysis requires more complicated instrumentation than other methods. The method does not distinguish chromate from other forms of chromium.

Example Applications:

- CPT deployment of LIF for in situ measurements of organic compounds
- Trace analysis of heavy metals in soils
- Laboratory studies of surface speciation of uranium

Deployment Platforms:

Laboratory/Field Laboratory:	Research instrumentation
Field Deployable:	Not developed
Subsurface/In situ:	CPT deployment for organic compounds

State of Development: Laboratory instrumentation is well developed, but methodologies for chromium analysis are not routinely used. Combined LIBS-LIF methods have been demonstrated in the laboratory.

No field deployable systems for metals are known.

LIF has been deployed for in situ analysis of organics but not metals (Bujewski and Rutherford 1997). No combined LIBS-LIF methods have been demonstrated in situ.

Application at Hanford: Combined LIBS-LIF systems appear to be practical and have some advantages over standard LIBS. However, the LIBS-LIF development lags field deployment of LIBS. This may be a viable alternative if LIBS cannot meet project performance targets.

A.3 Raman Spectroscopy

Category: Chemical Analysis

Laboratory/field laboratory:	Commercially available
Stand-alone field instrument:	Commercially available
In situ/down hole:	Possible
Target Analyte:	Chromate

Operating Principle: When monochromatic light strikes a molecule or surface, most of the reflected light is reflected back at the same wavelength through elastic Rayleigh scattering. However, a small portion interacts with the electron cloud of the material and is subject to inelastic Raman scattering and is reflected at a different wavelength. The wavelength is sensitive to the vibrational and other energy modes of the material and thus provides information on the molecular bonds.

Chromate in solution and chromate solids show characteristic Raman spectra that can be distinguished from those of trivalent chromium compounds. The dichromate spectra are also distinct from chromate (Heyns et al. 1999; Ramsey et al. 2001; Kikuchi et al. 2005). The method is non-destructive and rapid. Raman spectra can be measured through transparent materials such as glass containers or sapphire windows. The laser light may be transmitted to the material and the signal returned through fiber optics. The Raman signal is generally very weak but recent advances in instrumentation have increased sensitivity and made it possible to develop rugged, field-deployable systems. Spectral libraries have been developed to identify many compounds.

Surface-enhanced Raman spectroscopy (SERS) is a method that can enhance the Raman signal by many orders of magnitude. The material being analyzed is placed in contact with a roughened metal surface or colloidal metal particles. Thus, SERS is more practical for liquid than solid environmental samples. SERS spectra for chromate have been investigated in the laboratory (Feilchenfeld and Siiman 1986). As a further refinement, the use of a cationic-coated silver substrate for SERS has been investigated for measurement of chromate and other oxyanions by the Space and Naval Warfare Systems Center (2003). That work, funded under SERDP, was aimed at developing a sensor for groundwater monitoring.

Another approach to increasing the sensitivity of Raman spectroscopy is resonance Raman spectroscopy. This requires the use of a laser tuned to a specific wavelength for the compound of interest. The resonance Raman effect on chromate in aqueous solution and solids was investigated by Kiefer and Bernstein (1972). It appears that little other development work of this approach for chromate has taken place.

Advantages: Raman spectroscopy is rapid, non-destructive, does not typically require extensive sample preparation, and provides information on the structure of the compound (e.g., chromate vs. other forms) rather than just elemental analysis.

Limitations: Background color may interfere with the Raman signal. Fluorescence also may interfere. Spectral libraries may need to be developed for the compounds of interest. The weak signal for normal Raman spectroscopy limits the detection of trace compounds. SERS requires contact of the sample with a microscopically rough or colloidal metal surface. Resonance Raman spectroscopy requires tuning the laser to the appropriate wavelength.

