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Chemical Analyses in Support of Yucca Mountain Studies

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DOCUMENT CHANGE NOTICE (DCN)

DCN No. 1 **dated** [see latest approval date below]

to Document No. SIP-UNLV-034, **Revision** 1, **Effective Date:** 12/15/04. of 4/10/06

Document Title: Chemical Analyses in Support of Yucca Mountain Studies

Identify applicable affected page, section, paragraph, attachment, exhibit, table, figure, or other:

Replace the following:

5. STANDARDS, PROCUREMENTS AND QUALITY CONTROL

4th Paragraph:

For the Nye County Tracer Test,

With:

For Tracer Tests and Batch Test Studies,

Author: Julie Bertoia QAS 4-7-06

Approved by:

PI: [redacted] Date: 6 APR 06
(Signature)
Print name: Klaus Stetzenbach

QA Manager: [redacted] Date: 4-7-06
(Signature)
Print name: Amy Smiecinski

QA Manager evaluated acceptability that it does not violate quality requirements, and for impacts to other procedures; signature above documents this evaluation as successfully completed.

Attach this DCN as first page of hard copies of document, if any.

University and Community College System of Nevada (UCCSN)

Scientific Investigation Plan (SIP)

Task Title:	**CHEMICAL ANALYSES IN SUPPORT OF YUCCA MOUNTAIN STUDIES**
Task Number:	**ORD-FY04-010**
Document Number:	**SIP-UNLV-034**
Revision:	1
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Project Director

REVISION HISTORY

Revision Number	Effective Date	Description of Revision
0	**04/01/04**	Initial issue under cooperative agreement DE-FC28-04RW12232. This task is a continuation of Task 8 under cooperative agreement DE-FC28-98NV12081 and previous scientific investigation plans SIP-UNLV-001 and SIP-UNLV-005.
1	**12/15/04**	Updated SIP to incorporate Nye County Tracer Testing requirements in sections 1, 3-7, and 9-14.

1. SCOPE AND OBJECTIVES

The objective of this task "Chemical Analyses in Support of Yucca Mountain Studies" is to provide the Department of Energy (DOE) with data and reports from comprehensive chemical analyses of waters sampled from the wells of the Nye County Early Warning Drilling Program (NCEWDP), the Inyo County's Drilling Program, and the Nye county Tracer Test. In addition, this task will be used to provide other laboratory support needs as they arise within the Yucca Mountain Project. This support is provided by the Harry Reid Center for Environmental Studies (HRC) at University of Nevada, Las Vegas (UNLV), which is part of the University and Community College System of Nevada (UCCSN).

Major cations, anions, trace elements, rare earth elements, alkalinity, pH and conductivity will be quantified in groundwater for both Inyo and Nye County's Drilling Programs and submitted to the Technical Data Archive (TDA). These geochemical results will be used to address the degree of communication and the inter-relationships of the different aquifers sampled. As the spatial coverage of the geochemical data extends further downgradient of Yucca Mountain, the evaluations include identifying viable groundwater flow paths and groundwater mixing.

For the Nye County Tracer Test, the HRC will provide chemical analysis for the tracer test being conducted at Site 22S. The specific tracers used for testing will be selected by Nye County. Once the specific suite of tracers has been selected, analytical procedures will be developed to optimize the analyses. Samples will then be analyzed for these tracers throughout the testing period. The concentrated initial tracer solutions (injectate solutions) will also be prepared by HRC under this task. This work is subject to University and Community College System of Nevada (UCCSN) Quality Assurance (QA) Program requirements. This SIP presents an independent confirmatory study supporting previously gathered information.

