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Redox scale for assigning an oxidizing/reducing potential to groundwater: Method development and initial results

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REDOX SCALE FOR ASSIGNING AN OXIDIZING/REDUCING POTENTIAL TO GROUNDWATER: METHOD DEVELOPMENT AND INITIAL RESULTS

- TASK 33 -

FINAL REPORT

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TABLE OF CONTENTS

1	Overview	3
2	List of Tables	4
3	List of Figures	4
4	Introduction	5
5	Method Development	7
6	Sample Collection	18
7	Sample Custody	19
8	Control of Electronic Data	19
9	Results and Discussion	20
10	Conclusion	25
11	References	26
	Appendix I	27
	Appendix II	30
	Appendix III	32
	Appendix IV	34
	Appendix V	36
	Appendix VI	38
	Appendix VII	40

OVERVIEW

This report outlines the progress on Task 33 of the Department of Energy's Yucca Mountain Cooperative Agreement with the University and Community College System of Nevada (UCCSN). The task is titled "The Experimental Determination of a "Redox Scale" for Assigning an Oxidizing/Reducing Potential to Groundwater from Wells in the Nye County Early Warning Drilling Program: A Scale for Predicting the Solubility and Mobility of Elements Commonly Found in Nuclear Wastes". The purpose of the research was to determine the concentrations of the various electrochemical oxidation states or redox species of eleven elements in groundwater samples collected from the Nye County wells. The method of separation and quantification of the oxidation states depended on an ion chromatograph coupled to a highly sensitive inductively coupled plasma mass spectrometer. At the end of the task, methods had been developed for 10 of the 11 elements: antimony, arsenic, chromium, copper, manganese, molybdenum, selenium, tungsten, uranium and vanadium. A satisfactory method for determining the redox species for iron was not obtained. This report details the method development and presents Q'd data for arsenic and chromium. The oxidation/reduction potential of the groundwater samples in volts, or the E_h, was calculated from the arsenic redox species determinations and thermodynamic relationships. No correlation was observed between the calculated E_h and the percent of arsenic in its most oxidized state, the plus five state. Informational results are also presented which identify the redox species present for the other eight elements in the groundwater samples from Nye County. The major hurdle of the project, method development, was overcome. Future advances, such as the inclusion of the redox species of iron, cobalt, thallium and rhenium could be realized with a minimum investment of time. Likewise, examination of groundwater sample preservation techniques, which "lock in" the redox species present in the groundwater at the time of sampling, for the elements other than arsenic and chromium, for which very satisfactory techniques already exist, would also proceed rapidly. Although a "practical" redox scale was not developed, with the progress made on Task 33, there is little that stands in the path for achieving that goal.

LIST OF TABLES

Table 1	Ion Chromatography Conditions for the Separation of Element Species	8
Table 2	ICPMS Conditions for the Detection of Element Species	8
Table 3	Ion Chromatography Gradient Program for the Separation of Vanadium Species	15
Table 4	Concentrations in ppb for Redox Species of Arsenic and Chromium	20
Table 5	E_h in Volts Calculated from the Redox Species of Arsenic	23

LIST OF FIGURES

Figure 1	IC-ICPMS Instrument Set-up	7
Figure 2	Dynamic Reaction Cell Technology	8
Figure 3	Separation of As(III) and As(V) Species using IC-ICPMS	9-10
Figure 4	Separation of Mo(VI) and W(VI) Species by IC-ICPMS	11
Figure 5	Separation of Cr(III) and Cr(VI) using IC-ICPMS	12-13
Figure 6	Separation of Antimony, Copper, Manganese, and Uranium Species using IC-ICPMS	14
Figure 7	Separation of Se(IV) and Se(VI) Species using IC-ICPMS, 3 ppb Standard	15
Figure 8	IC-ICPMS Separation of Vanadium Species using IC-ICPMS	16
Figure 9	Concentrations of As (III) and As(V) in Southern Nevada Groundwater	21
Figure 10	Concentrations of Cr (III) and Cr (VI) in Southern Nevada Groundwater	21
Figure 11	Percent Oxidized Arsenic (As (V)) versus the Eh Calculated from the Arsenic Redox Species	24

INTRODUCTION

The Nye County Early Warning Drilling Program (NCEWDP) was initiated as part of the Nye County Nuclear Waste Repository Project Office (NWRPO) Yucca Mountain Oversite Program. The purpose of this program is to establish a groundwater monitoring system to protect the residents of Nye County in Amargosa and Pahrump Valleys against potential radionuclide contamination. The project involves drilling of several wells south of Yucca Mountain, which is proposed to be the repository for the nation's high and low level nuclear waste. Groundwater wells in the NCEWDP are located in Amargosa Valley, NV and on the Nevada Test Site (NTS), both approximately 90 miles northwest of Las Vegas, NV.

The Harry Reid Center for Environmental Studies (HRC) at the University of Nevada, Las Vegas (UNLV) has been actively involved in the analysis of groundwater from wells that are part of the NCEWDP for trace elements, major cations, major anions, and oxidation states of several elements. The information obtained from these analyses provides hydrochemical information, which can be used to help understand the groundwater system in the region surrounding Yucca Mountain.

Over the last quarter of a century there has been much discussion about the utility of the measured oxidizing/reducing potential, or E_h, in natural waters as a valid indicator of the actual redox condition, and its use to predict the distribution of a soluble element between its various oxidation state species or redox couples (Stumm and Morgan, 1970; Cherry, 1979; Lindberg and Runnells, 1984). The Eh is a value based on thermodynamic quantities such as the free energy (ΔG) and chemical equilibrium constants (K). The limitations of E_h-pH relationships are:

1) Eh is actually difficult to measure. Typically a platinum electrode is used, however, most redox couples do not react on a platinum surface at near-neutral pH values. Groundwater samples from wells in the NCEWDP have measured pH values from about 7.2 to 8.2.
2) Natural systems are rarely in equilibrium, a necessary assumption in a thermodynamically controlled system. It is estimated that the equilibration time for many environmentally important reactions is on the order of years to centuries.

The objective of Task 33 was to gather information with which to construct an experimental redox scale for the groundwaters collected from the NCEWDP. This attempt was based on measuring the concentrations of the common oxidation state species, or redox couples, for 11 elements. The elements are: antimony (Sb), arsenic (As), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), selenium (Se), tungsten (W), uranium (U), and vanadium (V). It was postulated that the redox species information from all 11 elements could be used to create a "practical" redox potential, which did not rely on thermodynamic assumptions, for each groundwater sample (location, site and depth). Subsequently, this "practical" redox potential could be utilized to predict whether an element, not measured, such as plutonium, neptunium or technetium, would be likely to exist in reduced or oxidized forms. Such information would facilitate predicting the mobility of an element (its solubility or affinity for solid surfaces). It was also postulated that this approach would be successful since this "practical" scale would be based on measurements of the redox species of 11 elements at very low concentrations from about 10^{-7}M to 10^{-11}M, concentrations not likely to react at the surface of a platinum electrode (at circumneutral pH's) used to obtain the E_h measurement.

The instruments that were employed to measure the concentrations of the redox species for all of the proposed elements, except iron, were an ion chromatograph coupled to an inductively coupled plasma mass spectrometer (IC-ICPMS). The combined unit is called an IC-ICPMS. With this combination of a separation device (the IC), whose effluent goes into a sensitive detector (the ICPMS), two tenths of a milliliter (0.2 mL) of groundwater could be injected directly into the IC and the results for one or more elements recorded simultaneously by the ICPMS. The method development results are presented in the next section.

METHOD DEVELOPMENT RESULTS

Groundwater samples were analyzed using IC-ICPMS (Figure 1). All samples, standards and groundwater, were directly injected into the IC and were carried through the analytical column by a liquid eluent. An anion or cation exchange column separates the various redox species based on their affinity for the column resin. Species that do not interact with the column resin elute first, whereas those that strongly interact with the column resin elute later. The liquid effluent from the column travels to the ultrasonic nebulizer (USN) where a stream of argon gas converts it into a fine aerosol. Ultrasonic sample nebulization enhances sample ionization by introducing a dry aerosol into the torch, and thus increases signal, relative to traditional cross-flow nebulization. Still, approximately 70% to 80% of the sample goes into the waste container. The remainder 20-30 % is injected into the ICP torch region where it is desolvated, atomized, and ionized. The ion beam then enters the Dynamic Reaction Cell (DRC) where certain molecular ion interferences, such as ArC^+ and $ArAr^+$, are eliminated (Figure 2). By introducing a reactive gas, such as ammonia, argon polyatomic ions are able to be removed from the ion beam, via a charge transfer reaction, while the analyte of interest is able to pass through the DRC unaffected. The remaining ion beam enters the mass spectrometer region where the analyzing quadrupoles focus and filter the ion beam so that only pre-selected ions with a certain mass-to-charge ratio (m/z) are able to pass through and reach the detector. The detector records the number of ions counted per second and records this as an intensity. A computer displays the output as a chromatogram showing intensity versus time.