Example Applications:

- Hydrocarbon/chlorinated solvent dense non aqueous phase liquid (DNAPL) characterization
- Mineral/gemstone identification
- Drug identification
- Landmine detection
- Natural organic material characterization
- Art and archaeological artifact authentication
- Detection of biological spores

Deployment Platforms:

Laboratory/Field Laboratory: Laboratory grade instruments are widely available and relatively compact instruments may be deployed in field laboratories.

Field Deployable: Portable, self-powered field deployable instruments have been developed by a number of manufacturers. The primary markets include pharmaceutical and other product testing, drug interdiction, military, and homeland security. The major applications are for relatively pure or high concentration materials due to the detection limits. Field deployable SERS air samplers for land mine detection have been tested. SERS water sampling instrumentation has been developed for some applications.

Subsurface/In situ: A cone-penetrometer based Raman system has been tested for DNAPL (trichloroethene and tetrachloroethene) analysis (Rossabi et al. 2000). Research on groundwater monitoring applications for anions including chromate using SERS has been performed by the Space and Naval Warfare Systems Center (2003) and Farquharson (2002). It should be noted that many of the elements of a remote laser-induced breakdown spectroscopy (LIBS) system, such as fiber optics are similar to Raman systems, so modifications to change measurement systems or even to deploy multiple technique systems may be possible.

State of Development: Field deployable and portable normal Raman spectroscopy systems are commercially available. These may not have the detection capabilities needed for analysis of chromate in soils. It appears that most components needed for SERS are commercially available, although the commercial products have not been documented or optimized for chromate analysis. Currently, SERS appears to be restricted to liquid chromate samples. Resonance Raman spectroscopy for chromate needs further development prior to testing in environmental applications.

Subsurface analysis has been demonstrated using CPT systems. To our knowledge, Raman spectroscopy has not been tested with other subsurface access systems.

Application at Hanford: Further evaluation of Raman spectroscopy for characterization activities at Hanford is warranted because of its ability to distinguish trivalent chromium from chromate for rapid analysis.

The direct measurement of chromate in soils could be evaluated relatively easily using existing laboratory instrumentation at PNNL and through cooperation with manufacturers of field-portable instruments. SERS analysis is a practical alternative that would require a somewhat greater amount of method development. SERS could be applied for rapid field screening of water extractions of sediment samples brought to the surface. SERS methods for aqueous samples would also be valuable when tracking groundwater contamination back to the source and for evaluating the effects of reduction induced by drilling.

In situ measurements are limited by depth of CPT penetration for currently available systems, but may be useful for some studies. It is likely that LIBS would be a more practical alternative in the short-term. Experience with Raman measurements of sediment samples brought to the surface would help determine if in situ measurements are worth further development.

A.4 X-Ray Fluorescence (XRF)

Category: Chemical Analysis

Laboratory/field laboratory:	Commercially available
Stand-alone field instrument:	Commercially available
In situ/down hole:	Possible
Target Analyte:	Chromium

Operating Principle: XRF provides atomic identification and quantification by ejecting the inner-shell electrons of the atom using high energy x-rays or gamma rays. As electrons repopulate those orbitals, photons with energies characteristic of the atom are released. Detection of the photons is made with either an energy dispersive spectrometer or a wavelength dispersive spectrometer.

Advantages: XRF analysis is non-destructive and multi-element capabilities are possible. Solids or liquids can be analyzed although typical applications are for solid analysis. XRF is a surface analysis technique, which can be an advantage for some applications.

Limitations: Detection limits are relatively high. As a surface analysis, technique, the results may not be comparable to bulk analytical methods. The use of ionizing radiation and radiation sources requires certain safety procedures. Field method results should be considered qualitative. XRF only measures total chromium, not chromate.

Example Applications:

- Chromium, copper, arsenic in CCA wood preservative
- Field screening of chromium contaminated soil
- Analysis of steel alloys
- Heavy metals in plastics

Deployment Platforms:

Laboratory/Field Laboratory: Commercially available
Field Deployable: Hand-held field instruments are commercially available
Subsurface/In situ: CPT deployment demonstrated

State of Development: Laboratory XRF instrumentation and methods are well established. For chromium contamination, other laboratory methods are available at better sensitivity.