2. PREVIOUS WORK

During the previous cooperative agreement, the HRC collected approximately 80 samples from wells of the NCEWDP and seven samples from wells and springs in support to Inyo County. These samples were analyzed for a variety of chemical compositions as described in the final report for Task 8 "Support for the Nye County Early Warning Drilling Program". Geochemical evaluation of samples collected from the wells of the NCEWDP over the period of May 1999 through May 2000 is described in the qualified, "Q", report titled "Preliminary Geochemical Evaluation of Groundwaters from Wells of the Nye County Early Warning Drilling Program" (Farnham et. al., 2002). Support to the tracer testing at the Alluvial Tracer Complex (ATC) was also provided under this task. The HRC was responsible for assisting in tracer selection, preparing the high concentration injectate solutions, and analyzing the approximately 3000 samples collected during the test for the tracers. Task 8 resulted in a total of fourteen submittals of "Q" data to the UCCSN Technical Data Archive (TDA) / Technical Data Management System (TDMS). All quality assurance controls were applied in concurrence with the UCCSN QA Program requirements.

3. APPROACH AND SAMPLES

Implementing procedures (IPs), approved by the UCCSN Quality Assurance Program, will be followed for sample collection (other than tracer samples) and analysis. Routine work is described in IPs. All non-routine work without an associated IP will be documented in the scientific notebook as described in "Scientific Investigation Control", QAP-3.0.

Water samples, collected from the wells of the NCEWDP and Inyo County, in accordance with QAP-8.0 "Identification and Control of Items and Samples," are collected by either filtering the sample through a 0.45 um filter capsule using a peristaltic pump into polyethylene containers or by attaching the

filter directly to the end of the pump tubing provided by the client in accordance with IPLV-8.3 "Groundwater Sample Collection and Control." Spring water samples are collected and treated according to IPLV-059 "Collection of Spring Water Samples and Measurement of Conductivity, Alkalinity, and pH." Bar-codes are placed on the sample containers as well as the sample collection forms in accordance with QAP-8.1 "Sample Collection." Sample transfer is controlled according to QAP-8.2 "Sample Transfer." The concentrations of the trace elements, major cations, and major anions, as well as iodide and fluorinated benzoate tracers, will be measured in UNLV laboratories using an Inductively Coupled Plasma Mass Spectrometry System (ICP-MS), an Inductively Coupled Plasma Atomic Emission Spectrometry System (ICP-AES), a Flame Atomic Absorption Spectrometry System (AA), High Performance Liquid Chromatography System (HPLC), and an Ion Chromatography System (IC), respectively. Preconcentration of samples for analysis of rare earth elements, following IPLV-030 "Preconcentration of Rare Earth Elements", may be performed. Measurements that are usually taken in the field include conductivity, pH, and alkalinity. These measurements are made on un-filtered samples according to IPLV-012 "Measurement of Conductivity, Alkalinity, and pH in Water Samples." A field portable conductivity meter will be used to measure conductivity. A digital titrator will be used for alkalinity measurements, and pH will be measured using a field portable pH meter. Alkalinity may be measured either in the field or in the lab.

For the Nye County Tracer Test, Nye County and Sample Management Facility (SMF) personnel will perform all field work including injection of the tracer solutions as well as sample collection. A portion of the final tracer solution used for the injection will be transferred to the Harry Reid Center for Environmental Studies (HRC). Once samples are received at the HRC (under Chain of Custody) , implementing procedures (IPLVs), approved by the UCCSN QA Program, will be followed for all sample control and analysis. The instrumentation used to quantify the tracers will depend on the particular tracer. Fluorinated benzoate tracers will be analyzed using a high performance liquid chromatograph (HPLC) with an ultraviolet (UV) detector. Bromide will be analyzed using an ion chromatograph (IC) with a conductivity detector. Iodide will be analyzed using either an ion chromatograph (IC) with either a UV detector or a conductivity detector or an HPLC with a UV detector. Lithium will be analyzed using an inductively coupled plasma mass spectrometer (ICP-MS). Instrumentation may be changed during the course of the project and will be documented in the scientific notebook. Method development work will be performed to determine optimal conditions for the analysis of tracers selected for testing. The mobile phase solvents used for the HPLC and IC are not quality affecting. This includes the pH adjustment of the buffer solutions. The quality of the mobile phase solvents is determined through the quality control requirements for calibrations described in the IPLVs.