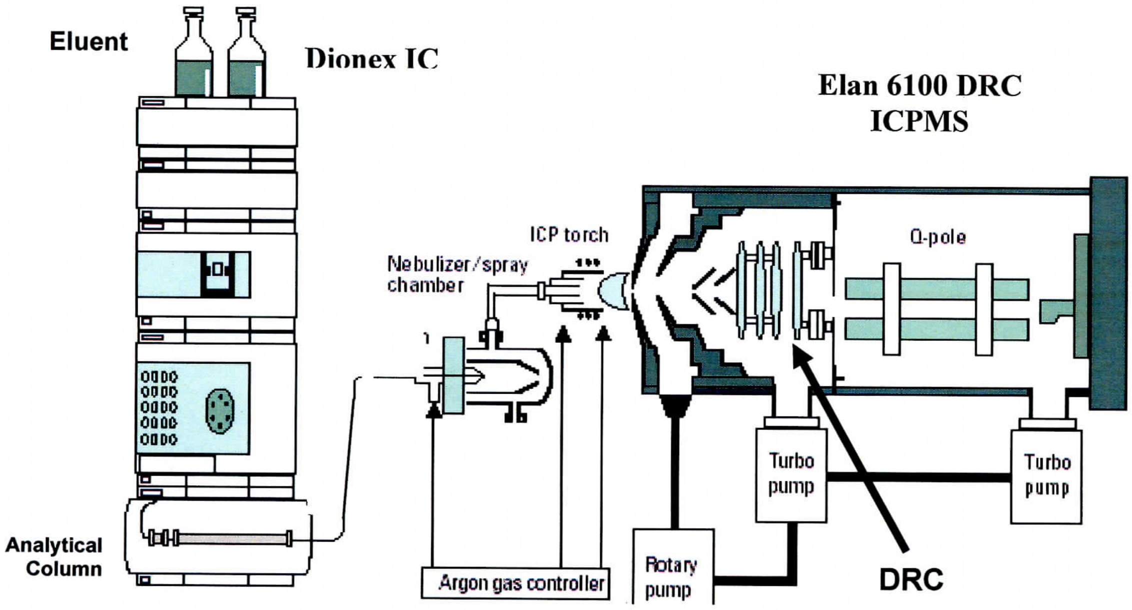
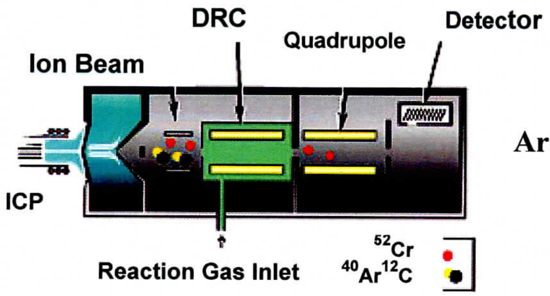


Figure 1: IC-ICPMS Instrument Set-up



$$ArC^+ + NH_3 \rightarrow ArC + NH_3^+$$

Figure 2: Dynamic Reaction Cell Technology

Four methods were developed for the separation and detection of the redox species of ten elements. Ion chromatography conditions for each method are listed in Table 1. Inductively coupled plasma mass spectrometry conditions are listed in Table 2.

Table 1: Ion Chromatography Conditions for the Separation of Element Species

Element	**Eluent**	**Column**	**Flow Rate (mL/min)**	**Suppressor**	**Regeneration Solution**
As, Mo, W	1.8 mM Na_2CO_3 1.7mM $NaHCO_3$	Analytical:AS9-SC Guard: AG9-SC	2.00	As- ASRS 4mm 50 mA	As- 0.0125 M H_2SO_4
Cr	1% HNO_3	Analytical:AS-14 Guard:AG-16	2.00	N/A	N/A
Sb, Cu, Mn, Se, U	5% HCl	Analytical:CS5A Guard: CG5A	1.20	N/A	N/A
V	See Table 3	Analytical: CS5A Guard: CG5A	1.20	N/A	N/A

Note: Sample injection volume was 200 µL for all methods

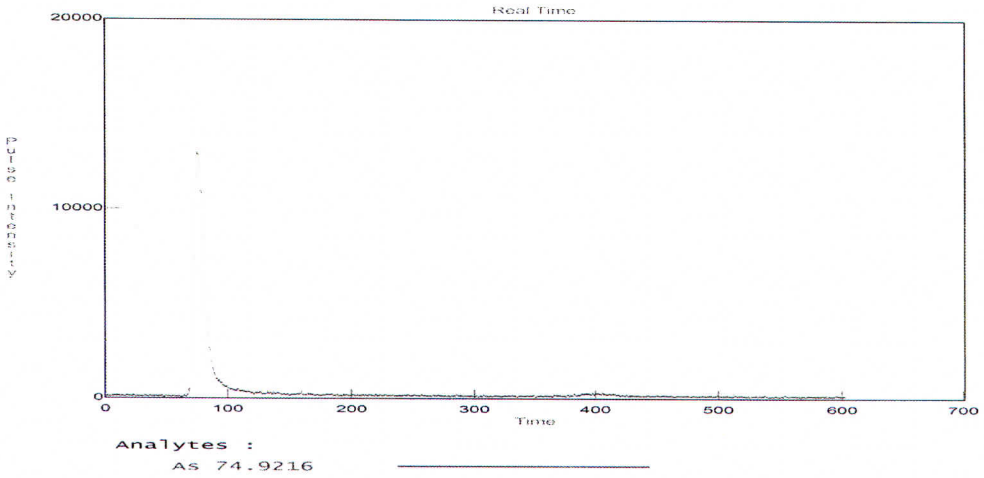
Table 2: ICPMS Conditions for the Detection of Element Species

	As	Mo	W	Mn	Cu	Sb	Se	U	V	Cr
Nebulizer	← ULTRASONIC →									
DRC Flow	Not used	Not used	Not used	0.5 mL/ min	0.5 mL/ min	0.5 mL/ min	0.5 mL/ min	0.5 mL/ min	0.5 mL/ min	0.5 mL/ min
Monitored Mass(es)	m/z = 75	m/z = 98	m/z = 184	m/z = 55	m/z = 63	m/z = 121	m/z = 82	m/z = 238	m/z = 51	m/z = 52, 53

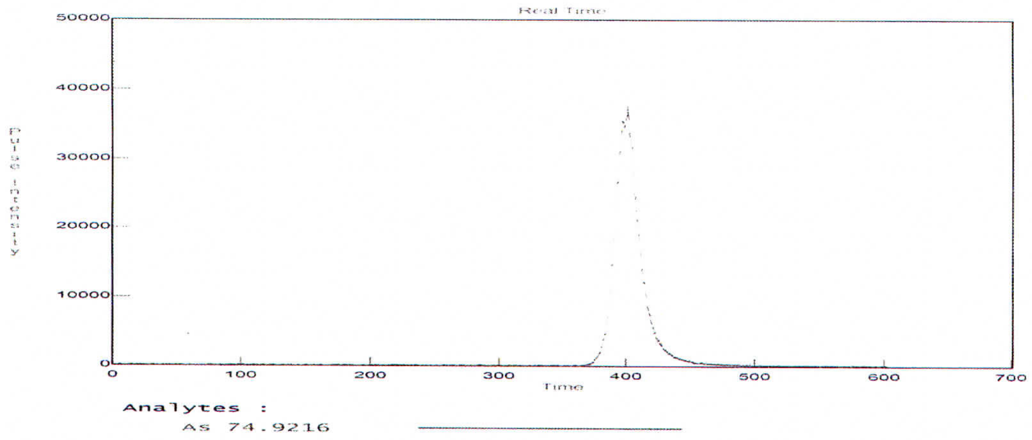
Arsenic, Molybdenum, and Tungsten

Arsenic

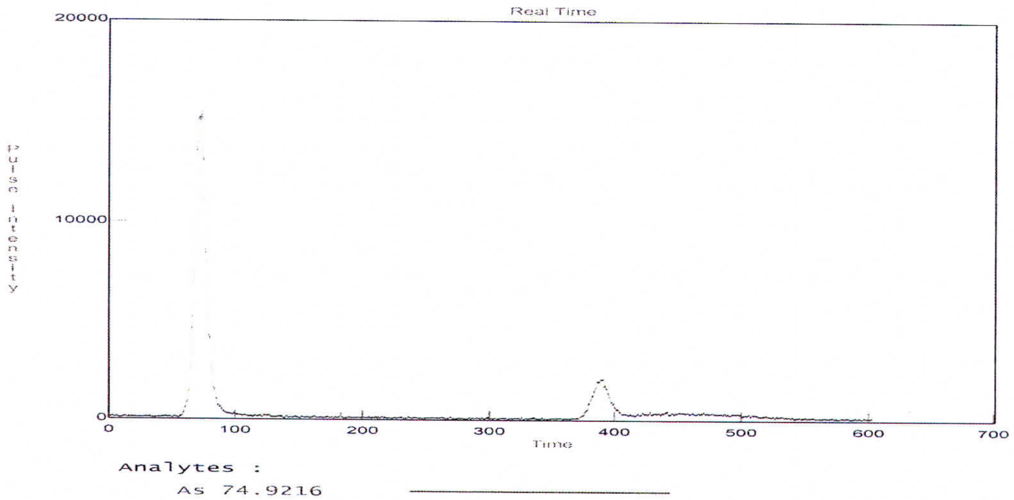
The anion exchange column Dionex AS9-SC and guard column AG9-SC were used to separate arsenite (As(III)) and arsenate (As(V)) using a 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ isocratic eluent at a flow rate of 2.00 mL/min. **Note: Roman numerals are used to denote the number of positive charges carried by the element of interest. As(III) tells us that arsenic carries three positive charges. The higher the Roman numeral, the more oxidized. The designation does not necessarily indicate the chemical form.** The effluent from the column was passed through the Dionex ASRS 4mm suppressor in order to prevent excessive salt precipitation on the ICPMS cones. It then entered the ICPMS where the arsenic species were detected at m/z 75. Under these conditions it was found that As(III) had a retention time of 90 seconds and As(V) had a retention time of 400 seconds (Figure 3).