Field deployable XRF instruments are widely available from several manufacturers and have been extensively evaluated for environmental applications. Field instruments are regularly used for screening of surface and near-surface soils by Washington Closure Hanford.

Development work has been performed for total reflection x-ray fluorescence (TXRF) for field-deployable systems with greater sensitivity than standard XRF (Stosnach 2006). The samples required grinding to a fine grain size before being mounted on a quartz glass sample carrier. Detection limits were improved to ~30 mg/kg by using a larger detector and sample size.

Subsurface in situ methods for XRF have been tested. Elam et al. (2000) tested a CPT-deployed XRF system for lead analysis as part of the Site Characterization and Analysis Penetrometer System (SCAPS) system. Testing of an XRF module in a CPT system in the 200 East Area of Hanford was successful but chromium was not one of the species investigated (U.S. Department of Energy 2000b).

Application at Hanford: Field XRF instrumentation is valuable for detecting relatively high levels of chromium contamination in soil samples. According to WCH personnel, they are achieving a detection limit of approximately 50 μg/kg using a hand-held instrument. Thus, TXRF does not appear to offer significant advantages at its current state of development.

It does not appear that down-hole XRF has any major advantages over LIBS. However, XRF may be a viable alternative if LIBS is found to be unsuitable.

A.5 Ultraviolet Absorption Spectroscopy

Category: Chemical Analysis – liquid

Laboratory/field laboratory: Yes
Stand-alone field instrument: Possible
In situ/down hole: Possible (for groundwater)

Target Analyte: Chromate

Operating Principle: Chromate absorbs ultraviolet light at a wavelength of 373 nm (Tao et al. 2002). The absorption is relatively weak at concentrations of interest in groundwater, so either a long light path (Tao et al. 2002) or a flow-through preconcentration step (Egorov et al. 2006) is required.

Advantages: Direct measure of chromate in solution with no added chemicals. Rapid analysis.

Limitations: Has not been fully tested in field conditions. Possible issues with particulates.

Example Applications:

- Long-term monitoring

Deployment Platforms:

Laboratory/Field Laboratory: Has been tested
Field Deployable: Possible but may not offer major advantages over other technologies.
Subsurface/In situ: Not fully developed

State of Development: Laboratory testing only. Fully deployable systems have not yet been developed.

Application at Hanford: Currently not suitable for vadose zone investigations but may be valuable for groundwater monitoring.

A.6 Stripping Voltammetry

Category: Chemical Analysis – liquid

Laboratory/field laboratory: Available
Stand-alone field instrument: Has been developed for lead
In situ/down hole: Not currently available

Target Analyte: Chromate

Operating Principle: The analyte is concentrated on the electrode surface and subsequently stripped off by applying a voltage. The concentration is related to the diffusion current as the analyte is stripped (Hanrahan et al. 2004).

Advantages: Extremely sensitive; low detection limits.

Limitations: Standard methods require a mercury drop electrode and chemical additions to the sample. Methods are under development to use more stable and safer electrodes (e.g., Lin et al. 2005).

Example Applications:

- Chromate in river water and groundwater.

Deployment Platforms:

Laboratory/Field Laboratory: Laboratory instrumentation is readily available.
Field Deployable: Has been demonstrated. Development is ongoing.
Subsurface/In situ: Under development

State of Development: Laboratory instrumentation is a well-established technology. Chromate analysis in a field laboratory was successfully demonstrated during a site investigation at Sandia National Laboratory (Olsen et al. 1994). A hand-held instrument for analysis of lead in water has been developed (Yarnitzky et al. 2000). An in situ microsensor for analysis of chromium and uranium in groundwater has been designed and tested (Wang 2000).

Application at Hanford: Stripping voltammetry is extremely sensitive but probably does not offer significant advantages for vadose zone characterization studies.