Any special environmental conditions required such as refrigeration of samples for preservation are described in the corresponding IP or scientific notebook. Any processes not addressed in the IP will be documented in the scientific notebook. Special controls to be used in sample collection and analysis are specified in the corresponding Implementing Procedures. The skills of the chemists (investigators and analysts) performing these measurements are outlined in their position descriptions. Special training requirements for this work beyond the experience and education requirements of each employee's position description are specified in those IPs for which an initial demonstration of capability is required. Familiarity with the instrument systems and procedures is required prior to running specialized instrumentation.

4. INTERFACE CONTROLS

Quarterly reports will be submitted summarizing the progress of the study. Concentration data for the field samples will be reported to the Technical Data Archive (TDA) following internal verification and technical review. When samples are submitted to the TDA, the sample results will be reported by site, bar code ID, sample collection date, and depth or zone sampled, where applicable.

External Interfaces

DOE Technical Task Representative: Drew Coleman
Sampling coordinator: Kathy Gilmore (Nye County Waste Repository Project Office**)**

Internal Interfaces

Cooperative Agreement Project Director: Raymond Keeler
PI: Klaus Stetzenbach
Investigators: Jeanette Daniels, Julie Bertoia
Analysts: Caixia Guo, Tatjana Jankovic**,** Kazumasa Lindley, James Cizdziel,
Students: Jennifer Petchsaiprasert, Joseph Lloren, David Edwards, Mose Ohia, Emily Ishkanian

5. STANDARDS, PROCUREMENTS AND QUALITY CONTROL

Determination of precision and accuracy of the analytical measurements is described in each corresponding IP. Precision is addressed through the use of field and laboratory duplicates. Accuracy is addressed using initial calibration checks. For each instrument system, the calibration curve is checked with a standard from an external source. National Institute for Standards and Technology (NIST) traceable standards will be used, when available, as described in each applicable IP. For instance, NIST traceable standards are used as calibration and check standards for the ICP-MS, and the AA.

Lot numbers and manufacturers of all analytical standards are documented or referenced in the scientific notebook. Analytical standards, either calibration or calibration check standards, will be procured from a supplier on the QSL unless otherwise noted in this SIP. Calibrations of pipettors are checked annually; calibrations and calibration checks will be performed by HRC staff in accordance with IPLV-017 “Pipettor Use and Calibration Check” or by an organization on the QSL. Calibration items and services are procured in accordance with QAP-7.0. Balances are calibrated annually by a qualified supplier. The reference mass set used to check working mass sets is calibrated every two years by an organization on the Qualified Supplier List (QSL). No subcontractors will be used on this task.

Representativeness of the measurements made on the groundwater samples is determined by evaluating the accuracy and precision. Representativeness of the samples to the aquifer groundwater can not be determined mathematically and is therefore the largest uncertainty associated with this task. Representativeness is associated with the condition of the borehole and is addressed by collection and analysis of multiple samples collected from the same borehole at different times as well as training of sample collection personnel to IPLV-8.3.

See DCN #1 ~~For the Nye County Tracer Test,~~ standards used to quantify the tracers in the field samples will be prepared directly from the tracer stock used for field testing rather than from NIST-traceable standards or other high-quality standard that is intended to allow absolute concentration measurement. Most of the chemicals used as tracers are not available from NIST or qualified suppliers. This is not important, however, considering the nature of a tracer test. When tracer transport experiments are interpreted, it is not necessary to know the absolute concentration of tracers in the samples collected, but rather it is important to know tracer concentrations relative to the amount that was injected. Using material from the bulk stock to prepare standards will inherently contain any interferences that are present in the samples to be analyzed. Standards prepared from this same stock will therefore more accurately represent the condition of the samples than if a high purity standard is used. Results of the analyses are quality-affecting. An initial calibration check is prepared by someone other than the individual that made the calibration standards to check accuracy of the calibration standards.

6. IMPLEMENTING PROCEDURES / SCIENTIFIC NOTEBOOKS

Separate scientific notebooks will be used to document measurements made by each instrument (ICP-MS, AA, IC, HPLC). Listed below are all implementing procedures for this task. The specific IP associated with the measurements described in each notebook will be identified within that notebook.