3a: As(III) 10ppb Standard



3b: As(V) 10 ppb Standard



3c: Groundwater Sample 7SC Zone 1 Filtered Unacidified

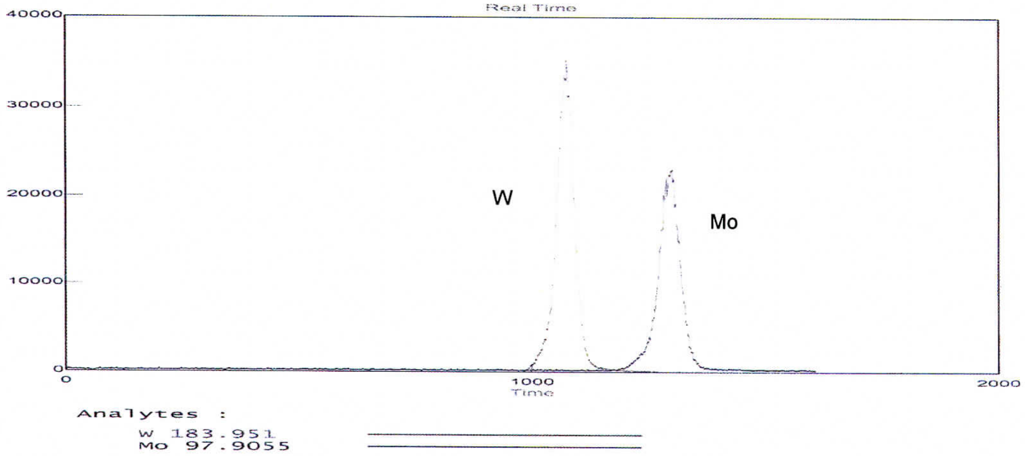
Figure 3: Separation of As(III) and As(V) Species using IC-ICPMS
(For informational purposes only)

Molybdenum

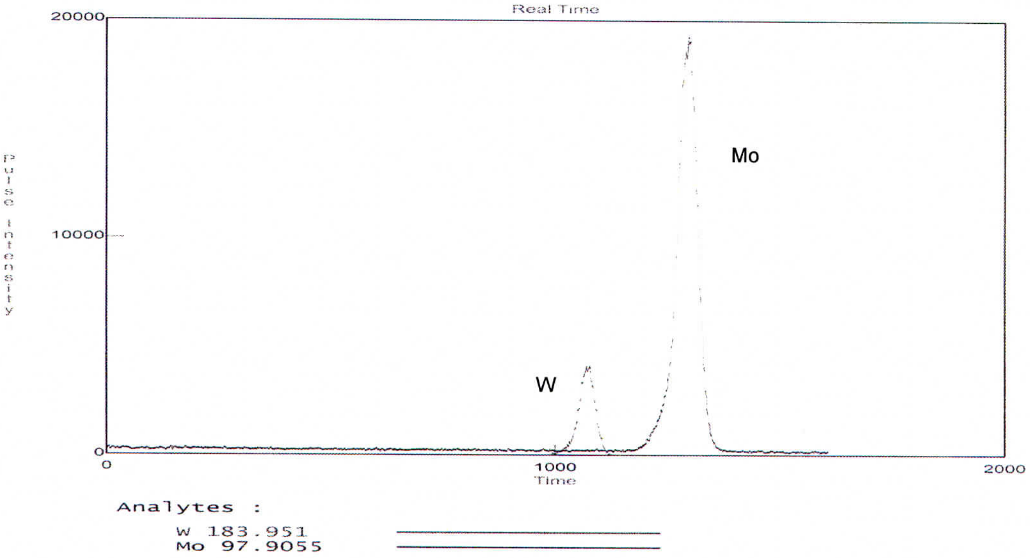
The anion exchange column Dionex AS9-SC, guard column Dionex AG9-SC and the 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ isocratic eluent at a flow rate of 2.00 mL/min were also used to separate the molybdenum species. However, no suppressor was used due to the possibility that molybdenum cationic species may be lost or exchanged within the suppressor. As a result, the effluent from the column was directly injected into the USN and the ICPMS detected molybdenum ions at m/z 98. Molybdate (Mo(VI)) was the only molybdenum species that was detected in the groundwater. Under these conditions, it was found to have a retention time of 1300 seconds (Figure 4).

Tungsten

Tungsten species were separated using the same anion exchange column Dionex AS9-SC and guard column Dionex AG9-SC and the 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ isocratic eluent at a flow rate of 2.00 mL/min. As with the molybdenum separation, no suppressor was used in the analysis of tungsten. The effluent from the analytical column directly entered the USN and into the ICPMS where tungsten was detected at m/z 184. Only tungstate (W(VI)) was detected in the groundwater well samples and had a retention time of 1100 seconds (Figure 4).



4a: Mo and W 5ppb Standard, W(VI) elutes at 1100s and Mo(VI) elutes at 1300s

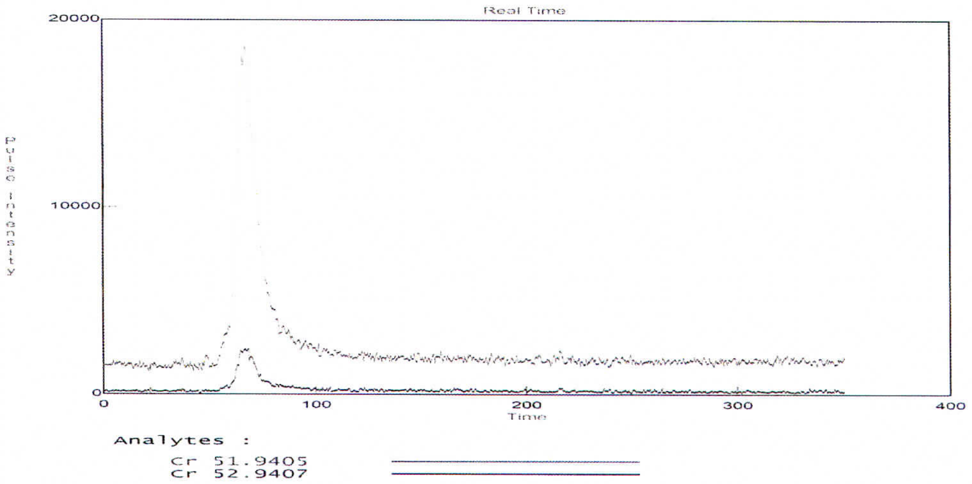


4b: Groundwater Sample 22S Zone 4 Unacidified Unfiltered

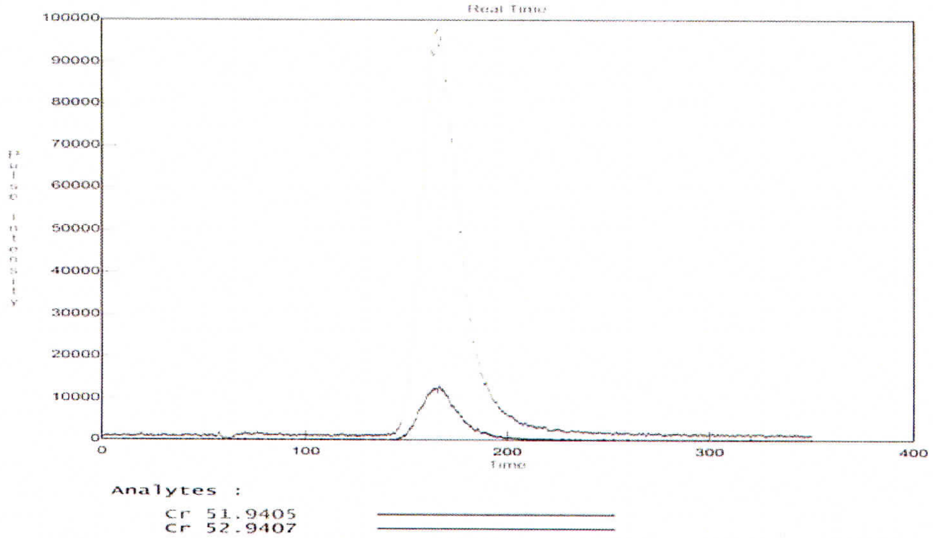
Figure 4: Separation of Mo(VI) and W(VI) Species by IC-ICPMS
For informational purposes only

Chromium

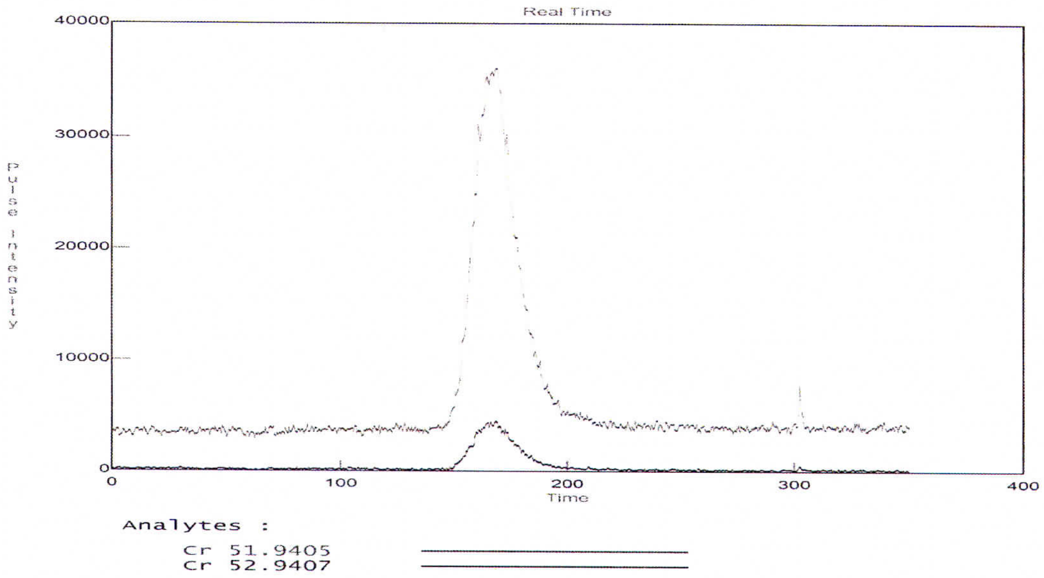
The two most common oxidation states of chromium are Cr(III) and Cr(VI). By using the anion exchange column Dionex AS-14 and the guard column Dionex AG-16 with a 1% HNO_3 isocratic eluent at 2.00 mL/min, these two chromium species were separated with a relatively short run time. By setting the DRC flow rate of NH_3 at 0.5 mL/min to eliminate ArC^+ interferences at m/z 52 and 53, chromium species were able to be measured with low background counts and hence low detection limit. Cr(III) was found to have a retention time of 75 seconds and Cr(VI) was found to have a retention time of 175 seconds (Figure 5).