A.7 Ion Chromatography

Category: Chemical Analysis – Liquid

Laboratory/field laboratory:	Commercially available
Stand-alone field instrument:	No
In situ/down hole:	No

Target Analyte:	Cation or anionic species in solution

Operating Principle: Species are separated by ion chromatography and detected with a conductivity or other detector.

Advantages: Quantitative, multi-species analysis. EPA and other well established methods are available for chromate and trivalent chromium (e.g., EPA SW-846 method 7199).

Limitations: Not readily deployable in the field. Needs an aqueous sample. Relatively slow.

Example Applications:

- Chromate in water and solid waste digests

Deployment Platforms:

Laboratory/Field Laboratory: Commercially available
Field Deployable: Not developed
Subsurface/In situ: Not developed

State of Development: Laboratory instrumentation and methods are well established (Jackson and Chassaniol 2002).

Application at Hanford: Unlikely to offer significant advantages over other technologies for vadose characterization. Not recommended to pursue further at this time.

A.8 Capillary Ion Electrophoresis

Category: Analytical Chemistry – water

Laboratory/field laboratory:	Commercially available
Stand-alone field instrument:	Not currently available
In situ/down hole:	Not currently available

Target Analyte:	Chromate or other ions

Operating Principle: Ions in solution are separated by flow through a capillary tube under an electrical field. The separation is related to their charge and frictional forces in the capillary. Detection can be performed in a number of ways. UV absorption of an added chromate electrolyte is often used in the analysis of other anions but chromate can also be measured as the analyte.

Advantages: Sensitive and selective. Amenable to miniaturization (Dittrich et al. 2006).

Limitations: Aqueous phase analysis only. Requires carrier solution.

Example Applications:

- Separation and analysis of biological materials
- Chromate in water

Deployment Platforms:

Laboratory/Field Laboratory: Well established
Field Deployable: Potentially
Subsurface/In situ: Potential application for water samples

State of Development: Two recent articles report the use of electrophoresis for chromate analysis (Xu et al. 1997; King et al. 2004). Further work is needed for microchemical analysis systems.

Application at Hanford: Electrophoresis does not appear to offer advantages over other technologies for vadose zone investigations.

A.9 Soil Conductivity Probe

Category: Soil Physio-Chemical Property Measurement

Laboratory/field laboratory: Commercially available
Stand-alone field instrument: Commercially available
In situ/down hole: Commercially available

Target Analyte: Soil moisture/ionic contamination

Operating Principle: Soil conductivity the inverse of the electrical resistivity and is measured through a series of electrodes in contact with the soil and connected to measurement circuitry. Conductivity is sensitive to changes in lithology, soil moisture, and contaminants that are present as ionic species.

Advantages: Soil conductivity measurements are simple, inexpensive, and easy to deploy.

Limitations: Conductivity is an indirect indicator of contamination and moisture that may be related to contamination. It is sensitive to a variety of factors, so care must be taken in interpreting the data.

Example Applications:

- Identification of lithologic and soil moisture changes
- Identification of groundwater contamination
- Location of permeable reactive barriers

Deployment Platforms:

Laboratory/Field Laboratory: Possible
Field Deployable: Commercially available
Subsurface/In situ: Commercially available

State of Development: Soil conductivity measurements deployed in the subsurface using a Geoprobe® were reported by Beck et al. (2000). They were able to locate a zero-valent iron barrier and a chromium groundwater plume through the measurements.

Application at Hanford: Measurement of soil conductivity would likely be most productive if it could be used in conjunction with other characterization technologies. Subsurface measurements require CPT, Geoprobe, or other access method.

Soil conductivity may be a useful method for locating changes in subsurface lithology that can produce capillary breaks leading to higher contaminant concentrations.

A.10 Down-Hole Neutron Moisture Measurement

Category: Geophysical Logging

Laboratory/field laboratory:	Not Applicable
Stand-alone field instrument:	Not Applicable
In situ/down hole:	Commercially Available
Target Analyte:	Soil moisture content

Operating Principle: Several methods are available for in situ measurements of soil moisture. At Hanford, the most commonly used is active neutron logging where a neutron source and detectors are deployed through the well casing or push rod in the subsurface.