I. Analytical & Top-Loading Balance Use, IPLV-003
II. High Performance Liquid Chromatograph Operation, IPLV-004
III. Batch Testing of Organic Tracers, IPLV-005
IV. Groundwater Sample Collection and Control, IPLV-8.3
V. Measurement of Inorganic Anions in Water Samples by the Ion Chromatography System, IPLV-008
VI. Measurement of Trace Elements in Water Samples by Inductively Coupled Mass Spectroscopy (ICP-MS), IPLV-009
VII. Measurement of Major Cations in Water Samples by the Flame Atomic Absorption Spectrometry System, IPLV-011
VIII. Measurement of Conductivity, Alkalinity, and pH in Water Samples, IPLV-012
IX. Pipettor Use and Calibration Check, IPLV-017
X. Preconcentration of Rare Earth Elements, IPLV-030
XI. Collection of Spring Water Samples and Measurement of Conductivity, Alkalinity and pH, IPLV-059

7. EQUIPMENT

The specific equipment, described in 3.0, used for each measurement will be documented in the scientific notebook. Documentation will include the instrument manufacturer, model, and serial number as well as all applicable instrument manuals. The calibration, accuracy, and precision requirements for all equipment are described in the corresponding IP. Relative calibration of all analytical instruments, that is, establishment of an analytical instrument response curve is performed in-house prior to use. The manufacturer and lot number of each chemical used to calibrate, in relative terms, the instrument systems will be recorded in the applicable scientific notebook. Instruments or equipment used are under the constant surveillance of at least one task member or kept in a limited access laboratory to prevent loss or tampering of instrumentation. All other instruments and equipment are calibrated by suppliers as described in Section 5. Calibration checks are conducted in-house in accordance with IPs.

8. HOLD POINTS / DECISION POINTS

There are no prerequisites or hold points associated with this task. Decision points associated with the analytical measurements are addressed by use of quality controls to indicate when there is an analytical or other problem which needs action described in the IPs.

9. SOFTWARE, MODELS and ELECTRONIC PROTECTION

Software to be used is exempt from the qualification process in QAP-3.2 . The software packages used in this study include 1) The analytical instrumentation software used for data acquisition, and 2) Spreadsheet software such as Quattro Pro or Excel for data reduction. Use of the analytical instrumentation data acquisition and spreadsheet software will be documented or referenced, along with the specific version used, in the instrument scientific notebook. Electronic data is controlled according to QAP-3.1 and the control of data is addressed in each IPLV that involves electronic data management, primarily instrument system IPLVs. No models are used on this work. Raw and reduced data as described will be controlled in accordance with QAP-3.1. by being stored on password protected computers in locked rooms. The data will be backed up to the HRC server on a regular basis. The final verified

spreadsheet of reduced data for submittal to the TDA will also be controlled in accordance with QAP-3.1. Records that are in-process are protected by being backed up onto the computer server if electronic, or if the data is in hard copy form, it is stored in a fire-rated safe until submission to the TDA.

10. DATA REDUCTION AND REPORTING

Reduced data for the analyte concentrations of the field samples will be reported to the Technical Data Archive (TDA) following internal verification and technical review in accordance with QAP-3.6. All sample results will be reported by site, bar code ID, sample collection date, and depth or zone sampled, where applicable. Reduction of data involves calculating the concentration of the analytes in each sample based on the slope and intercept of an instrument response curve. Data reduction also includes calculating averages when multiple measurements are made on the same sample.

For the Nye County Tracer Test, data packages consisting of the hard copies of raw data generated from each instrument will be referenced by the analysis date and will be attachments to the scientific notebook. Data recording requirements for each scientific notebook are described in the corresponding IPLV. A summary of the data generated from each instrument (described in section 2.0) is exported to a spreadsheet (Microsoft Excel) where final data reduction is performed. Reduction of data involves calculating the concentration of the tracers in each sample based on the slope and intercept of an instrument response curve and also calculating averages when multiple injections are made from the same autosampler vial. A hard copy of the spreadsheet containing the reduced data will be included in the data package. The concentration of the tracer is generally calculated using the analytical instrumentation software but may be calculated using a spreadsheet software package (Microsoft Excel). The calculation of averages is performed using the spreadsheet software. Following data reduction, the spreadsheet file will be labeled as preliminary and sent to the external PIs. The reported results will include sample name, tracer concentration, bar code ID, and analysis dates. Data will be submitted to the TDA following technical and QA verification.