5a: Cr(III) 4ppb Standard



5b: Cr(VI) 4 ppb Standard



5c: Groundwater sample 22PB Deep Filtered Unacidified

Figure 5: Separation of Cr(III) and Cr(VI) using IC-ICPMS
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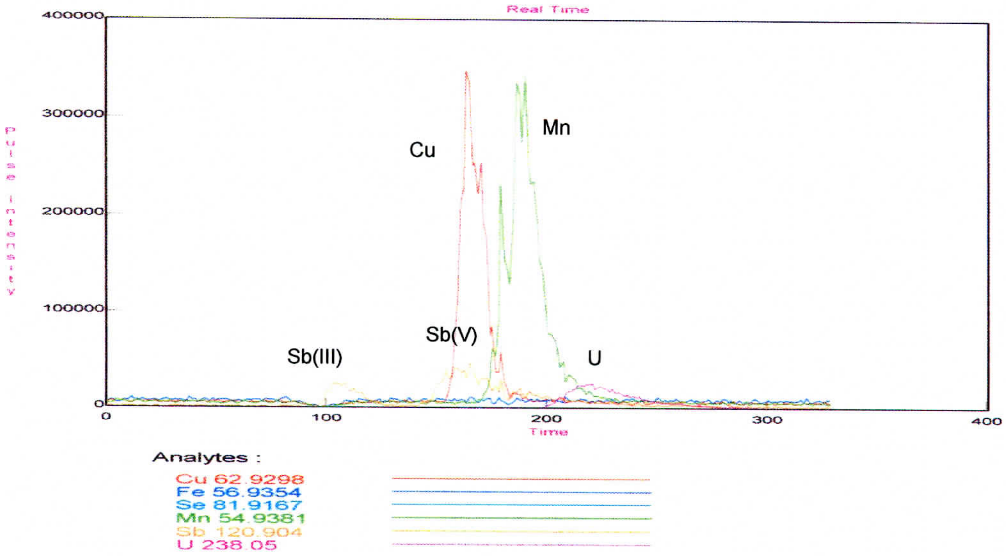
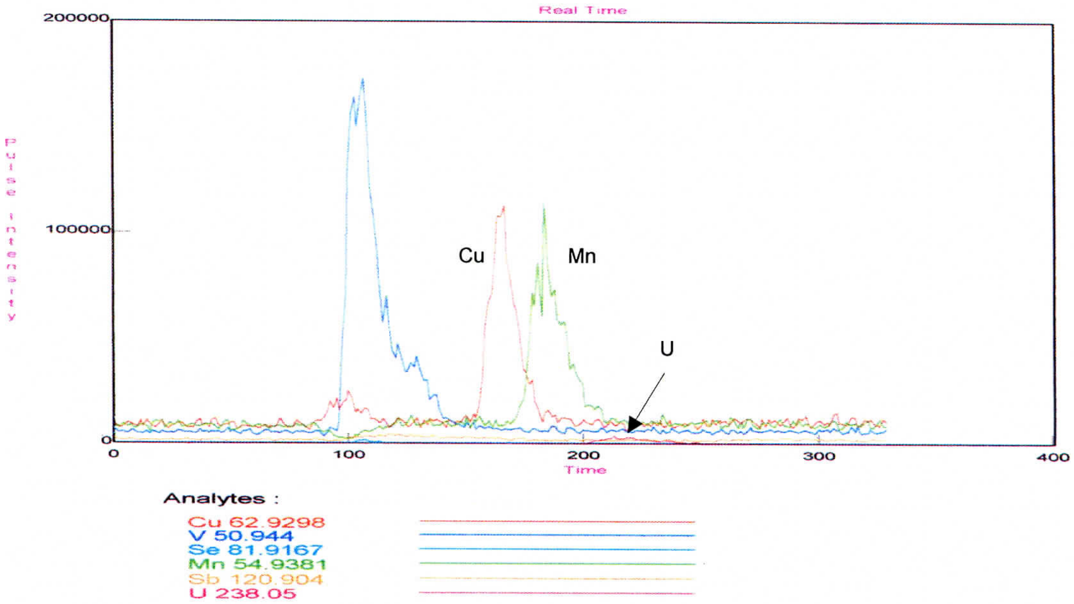
<u>Antimony, Copper, Manganese, Selenium, and Uranium</u>

Cation exchange chromatography was used to separate the species of antimony, copper, manganese, selenium and uranium. Separation was achieved by using the Dionex CS5A analytical column and the Dionex CG5A guard column with the 5% HCl eluent run isocratically at a flow rate of 1.20 mL/min and the DRC NH_3 flow set at 0.5 mL/min. Retention times were as follows: Sb(III), 125 seconds; Sb(V), 175 seconds; Cu(II), 175 seconds; Mn(II), 200 seconds; U(VI) 225 seconds (Figure 6); Se(VI), 110 seconds; and Se(IV) 160 seconds (Figure 7). Upon further analysis of the groundwater samples, it was found that another copper, possibly Cu(I), eluted under these conditions and had a retention time of 100 seconds.



6a: Antimony, Copper, Manganese, and Uranium, 5 ppb Standard



6b: Groundwater sample 22PB Shallow Filtered Unacidified

Figure 6: Separation of Antimony, Copper Manganese, and Uranium Species using IC-ICPMS
For informational purposes only

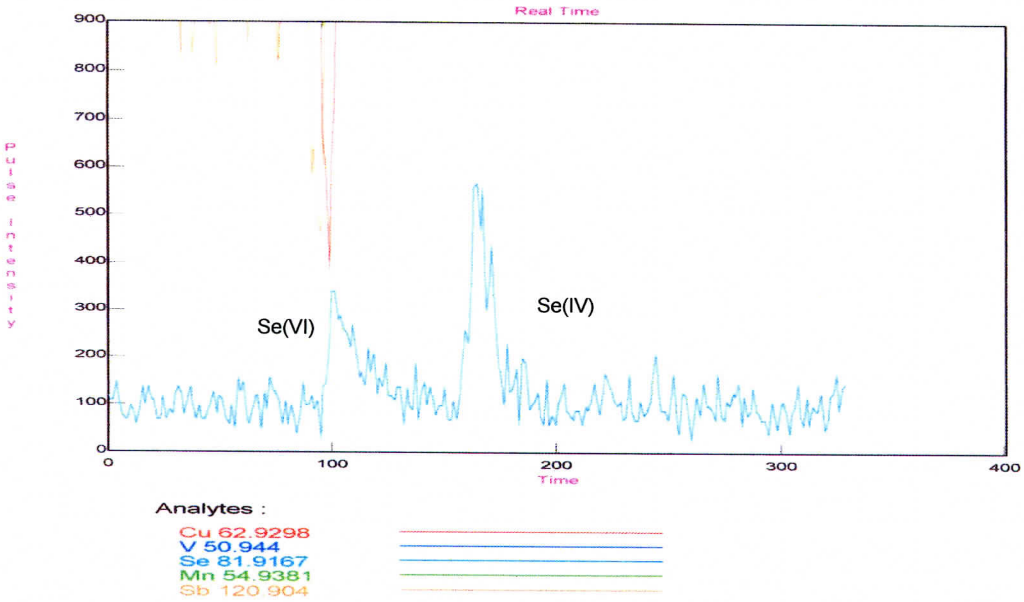


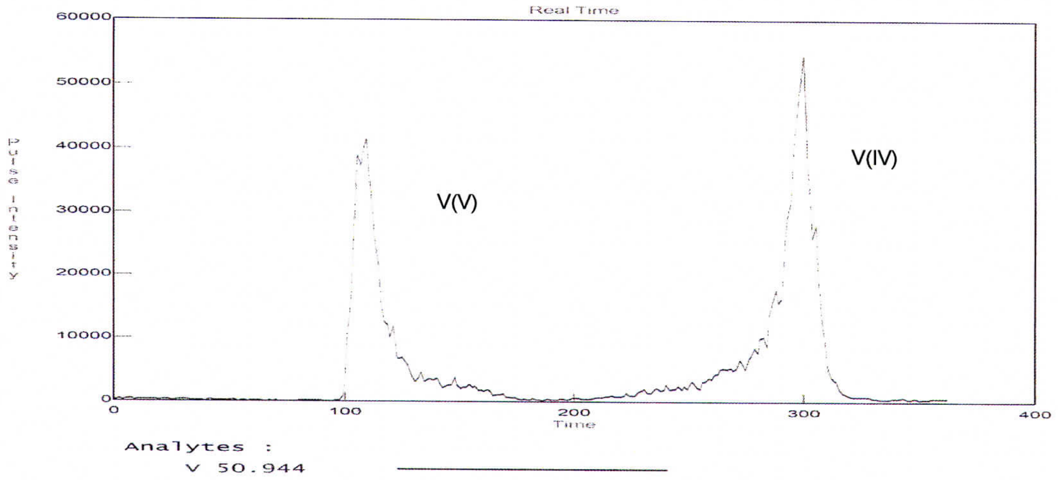
Figure 7: Separation of Se(IV) and Se(VI) Species using IC-ICPMS, 3 ppb Standard
For informational purposes only

Vanadium

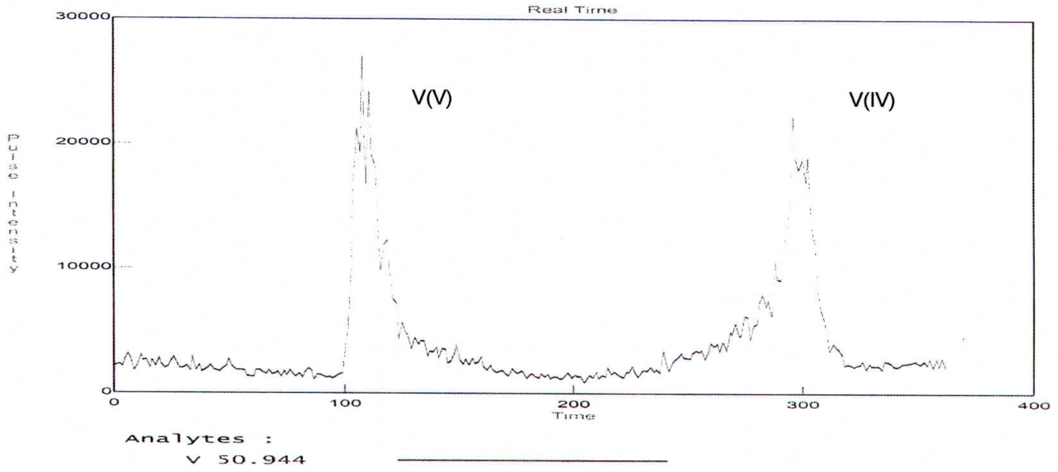
By using the Dionex CS5A cation exchange analytical column, the Dionex CG5A guard column, and a DRC flow rate of NH_3, the two species of vanadium, V(V) and V(IV), were able to be separated. The gradient program listed in Table 3 with a flow rate of 1.20 mL/min, was used to separate the two vanadium species in a relatively short run time. It was found that V(V) had a retention time of 110 seconds and V(IV) had a retention time of 300 seconds (Figure 8).