A source of fast neutrons, typically americium and beryllium, is placed down hole with one or more He-3 neutron detectors. The fast neutrons are slowed to thermal neutron velocity (thermalized) by the soil. Interaction with hydrogen in the soil moisture is the main factor in thermalizing the neutrons so the thermal neutron flux at the detector is a function of the soil moisture. The system should be calibrated for soil of similar type.

Advantages: These in situ measurements interrogate a reasonably large volume of soil, ~1 m, around the probe (as compared to localized soil sampling). A continuous or stop-and-acquire logging technique can be used, depending on the precision desired. The method is suitable for moisture contents typical of Hanford sediments. May be deployed through a variety of boreholes including CPT.

Limitations: Procedures and permits must be in place for handling neutron source. Subsurface access is required through borehole. Application to defining vadose contamination plumes assumes there is a moisture anomaly associated with the contamination and that there are not other non-contaminated moisture anomalies. Knowledgeable staff needed for data acquisition and interpretation.

Example Applications:

- Near surface soil moisture measurements for crop studies
- In situ moisture logging at tank farms for leak detection
- In situ logging for contaminant studies

Deployment Platforms:

Laboratory/Field Laboratory: Possible
Field Deployable: Not applicable
Subsurface/In situ: Commercially available

State of Development: Neutron moisture logging is a fully mature technology. Instruments and operators are available through Hanford-trained subcontractors and are routinely used on Site (e.g., Horton and Randall 2000). A calibration facility for Hanford sediments exists on Site.

Application at Hanford: The application to delineation of contamination in the deep vadose zone at Hanford depends on a correlation between moisture and contaminant concentration. Contamination associated with elevated soil moisture at distance from sources has been documented (e.g., DePaolo et al. 2004). If higher moisture zones can be identified they are desirable targets for sampling since chromate is generally highly soluble. Thus moisture logging can complement other methods during subsurface investigations.

A.11 Electromagnetic Geophysical Surveys

Category: Vadose/Geophysics/Near-Surface

Laboratory/field laboratory: Field laboratory
Stand-alone field instrument: Stand-alone
In situ/down hole: In situ

Target Analyte: Electrical conductivity/resistivity

Operating Principle: An induced magnetic field is distorted by the conductive body in the subsurface and is detected by the receiver of the instrument to identify a conductive anomaly in a more resistive host body.

Electromagnetic geophysical surveys involve the propagation of continuous-wave or transient electromagnetic fields in and over the earth. There is a close relationship between the transmitter, receiver, and buried conductor in the EM field situation, and a trio of circuits is coupled by electromagnetic induction. In a few EM ground systems the source energy may be introduced into the ground by direct contact, although generally inductive coupling is used; invariably the detection receives its signal by induction (Telford et al. 1990).

Advantages: Interrogates the entire area surrounding a contaminated region. Simple to deploy and covers large areas in short timeframe. Reconnaissance survey can provide qualitative background conductivity data for geophysical methods having a deeper investigative focus (e.g., seismic reflection/refraction, electrical resistivity).

Limitations: Electrical conductivity varies by the amount of clay, water, and salinity in the soil. If the contaminant plume is located at the fringe of either a clay source or near the water table, the technique is unable to produce unique solutions without modeling and inversion. Results at the limits of detection, when they are available, are not always clear and unambiguous. Requires the use of supplemental characterization information from boreholes and other near-surface geophysics of comparable depth of investigation (i.e., magnetometry, ground-penetrating radar).

Example Applications:

- BC Cribs and Trenches, 2004
- Several, by all Hanford contractors over the last 10 years.

Deployment Platforms:

Laboratory/Field Laboratory: Not applicable
Field Deployable: Yes
Subsurface/In situ: Surface technique

State of Development: The method has been in use in the minerals and environmental industry for several decades; commercially available. Has been applied at the Hanford BC Cribs and Trenches (Rucker and Sweeney 2004).