11. VERIFICATION AND REVIEWS

Internal verification of all data will be performed by someone other than the originator to check compliance to the procedures and to verify the accuracy of data reduction, transfer and manual entry. Internal technical review will be performed and documented on the data, scientific notebooks, and all reports generated in this task. Any report of data generated without full internal verification will be labeled as “preliminary” data.

12. SCHEDULE OF WORK

1. Submit SIP for QA review due 03/15/04
2). Approval of SIP due 04/15/04
3). Purchase of HPLC due 04/30/04
5). End Data Collection/testing/measurements due 05/30/08
6). Complete Data Reduction/Analyses due 06/30/08
7). Submit Scientific Notebook for Technical Review due 07/10/08
8). Submit Scientific Notebook for QA Review due 07/10/08
9). Final TDA submittal for data supporting final report due 07/30/08
10). Complete Final Calibrations/Calibration Checks due 07/09/08
11). Submit Final Report for Technical Review due 08/29/08
12). Submit Final Report for QA Review due 08/29/08

13). Submit Final Report to DOE due 09/30/08
14). Final Records Submittal to DCC due 09/30/08
15). Funding Ends 09/30/08

13. RECORDS AND SUBMITTALS

QA Records

QA records are handled in accordance with QAP-17.0 "Quality Assurance Records" and in-process records are stored in a fire-rated safe until transmittal. Records designated as QA records in the UCCSN QAPs and IPLVs listed include, but are not limited to:

1. Hard copies and/or electronic media containing raw data including calibrations and Quality Control (QC) results for each instrument system.
2. Calibration and checks for each balance and pipettor used to collect or produce quality affecting data for this study.
3. Scientific Notebooks including attachments if applicable.
4. Data Review Check Sheets.
5. Chain of Custody Forms.
6. Field Forms and Data Checklists
7. Copies of deliverables.

Submittals

Submittals are given to the HRC Administrative Task PI for submittal to DOE in accordance with the cooperative agreement.

1. Quarterly progress reports and technical reports containing Q data consisting of hard copies containing reduced concentration data.

14. OTHER REQUIREMENTS

Potential sources of error and uncertainty are addressed in the associated IPLV. This task does not perform field surveys. In a study of this nature, the majority of error is generally attributed to field sample collection and handling rather than to laboratory analysis. Scheduling for sample collection is coordinated by the Nye County Waste Repository Project Office.

15. REFERENCES

1. IPLV-003, "Analytical & Top-Loading Balance Use"
2. IPLV-004, "High Performance Liquid Chromatograph Operation"
3. IPLV-005, "Batch Testing of Organic Tracers"
4. IPLV-8.3, "Groundwater Sample Collection and Control"
5. IPLV-008, "Measurement of Inorganic Anions in Water Samples by the Ion Chromatography System"
6. IPLV-009, "Measurement of Trace Elements in Water Samples by Inductively Coupled Mass Spectroscopy (ICP-MS)"

7. IPLV-011, “Measurement of Major Cations in Water Samples by the Flame Atomic Absorption Spectrometry System”
8. IPLV-012, “Measurement of Conductivity, Alkalinity, and pH”
9. IPLV-017, “Pipettor Use and Calibration Check”
10. IPLV-030, “Preconcentration of Rare Earth Elements”
11. IPLV-059, “Collection of Spring Water Samples and Measurements of Conductivity, Alkalinity and pH”
12. QAP-3.0, “Scientific Investigation Control”
13. QAP-3.1, “Control of Electronic Data”
14. QAP-3.2, “Software Management”
15. QAP-3.6, “Submittal of Data”
16. QAP-7.0, “Control of Quality-Affecting Procurement and Receipt”
17. QAP-8.0, “Identification and Control of Items and Samples”
18. QAP-8.1, “Sample Collection”
19. QAP-8.2, “Sample Transfer”
20. QAP-17.0, “Quality Assurance Records”