Table 3: Ion Chromatography Gradient Program for the Separation of Vanadium Species

Time (min)	%DI	%HCl (5%)
0.00	60	40
0.15	100	0
3.00	0	100
5.00	0	100
5.01	60	40
10.00	60	40



8a: Vanadium Standard 10ppb



8b: Groundwater sample 22S Zone 1 Filtered Unacidified

Figure 8: IC-ICPMS Separation of Vanadium Species using IC-ICPMS
For informational purposes only

Each method was calibrated with a minimum of three calibration standards, which were chosen so as to bracket the sample concentrations. Calibration standards were individually available for As(III), As(V), Cr(III), and Cr(VI) and thus, those species were calibrated separately. For copper, manganese, molybdenum, tungsten an uranium species Cu(II), Mn(II), Mo(VI), W(VI), and U(VI) were confirmed from a standard containing a mixture of antimony, arsenic, chromium, copper, manganese, molybdenum, selenium tungsten, uranium, and vanadium and calibrated using this standard only. A continuing calibration check (CCC) was performed at the end of each analysis to ensure that the instrument signal had not drifted throughout the analysis and the calibration curve remained valid.

For antimony, selenium and vanadium, two peaks were observed with the multi-element standard mentioned above, however individual element standards were unavailable for calibration of the two species, thus, different oxidation states were determined using dissolved solid standards. A correction factor was used to determine the concentrations of the different species of antimony, selenium and vanadium to account for the elution of the two species with one standard. For selenium, the total peak area was calculated from the sum of the areas of the two eluted peaks of Se(IV) and Se(VI). A ratio of the single peak area of Se(IV) and Se(VI) peaks with respect to the total area was determined for each standard in the calibration curve. The ratios for the three calibration standards were averaged for Se(IV) and Se(VI) and this average ratio was multiplied by raw Se(IV) and Se(VI) concentrations to give the reported concentrations.

All acquired data and reduced data were technically and QA reviewed to verify the accuracy of the results.

SAMPLE COLLECTION

Groundwater samples were collected from August-October 2002 and February-May 2003 on a schedule proposed by the Nye County Nuclear Waste Repository Project Office (NWRPO) for wells of the Nye County Early Warning Drilling Program (NCEWDP). In 2002, a total of seventeen wells were sampled for filtered and unfiltered unacidified samples, fourteen wells for filtered dry ice preserved, and sixteen for unfiltered dry ice preserved. In 2003, filtered samples were collected from five wells and unfiltered samples were collected from four wells. Duplicate samples were collected from a total of ten wells in 2002-2003 and were analyzed identical to original samples in order to determine analytical reproducibility.

Sample bottles were cleaned using ultra-clean methods. The bottles were rigorously washed five times with 18.3 MΩ-cm deionized water and allowed to air dry. Once cleaned, sample bottles were placed in plastic Ziplock-type bags to prevent contamination. Sample bottles were handled only with polyethylene gloved hands.

Prior to sample collection, wells were pumped for a minimum of three well volumes so that the collected samples were representative of the actual groundwater, not the water that has been sitting in the well for some time. Water samples were collected once the pH, conductivity, and total dissolved solids (TDS), measured via an in-line probe, were stabilized. Groundwater samples were collected following IPLV-8.3 "Groundwater Sample Collection and Control". This procedure describes the methods used to handle sample bottles, procedures for sample collection of filtered unacidified samples, and chain of custody control of the collected groundwater samples.

Groundwater was passed through a Teflon tube that was attached to an on-line 0.45 μm filter that was previously rinsed with one liter of groundwater before samples were collected. One sample bottle of volume 125 mL was collected at each well site and one 125 mL sample bottle is collected for a field duplicate. Sample bottles are rinsed three times with filtered groundwater in order to reduce any possible traces of contamination from bottle cleaning. Groundwater sample bottles were again placed in plastic Ziplock-type and immediately placed into an ice chest filled with an ice slurry. The samples were transported to the laboratory and stored in a refrigerator at approximately 4°C.

Additional samples, not described in IPLV-8.3, were collected from groundwater well sites for method development. Unfiltered unacidified samples consisted of groundwater taken directly from the pump tubing and not passed through a filter. These sample bottles were also rinsed three times with unfiltered groundwater and filled to the top so as to reduce head-space. The collected groundwater samples were placed in Ziplock-type bags and immediately placed in an ice slurry. Filtered and unfiltered samples immediately placed in dry ice were collected from groundwater wells sampled in 2002. Filtered groundwater samples were filtered through a 0.45 μm filter, as described above for the filtered unacidified samples, into a 20 mL scintillation vial, placed in a plastic Ziplock-type bag, and immediately placed in dry ice. Unfiltered groundwater samples consisted of 20 mL of unaltered groundwater collected in a scintillation vial and immediately frozen with dry ice. Upon return to the laboratory, unfiltered samples were placed in a refrigerator that was maintained at 4°C and filtered and unfiltered samples stored in dry ice were transferred to a freezer at approximately -2°C. The dry iced samples were completely thawed only when they were used for IC-ICPMS analysis.

Lab blanks were prepared in the laboratory using deionized water and were collected in a similar way as the samples except that they were not filtered. The bottles for the collection of the lab blank were rinsed three times with deionized water, filled with deionized water, and immediately placed in a refrigerator at approximately 4°C and only removed when they were analyzed. Field blank samples consisted of deionized water that was carried out into the field in 10-L cubic containers and filtered in the same manner as the groundwater samples, bagged, and placed in an ice slurry. These samples were also immediately placed in a refrigerator at approximately 4°C and were only removed at the time of analysis.

SAMPLE CUSTODY

Each sample bottle is labeled with the groundwater well site, the date of sample collection, and a unique barcode that is distributed and managed by the Sample Management Facility (SMF) so that an individual sample can be traced back to raw data. A chain of custody form, which travels with the sample bottles to and from the field, records the sample site, date and time of collection, sample bottle volume, and the sample barcode identifier. Upon return to the laboratory, collected groundwater samples are immediately checked for pH, using pH paper, to ensure that they are unacidified; this result is recorded on a chain of custody form. Samples are then transferred custody from a member of the sample collection team to the particular analyst assigned to measure the species present in the groundwater sample. Sample bottles are then immediately secured in a locked refrigerator maintained at approximately 4°C or in a freezer at approximately -2°C.

CONTROL OF ELECTRONIC DATA

Data was acquired on a daily basis using Elan 2.3.2 and transferred to TotalChrom 6.2.0 via ChromLink 1.8. Electronic data were controlled by the use of a password-protected computer whose access is limited to those working under Task 33. Data was stored on a network server, which is back up nightly, at most 24 hours after acquisition. Transferred data from the Elan 2.3.2 to the TotalChrom 6.2.0 were visually verified for accuracy and completeness at the time of transfer. Manually entered data were visually verified and checked for accuracy at the time of data review.

RESULTS and DISCUSSION

The IC-ICPMS method development was presented in the previous section and the actual concentration measurements for any redox species found in the NCEWDP groundwater samples are listed in Appendix I. Although methods were developed for 10 of the 11 elements, iron is the exception, we feel that the results only for arsenic and chromium are worthy of extended discussion because we are confident that the measurements were carried out before any changes in oxidation states of the redox species occurred. Now that methods for the other eight elements have been developed, little time will be needed to find sample preservation techniques that "lock in" the redox species so that the sample composition reflects that of the groundwater.

The Q'd results for arsenic and chromium are found in Table 4 and displayed in Figure 9 and Figure 10.

Table 4: Concentrations in ppb for Redox Species of Arsenic and Chromium

Sample Site	Filtered/ Unfiltered	SMF Sample ID***	Collection Date	pH*	[As(III)] (ppb)**	[As(V)] (ppb)**	[Cr(III)] (ppb)**	[Cr(VI)] (ppb)**
10P Deep	Filtered	00565386	8/27/2002	7.75	0.06	10.4	<0.015	0.4
10P Shallow	Filtered	00565361	8/27/2002	7.75	0.02	9.7	<0.015	0.5
10P Shallow Dup	Filtered	00565442	8/27/2002	7.77	0.02	9.7	<0.015	0.6
10S Zone 2	Filtered	00565445	9/11/2002	7.94	1.4	8.9	<0.015	0.6
10S Zone 2 Dup	Filtered	00565398	9/11/2002	7.89	1.7	8.6	<0.015	0.6
18P	Filtered	00565330	8/26/2002	8.19	0.14	7.6	<0.015	0.5
22PA Deep	Filtered	00565337	8/28/2002	7.44	0.05	4.2	<0.015	1.1
22PA Deep Dup	Filtered	00565380	8/28/2002	7.43	0.02	4.9	<0.015	1.3
22PA Shallow	Filtered	00565363	8/28/2002	7.64	0.05	5.9	<0.015	0.8
22PB Deep	Filtered	00565364	8/30/2002	7.84	0.04	5.5	<0.015	1.5
22PB Deep Dup	Filtered	00565496	8/30/2002	7.87	0.02	5.3	<0.015	1.1
22PB Shallow	Filtered	00565342	8/29/2002	8.03	0.07	4.3	<0.015	0.7
22PB Shallow Dup	Filtered	00565355	8/29/2002	8.00	0.09	4.3	<0.015	1.1
22S Zone 1	Filtered	00565234	9/11/2002	7.68	1.2	2.5	<0.015	0.1
22S Zone 2	Filtered	00565393	9/10/2002	7.95	2.0	2.0	<0.015	<0.023
22S Zone 2 Dup	Filtered	00565344	9/10/2002	7.99	2.2	2.1	<0.015	<0.023
22S Zone 3	Filtered	00565383	9/10/2002	7.95	1.8	2.1	<0.015	0.06
22S Zone 4	Filtered	00565339	9/9/2002	8.22	1.4	1.9	<0.015	0.4
22S Zone 4 Dup	Filtered	00565379	9/9/2002	8.20	1.5	2.0	<0.015	0.4
23 P Deep	Filtered	01017524	10/1/2002	8.75	0.09	20.5	<0.015	2.6
7SC Zone 1	Filtered	00565389	9/13/2002	7.38	11	0.33	<0.015	<0.023
7SC Zone 1 Dup	Filtered	00565415	9/13/2002	7.28	11.3	0.34	<0.015	<0.023
7SC Zone 2	Filtered	00565425	9/13/2002	7.16	1.9	0.03	<0.015	<0.023
7SC Zone 3	Filtered	00565435	10/3/2002	7.54	0.71	0.15	<0.015	<0.023
7SC Zone 3 Dup	Filtered	01017520	10/3/2002	7.61	0.71.	0.15	<0.015	<0.023
SF1	Filtered	00556382	2/26/2003	7.63***	0.14	31	<0.015	1.1
SF1 Dup	Filtered	00556389	2/26/2003	7.65***	0.21	45.3	<0.015	1.1
SF2	Filtered	00556398	2/26/2003	7.70***	0.07	29.9	<0.015	2.1
Travertine #2	Filtered	01019515	5/23/2003	7.77***	1.9	36.8	0.48	1.0
VH-1	Filtered	00575751	9/18/2002	8.09	2.1	16.9	<0.015	0.1
Warm Spring	Filtered	01017556	2/5/2003	7.54***	<0.011	3.9	<0.015	3.0
MDL	N/A	N/A	N/A	N/A	0.011	0.005	0.015	0.023