Evaluation for Hanford Vadose Zone Characterization: Consider for application based on previous results.

A.12 High-Resolution Resistivity (HRR)

Category: Vadose/Geophysics/Near-Surface

Laboratory/field laboratory:	Field laboratory
Stand-alone field instrument:	Stand-alone
In situ/down hole:	In situ
Target Analyte:	Ionic contaminants that provide an electrical resistivity or conductivity contrast with the surroundings

Operating Principle: High-resolution resistivity (HRR) is a pole-pole array configuration of electrical resistivity surveying that applies a specific and proprietary plotting methodology (owned by hydroGEOPHYSICS, Inc.) to apparent resistivity data. A pole-pole electrical resistivity array survey involves one current and one potential electrode in the field of measurement and the other two electrode poles at distances up to 10 times from the test area (Barnett et al. 2002).

Electrical energy is applied to the ground with a pair of current electrodes and the potential field generated in the earth by that current is measured by a pair of potential electrodes. Conductive anomalies are mapped in resistive bodies by carefully plotting the apparent resistivity, while more precise representations of the resistivity data are achieved through inversion of the apparent resistivity results.

Advantages: Interrogates the entire area surrounding a contaminated region. Inverted data of properly designed survey can provide plume geometries at depth.

Limitations: Electrical resistivity varies by the amount of clay, water, and salinity in the soil. The technique is best suited for small, discrete plume bodies. Multiple sources or distinct and closely spaced bodies can produce artifacts that confound interpretation without modeling and inversion. Surveys conducted in areas with cultural interferences such as piping and buried tanks can complicate data interpretation, sometimes, but rarely, making it difficult to converge on a unique solution. Requires the use of supplemental characterization information from boreholes and other near-surface geophysics of comparable depth of investigation (i.e., magnetometry, ground-penetrating radar).

Example Applications:

- Mock tank site tests, 2001 (Barnett et al. 2002)
- BC Cribs and Trenches, 2004
- T Tank Farm

Deployment Platforms:

Laboratory/Field Laboratory: Not applicable
Field Deployable: Yes
Subsurface/In situ: Cross borehole HRR has been used in the vicinity of T Tank Farm.

State of Development: The method has been in use in the minerals and environmental industry for several decades; commercially available. The method has been applied in the 200 Areas with some success.

Application at Hanford: Since chromate is an anionic contaminant, an HRR anomaly may be detectable in areas of vadose zone chromate contamination. Testing should be considered for potential areas of vadose zone chromate contamination.

A.13 Surface Nuclear Magnetic Resonance

Category: Vadose/Geophysics/Near-Surface

Laboratory/field laboratory: Not applicable
Stand-alone field instrument: Stand-alone
In situ/down hole: In situ

Target Analyte: Soil moisture

Operating Principle: Surface Nuclear Magnetic Resonance is similar to the approach used in medical applications: excitation of the spin of atomic particles to extract spectral information from a target through the use of magnetic fields. Because the amplitude of the Surface NMR signal is related to the number of hydrogen protons, this technique can be used to measure the subsurface water content of soils and formations (Yaramanci et al. 2002).

Surface coils are placed over the area to be interrogated and the primary coil is energized with a high voltage and current. The induced magnetic field excites the magnetic moment of the hydrogen protons in the subsurface water until the power is removed from the primary coil. The relaxation of the protons creates a voltage that is measured by one or several large coils.

Advantages: Interrogates the entire area surrounding a contaminated region. Provides a measure of water content in the subsurface.

Limitations: Highly dependant on conductivity data. NMR signal also impacted significantly by cultural noise (i.e., automotive electrical or overhead power lines). Requires the use of supplemental characterization information from boreholes and other near-surface geophysics of comparable depth of investigation (i.e., magnetometry, ground-penetrating radar).

Example Applications:

- A small-scale preliminary survey in the 300 Area.