As(III), As(V), Cr(III), and Cr(VI) measurement standard deviation <15%

* Data Source: DID# : 008IF.004

**Data Source DID# : 033JB.003

***Data Source: DID#:008IF.002

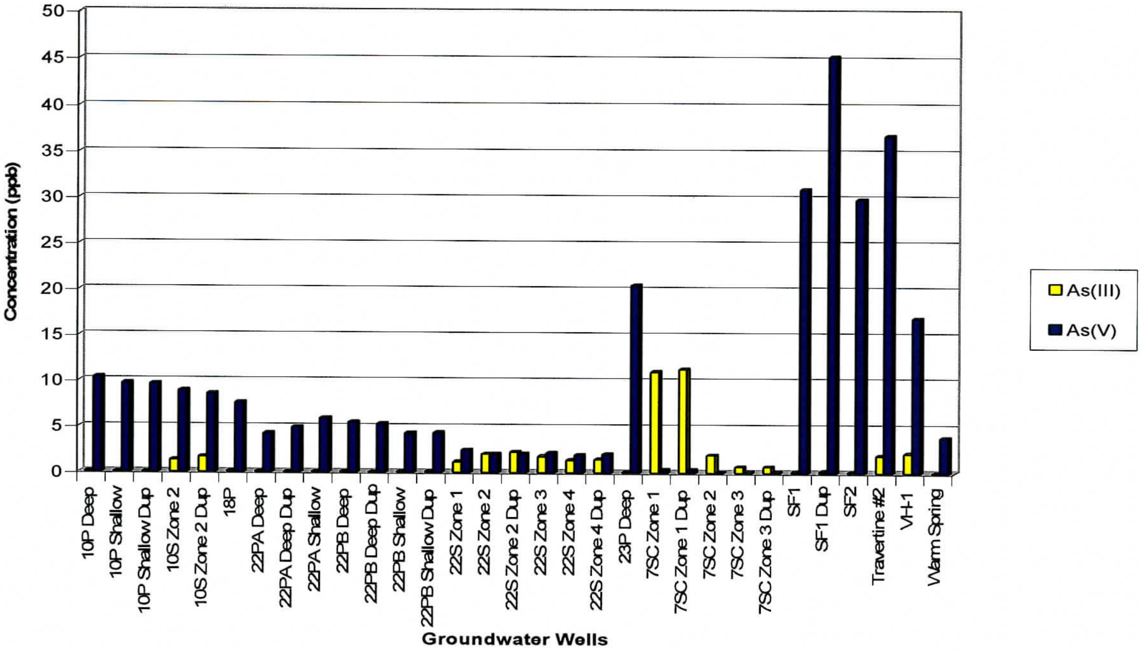


Figure 9: Concentrations of As (III) and As (V) in Southern Nevada Groundwater
Data Source: DID# 033JB.003

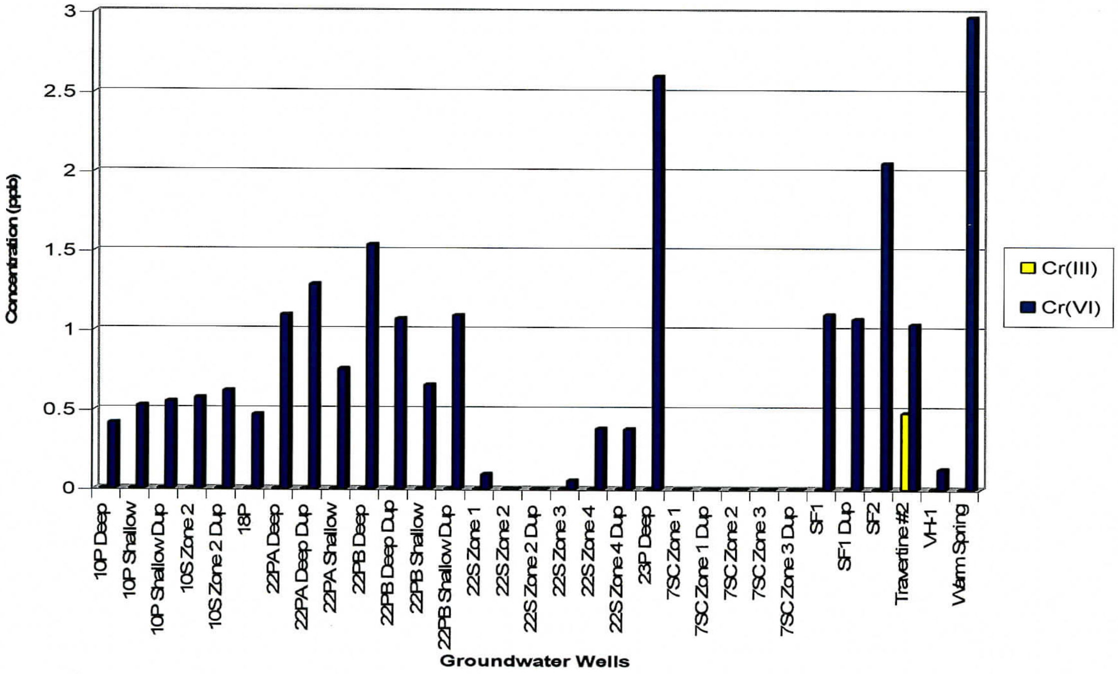


Figure 10: Concentrations of Cr (III) and Cr (VI) in Southern Nevada Groundwater
Data Source: DID # 033JB.003

It is evident from the table and figures that at all locations and sampling depths, with the exception of Travertine #2, Cr (VI) is the only species of chromium in these waters. At Travertine #2, there is about one third of the total chromium in the reduced state, Cr (III). On the other hand, the percentages of oxidized arsenic, As (V), are essentially 100% at some sample locations, for example: 10P, 22PA and 22PB samples, 23P Deep, SF1, SF2, and Warm Springs. Conversely, As (III) is the predominant redox species in a few of the wells, such as the 7SC samples. All of the samples collected from 22S have roughly equal amounts of As (III) and As (V). Thus, in the geographical region covered by the NCEWDP, the ratio of As (III)/As (V) varies considerably.

It is possible to calculate the E_h values for elements in samples that have measurable amounts of two redox species. The results for E_h calculated from As(III) and As(V) species are found in Table 5. Eh values were calculated from equation 1 and 2 from Cherry et. al.:

$$pE = 14.5 - 2pH - \frac{1}{2} \log [H_3AsO_3^0]/[HAsO_4^{2-}] \qquad (1)$$

$$E_h = 0.0591 * pE \qquad (2)$$

Equation 1 can be derived from the following series of equations:

$$H_3AsO_3 + H_2O \leftrightarrow HAsO_4^{2-} + 4H^+ + 2e^- \qquad (3)$$

$$K = [HAsO_4^{2-}][H^+]^4/[H_3AsO_3] \qquad (4)$$

$$E_h = E_o + (2.3RT/nF) * \log K \qquad (5)$$

Where $2.3RT/F = 0.0591$ V at 25°C

$$E_h = E_o + 0.0591/n * \log ([HAsO_4^{2-}][H^+]^4/[H_3AsO_3]) \qquad (6)$$

$$E_h = E_o + 0.0591/2 * \log([HASO_4^{2-}] + 4\log[H^+] - \log[H_3AsO_3] \qquad (7)$$

$$Eh = E_o + 0.0591/2 * \log[HAsO_4^{2-}] + 0.0591/2 * 4\log[H^+] - 0.0591/2 * \log[H_3AsO_3] \qquad (8)$$

$$E_h/0.0591 = E_o/0.0591 + \frac{1}{2} \log[HAsO_4^{2-}] + 2\log[H^+] - \frac{1}{2} \log[H_3AsO_3] \qquad (9)$$

$$pE = E_o/0.0591 - 2pH - \frac{1}{2} \log [H_3AsO_3]/[HAsO_4^{2-}] \qquad (10)$$