Deployment Platforms:

Laboratory/Field Laboratory: Not applicable
Field Deployable: Tested
Subsurface/In situ: Not applicable

State of Development: The method has received SBIR funding through the product development cycle. The vendor (Vista Clara) has visited the Hanford Site to perform noise surveys at the 100-D Area, the Central Plateau (between 200 West and 200 East behind a borrow pit), and in the 300 Area. The PI of Vista Clara performed a short survey in the 300 Area and produced a preliminary report.

Application at Hanford: The results of the SBIR should be evaluated when available to determine applicability to deep vadose characterization.

A.14 Partitioning Inter-Well Tracer Testing

Category: Vadose/Geochemistry/Process Engineering/

Laboratory/field laboratory:	Field laboratory
Stand-alone field instrument:	N/A
In situ/down hole:	In situ
Target Analyte:	Variable

Operating Principle: The partitioning tracer method is one of several components that comprise the subsurface air flow and extraction (SAFE) technologies. The partitioning inter-well tracer testing (PITT) method uses the principle of chromatographic separation through partitioning-induced flow retardation between partitioning and conservative (non-partitioning) tracers to quantify substances of interest in the swept zone (Cameron et al 2002). The choice of partitioning and conservative tracers is based on field pneumatic conditions, assumed target chemistry, and level of development for specific contaminant families (e.g., volatile or semi-volatile hydrocarbons versus dense ionic solutions). Tracers that partition into soil moisture may also be used to determine soil moisture content.

Advantages: Interrogates the entire area surrounding a contaminated region. Provided that subsurface characterization has been performed, including drilling of near-field boreholes with sediment samples and reconnaissance-grade near-surface geophysics (i.e., GPR with EM), the elution of the partitioning and conservative gases should provide quantitative data about a plume body at depth.

Limitations: Infrastructure intensive investigation. The method was originally considered for deployment as a Leak Detection Mitigation and Monitoring (LDMM) technology for the single-shell tank farm (Barnett et al. 2001). Air handling requirements at the 223E Facility required considerable power to drive the blowers necessary to establish and maintain the swept zone pressure gradient.

Example Applications:

- PITTs were completed in the vadose zone of a NAPL contaminated site at Kirtland Air Force Base in Albuquerque, New Mexico and at Sandia National Laboratory (Deeds et al. 1999; Mariner et al. 1999).
- Soil moisture measurements in a landfill

Deployment Platforms:

Laboratory/Field Laboratory: Not applicable
Field Deployable: Not applicable
Subsurface/In situ: Yes

State of Development: The method has been broadly applied in the oil industry but had only one experimental deployment at Hanford in 2000 at the 223E Facility (200 East Area Mock Tank, Cameron et al. 2002).

A number of recent studies have been performed for measurement of in situ soil moisture (Li and Imhoff 2005; Peng and Brusseau 2005; Han et al. 2006, 2007).

The state of development for the PITT method is well established for DNAPLs (e.g., Deeds et al. 1999; Mariner et al. 1999).

Application at Hanford: This is a viable method for determining soil moisture differences that may be associated with zones of contaminant infiltration and transport.

A.15 References

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Appendix B – Vendor Information

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This appendix contains information on vendors of services, instrumentation, or instrument components relevant to the technologies evaluated for application to characterization of chromate in the vadose zone at Hanford. This is not intended to be a comprehensive list and the vendors or equipment have not been evaluated for suitability to the applications of interest. Inclusion in this list does not constitute an endorsement.

Laser-Induced Breakdown Spectroscopy

Ocean Optics
830 Douglas Avenue
Dunedin, FL 34698
USA
Phone: (727) 733-2447
Fax: (727) 733-3962
http://oceanopticsbv.com/

Laser Analysis Technologies
P.O. Box 789
Bayswater ,VIC 3153
Australia
info@laseranalysis.com
Phone: +61(0)3 9729-6686
Fax: +61(0)3 9729-6656
http://www.laseranalysis.com/

StellarNet, Inc.
P.O. Box 1400
Oldsmar, FL 34677
USA
Phone: 1 (813) 855-8687
Fax: 1 (813) 855-0394
http://www.stellarnet-inc.com/

Raman Spectroscopy Systems

Control Development, Inc.
2633 Foundation Drive
South Bend, IN 46628
Phone: (574) 288-7338
Fax: (574) 288-7339
http://www.controldevelopment.com/

Raman Systems Inc.
3007 Longhorn Boulevard
Suite 105
Austin, TX 78758
USA
Phone: 1 (512) 719-9900
Fax: 1 (512) 719-9901
http://www.ramansystems.com

B&W Tek, Inc.
19 Shea Way, Suite 301
Newark, DE 19713
USA
Phone: (302) 368-7824
Fax: (302) 368-7830
http://www.bwtek.com/

Enwave Optronics, Inc.
18271 McDurmott Street, Suite A-1
Irvine, CA 92614
USA
Phone: (949) 955-0258
Fax: (949) 955-0259
http://www.enwaveopt.com/

Ahura Scientific, Inc.
46 Jonspin Road
Wilmington, MA 01887
Phone: 1 (978) 657-5555
Fax: 1 (978) 657-5921
http://www.ahurascientific.com/

DeltaNu
628 Plaza Lane
Laramie, WY 82070
Toll-free: (866) 301-6328
Phone: (307) 745-9148
Fax: (307) 745-9152
http://www.deltanu.com/

Ocean Optics
830 Douglas Avenue
Dunedin, FL 34698
USA
Phone: (727) 733-2447
Fax: (727) 733-3962
http://oceanopticsbv.com/

StellarNet, Inc.
P.O. Box 1400
Oldsmar, FL 34677
USA
Phone: 1 (813) 855-8687
Fax: 1 (813) 855-0394
http://www.stellarnet-inc.com/

XRF

Thermo Fisher Scientific, Inc.
NITON Analyzers Headquarters
900 Middlesex Turnpike
Building #8
Billerica, MA 01821
USA
Toll-free: (800) 875-1578
Phone: 1 (978) 670-7460
Fax: 1 (978) 670-7430
http://www.niton.com/

Innov-X Systems, Inc.
World Headquarters
100 Sylvan Road, Suite 100
Woburn, MA 01801
USA
Phone: 1 (781) 938-5005
Fax: 1 (781) 938-0128
http://www.innov-x-sys.com/company/overview

Omni Scientific Instruments, Inc
Phone: (228) 388-9211
http://www.omniinstruments.com/

Laser-Induced Fluorescence

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Phone: (978) 689-0003
Fax: (978) 689-3232
http://www.psicorp.com/

Soil Conductivity

Applied Research Associates, Inc.
4300 San Mateo Boulevard NE, Suite A-220
Albuquerque, NM 87110
Phone: (505) 881-8074
Fax: (505) 883-3673
http://www.ara.com

Geoprobe Systems
601 N. Broadway
Salina, KS 67401
Toll-free: 1 (800) 436-7762 or
(785) 825-1842
Fax: (785) 825-2097
http://www.geoprobe.com

Vironex
3 Owls Nest Road
Wilmington, DE 19807
Phone: (302) 661-1400
Fax: (302) 661-1460
http://www.vironex.com

High-Resolution Resistivity

hydroGEOPHYSICS, Inc.
2302 North Forbes Boulevard
Tucson, AZ 85745
Phone: (520) 647-3315
Fax: (520) 647-3428
http://www.hydrogeophysics.com/

Partitioning Interwell Tracer Testing

Neutron Logging

Three Rivers Geophysics
Kennewick, Washington 99338
Tel. (509) 735-3963

Applied Research Associates, Inc.
4300 San Mateo Boulevard NE, Suite A-220
Albuquerque, NM 87110
Phone: (505) 881-8074
Fax: (505) 883-3673
http://www.ara.com

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