Table 5: Eh in Volts Calculated from the Redox Species of Arsenic

Sample Site	Filtered/ Unfiltered	SMF Sample ID	Collection Date	pH ****	As(III) (ppb)*	As(V) (ppb)*	% As(V)	E_h Calc (Volts)**
10P Deep	Filtered	00565386	8/27/2002	7.75	0.057	10.374	99.5	+0.01
10P Shallow	Filtered	00565361	8/27/2002	7.75	0.022	9.708	99.8	+0.02
10P Shallow Dup	Filtered	00565442	8/27/2002	7.77	0.016	9.657	99.8	+0.02
10S Zone 2	Filtered	00565445	9/11/2002	7.94	1.351	8.926	86.9	-0.06
10S Zone 2 Dup	Filtered	00565398	9/11/2002	7.89	1.672	8.576	83.7	-0.06
18P	Filtered	00565330	8/26/2002	8.19	0.139	7.601	98.2	-0.03
22PA Deep	Filtered	00565337	8/28/2002	7.44	0.0455	4.244	98.9	+0.03
22PA Deep Dup	Filtered	00565380	8/28/2002	7.43	0.023	4.920	99.5	+0.05
22PA Shallow	Filtered	00565363	8/28/2002	7.64	0.045	5.908	99.2	+0.01
22PB Deep	Filtered	00565364	8/30/2002	7.84	0.039	5.469	99.3	-0.01
22PB Deep Dup	Filtered	00565496	8/30/2002	7.87	0.022	5.308	99.6	-0.002
22PB Shallow	Filtered	00565342	8/29/2002	8.03	0.074	4.289	98.3	-0.04
22PB Shallow Dup	Filtered	00565355	8/29/2002	8.00	0.086	4.330	98.1	-0.04
22S Zone 1	Filtered	00565234	9/11/2002	7.68	1.192	2.474	67.5	-0.04
22S Zone 2	Filtered	00565393	9/10/2002	7.95	2.046	2.031	49.8	-0.08
22S Zone 2 Dup	Filtered	00565344	9/10/2002	7.99	2.234	2.068	48.1	-0.09
22S Zone 3	Filtered	00565383	9/10/2002	7.95	1.790	2.147	54.5	-0.08
22S Zone 4	Filtered	00565339	9/9/2002	8.22	1.397	1.949	58.3	-0.11
22S Zone 4 Dup	Filtered	00565379	9/9/2002	8.20	1.472	2.043	58.1	-0.11
23 P Deep	Filtered	01017524	10/1/2002	8.75	0.09	20.5	99.6	N/A
7SC Zone 1	Filtered	00565389	9/13/2002	7.38	11.037	0.330	2.9	-0.06
7SC Zone 1 Dup	Filtered	00565415	9/13/2002	7.28	11.322	0.339	2.9	-0.05
7SC Zone 2	Filtered	00565425	9/13/2002	7.16	1.943	0.031	1.6	-0.05
7SC Zone 3	Filtered	00565435	10/3/2002	7.54	0.71	0.15	17.4	N/A
7SC Zone 3 Dup	Filtered	01017520	10/3/2002	7.61	0.71	0.15	17.4	N/A
SF1	Filtered	00556382	2/26/2003	7.63***	0.135	30.984	99.6	+0.02
SF1 Dup	Filtered	00556389	2/26/2003	7.65***	0.205	45.318	99.5	+0.02
SF2	Filtered	00556398	2/26/2003	7.70***	0.074	29.886	99.8	+0.02
Travertine #2	Filtered	01019515	5/23/2003	7.77***	1.886	36.814	95.1	-0.02
VH-1	Filtered	00575751	9/18/2002	8.09	2.138	16.903	88.8	-0.07
Warm Spring	Filtered	01017556	2/5/2003	7.54***	<0.011	3.9	100	N/A
MDL	N/A	N/A	N/A	N/A	0.011	0.005	N/A	N/A

[As(III)] and [As(V)] measurement standard deviation <15%

*Data Source: DID# 033JB.003
**Data Source: DID # 033JB.007
*** Data Source: DID# 008IF.002
****Data Source DID# 008IF.004

The values in the table for As(III) and As(V) represent the "total" concentrations of the possible chemical forms for these two oxidations states in aqueous solution. For example, under the mildly basic chromatographic conditions used for the determination of arsenic, As (III) is measured as AsO_3^{-3} (arsenite). These values are input as the total for all As (III) species and the distribution of As(III) between $As(OH)_3$ (or H_3AsO_3) , $H_2AsO_3^-$, $HAsO_3^{-2}$, and AsO_3^{-3} is determined using equilibrium constants and the corresponding pH values for each groundwater sample (Appendix V). The results show that, at the pH values for NCEWDP water, $As(OH)_3$ is by far the predominant species. Likewise, under the chromatographic conditions used for arsenic, As (V) is measured as AsO_4^{-3} (arsenate). These values are used as the total concentration for all As (V) species. The distribution of As (V) between H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{-2}$ and AsO_4^{-3} was calculated using equilibrium constants, total As (V), and pH of the groundwater sample (Appendix V). At the prevailing pH conditions in the NCEWDP wells, the predominant species include both the mono-protonated and di-protonated forms of As (V). The calculated concentrations of H_3AsO_3 and $HAsO_4^{-2}$ are used to calculate the pE. By multiplying pE by 0.0591, the Eh can be calculated. A negative E_h suggests available electrons or relatively reducing conditions and conversely, a positive E_h suggests relatively oxidizing conditions. The E_h axis (the y axis) of a typical E_h-pH plot ranges from about -0.8 volt to + 1.2 volt.

The calculated E_h values for the NCEWDP waters cluster around zero, suggesting conditions which are not reducing or oxidizing. Figure 11 shows a plot of percent arsenic in the oxidized form, As (V), versus the calculated E_h.

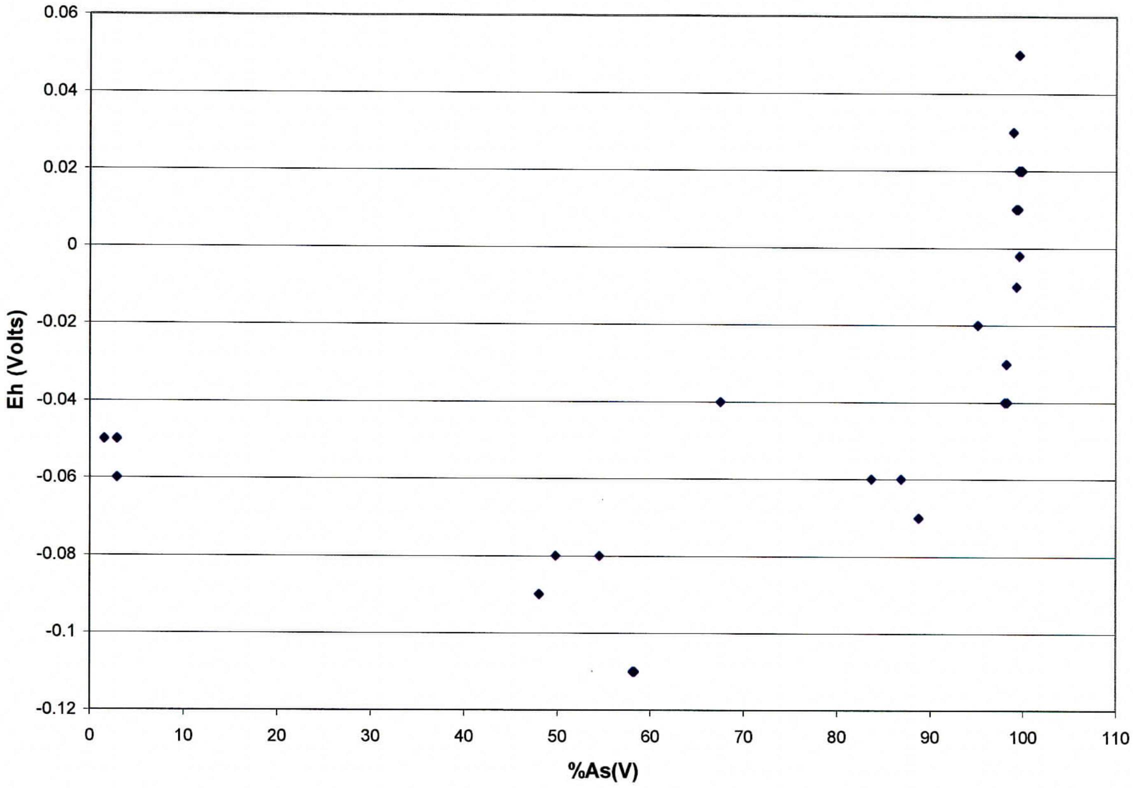


Figure 11: Percent Oxidized Arsenic (As (V)) versus the E_h Calculated from the Arsenic Redox Species
Data Source: DID# As 033JB.003
Data Source: DID# Eh 033JB.007

Although the highest percentages of As (V) in many of the groundwater samples are accompanied by the highest E_h values, some samples with almost all of the arsenic in the +5 state have E_h values as low as -0.04 volt. Moreover, at -0.06 volt, one finds samples ranging from less than 5% As (V) all the way up to 84% As(V). Thus, there is no clear correlation of E_h with pH. The lack of such a correlation is normally explained by suggesting that this natural water system is not in thermodynamic equilibrium, but under some type of kinetic control. Thus, the thermodynamic model, as most would agree, is not applicable to these environmental samples and the measured E_h not useful in predicting the redox species.

From the results in Appendix I for the other eight elements for which IC-ICPMS measurement conditions were found, there are several general observations. One must remember that these waters were used to test the methods although they had been kept unacidified at 4°C for many months by the time that the methods were developed. Thus, these observations are presented for informational purposes only. In addition to chromium, which exists almost exclusively as Cr (VI), five of the remaining elements appear to exist in a single oxidation state in the NCEWDP waters. They are: Cu as Cu(II), Mn as Mn(II), Mo as Mo(VI), W as W(VI), and U as U(VI). Except for manganese, all of the oxidation states represent the highest common state for all of these elements. On the other hand, the other three elements, Sb, Se and V, like arsenic have redox species distributions that sometimes favor the reduced state and sometimes the oxidized state, depending on sample location. One of these, antimony, is present in almost all of the samples in the reduced state, selenium generally exists in the oxidized state (Se (VI)), and vanadium seems to be distributed fairly evenly between, V (IV) and V (V).

CONCLUSIONS

In conclusion, a method, the IC-ICPMS, to measure the concentrations of the redox species of ten elements (antimony, arsenic, chromium copper, manganese, molybdenum, selenium, tungsten, uranium and vanadium) in groundwater has been developed and tested. Q'd results for arsenic and chromium are presented and discussed. The lack of a correlation between the E_h, calculated from the measured concentration of As (III) and As (V) and the pH, and the percent As (V) in the NCEWDP waters, point to a need for further research in this area of geochemistry to develop a "practical" method for predicting the oxidation state distribution for elements in groundwater. The experimental approach outlined is close to being able to collect the necessary data to do this. It could be broadened to include several other elements such as: rhenium (Re), a surrogate for technetium-99; cobalt, Co (II) and Co (III); thallium, Tl (III) and Tl(VI). We are close to having a method for possibly the most important element, iron, Fe (II) and Fe (III). Likewise, examination of groundwater sample preservation techniques, which "lock in" the redox species present in the groundwater prior to sampling, for the elements other than arsenic and chromium, could also proceed rapidly. From the approach reported in this report, there is hope that one can adequately describe the redox state of groundwater and predict the redox couple distribution for those elements available in nuclear waste. Although a "practical" redox scale was not developed, because of the progress on Task 33 few obstacles now stand in the path for achieving that goal.

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Appendix I

Filtered Unacidified Sample Concentrations

Sample Site	Filtered/ Unfiltered	SMF Sample ID	Collection Date	[As(III)] (ppb)*	[As(V)] (ppb)*	[Cr(III)] (ppb)*	[Cr(VI)] (ppb)*
10P Deep	Filtered	00565386	8/27/2002	0.057	10.4	<0.015	0.42
10P Shallow	Filtered	00565361	8/27/2002	0.022	9.7	<0.015	0.53
10P Shallow Dup	Filtered	00565442	8/27/2002	0.016	9.7	<0.015	0.55
10S Zone 2	Filtered	00565445	9/11/2002	1.4	8.9	<0.015	0.58
10S Zone 2 Dup	Filtered	00565398	9/11/2002	1.7	8.6	<0.015	0.62
18P	Filtered	00565330	8/26/2002	0.14	7.6	<0.015	0.47
22PA Deep	Filtered	00565337	8/28/2002	0.046	4.2	<0.015	1.1
22PA Deep Dup	Filtered	00565380	8/28/2002	0.023	4.9	<0.015	1.3
22PA Shallow	Filtered	00565363	8/28/2002	0.045	5.9	<0.015	0.76
22PB Deep	Filtered	00565364	8/30/2002	0.039	5.5	<0.015	1.5
22PB Deep Dup	Filtered	00565496	8/30/2002	0.022	5.3	<0.015	1.1
22PB Shallow	Filtered	00565342	8/29/2002	0.074	4.3	<0.015	0.66
22PB Shallow Dup	Filtered	00565355	8/29/2002	0.086	4.3	<0.015	1.1
22S Zone 1	Filtered	00565234	9/11/2002	1.2	2.5	<0.015	0.093
22S Zone 2	Filtered	00565393	9/10/2002	2.0	2.0	<0.015	<0.023
22S Zone 2 Dup	Filtered	00565344	9/10/2002	2.2	2.1	<0.015	<0.023
22S Zone 3	Filtered	00565383	9/10/2002	1.8	2.1	<0.015	0.055
22S Zone 4	Filtered	00565339	9/9/2002	1.4	1.9	<0.015	0.38
22S Zone 4 Dup	Filtered	00565379	9/9/2002	1.5	2.0	<0.015	0.38
23P Deep	Filtered	01017524	10/1/2002	0.094	20.5	<0.015	2.6
7SC Zone 1	Filtered	00565389	9/13/2002	11.0	0.33	<0.015	<0.023
7SC Zone 1 Dup	Filtered	00565415	9/13/2002	11.3	0.34	<0.015	<0.023
7SC Zone 2	Filtered	00565425	9/13/2002	1.9	0.03	<0.015	<0.023
7SC Zone 3	Filtered	00565435	10/3/2002	0.71	0.15	<0.015	<0.023
7SC Zone 3 Dup	Filtered	01017520	10/3/2002	0.71	0.15	<0.015	<0.023
SF1	Filtered	00556382	2/26/2003	0.14	31.0	<0.015	1.1
SF1 Dup	Filtered	00556389	2/26/2003	0.21	45.3	<0.015	1.1
SF2	Filtered	00556398	2/26/2003	0.07	29.9	<0.015	2.1
Travertine #2	Filtered	01019515	5/23/2003	1.9	36.8	0.48	1.0
VH-1	Filtered	00575751	9/18/2002	2.1	16.9	<0.015	0.13
Warm Spring	Filtered	01017556	2/5/2003	<0.011	3.9	<0.015	3.0

*Data Source: DID# 033JB.003

Sample Site	Filtered/ Unfiltered	SMF Sample ID	Collection Date	[Sb(III)]	[Sb(V)]	[Cu(II)]	[Mn(II)]	[Mo(VI)]	[Se(IV)]	[Se(VI)	[W(VI)]	[U(VI)]	[V(V)]	[V(IV)]
				(ppb)*	(ppb)*	(ppb)*	(ppb)*	(ppb)*	(ppb)*	(ppb)*	(ppb)*	(ppb)*	(ppb)*	(ppb)*
10P Deep	Filtered	00565386	8/27/2002	0.37	<0.088	<0.031	1.3	16.5	<0.415	1.8	15.4	0.48	10.5	5.3
10P Shallow	Filtered	00565361	8/27/2002	0.82	0.88	0.12	6.0	28.8	<0.415	2.0	2.6	0.52	3.2	4.3
10P Shallow Dup	Filtered	00565442	8/27/2002	0.70	<0.088	0.93	5.3	9.7	0.73	2.7	1.3	0.60	8.0	7.4
10S Zone 2	Filtered	00565445	9/11/2002	0.45	<0.088	<0.031	26.7	17.4	<0.415	1.9	3.5	0.45	7.9	4.3
10S Zone 2 Dup	Filtered	00565398	9/11/2002	0.31	<0.088	0.33	26.5	25.5	<0.415	1.9	3.3	0.57	10.3	7.4
18P	Filtered	00565330	8/26/2002	0.76	<0.088	<0.031	6.3	8.6	<0.415	<0.23	2.0	1.8	2.4	3.1
22PA Deep	Filtered	00565337	8/28/2002	0.34	0.40	0.44	3.2	9.0	<0.415	1.7	2.4	0.26	5.4	3.9
22PA Deep Dup	Filtered	00565380	8/28/2002	0.44	0.57	1.4	4.0	4.5	1.2	2.1	1.1	0.35	5.4	3.7
22PA Shallow	Filtered	00565363	8/28/2002	1.1	<0.088	0.074	2.9	29.2	<0.415	2.0	0.86	0.88	3.6	2.8
22PB Deep	Filtered	00565364	8/30/2002	<0.127	<0.088	0.33	2.2	7.9	0.58	<0.23	0.69	1.3	5.3	3.5
22PB Deep Dup	Filtered	00565496	8/30/2002	0.48	<0.088	1.2	2.3	9.6	1.2	2.7	1.0	1.2	2.7	2.4
22PB Shallow	Filtered	00565342	8/29/2002	<0.127	0.37	0.43	0.067	7.9	<0.415	2.4	0.60	0.73	5.1	3.7
22PB Shallow Dup	Filtered	00565355	8/29/2002	0.31	<0.088	1.2	1.1	6.5	0.90	2.9	0.71	0.72	3.4	2.9
22S Zone 1	Filtered	00565234	9/11/2002	0.37	<0.088	0.034	19.4	7.2	<0.415	1.3	0.56	0.25	2.9	2.9
22S Zone 2	Filtered	00565393	9/10/2002	0.28	<0.088	<0.031	20.7	10.4	<0.415	0.95	0.93	0.33	1.7	2.2
22S Zone 2 Dup	Filtered	00565344	9/10/2002	0.20	<0.088	<0.031	30.3	7.5	<0.415	0.71	0.56	0.19	1.7	1.0
22S Zone 3	Filtered	00565383	9/10/2002	0.34	0.48	0.17	25.5	6.6	<0.415	1.4	0.66	0.38	2.6	2.4
22S Zone 4	Filtered	00565339	9/9/2002	0.42	0.49	0.55	25.8	8.9	0.64	1.1	0.88	0.45	1.9	2.0
22S Zone 4 Dup	Filtered	00565379	9/9/2002	<0.127	<0.088	<0.031	24.1	9.7	<0.415	1.1	0.89	0.30	1.5	1.3
23P Deep	Filtered	01017524	10/1/2002	2.3	<0.088	0.28	0.12	41.3	<0.415	6.0	2.6	2.4	5.2	4.0
7SC Zone 1	Filtered	00565389	9/13/2002	0.52	<0.088	<0.031	0.22	6.0	<0.415	1.0	0.39	4.4	0.67	0.58
7SC Zone 1 Dup	Filtered	00565415	9/13/2002	0.59	<0.088	<0.031	8.4	4.9	<0.415	1.3	0.31	4.0	0.81	0.41
7SC Zone 2	Filtered	00565425	9/13/2002	0.49	0.64	<0.031	3.9	4.2	<0.415	0.98	0.15	3.9	0.53	0.24
7SC Zone 3	Filtered	00565435	10/3/2002	<0.127	0.29	<0.031	34.9	2.3	<0.415	<0.23	0.34	1.1	0.28	0.25
7SC Zone 3 Dup	Filtered	01017520	10/3/2002	<0.127	<0.088	0.097	71.3	2.6	<0.415	<0.23	0.38	1.4	<0.026	0.06
SF1	Filtered	00556382	2/26/2003	1.7	<0.088	1.8	0.39	N/A	1.2	2.1	N/A	4.2	12.6	7.6
SF1 Dup	Filtered	00556389	2/26/2003	1.9	<0.088	2.9	0.51	N/A	2.0	2.6	N/A	3.3	11.5	7.5
SF2	Filtered	00556398	2/26/2003	1.4	<0.088	1.1	0.13	N/A	1.1	<0.23	N/A	3.5	5.0	12.1
Travertine #2	Filtered	01019515	5/23/2003	<0.127	0.22	1.0	11.2	19.6	1.0	1.2	0.53	2.3	4.7	3.3
VH-1	Filtered	00575751	9/18/2002	0.73	<0.088	0.11	19.1	13.7	<0.415	1.4	6.3	2.6	3.7	3.3
Warm Spring	Filtered	01017556	2/5/2003	0.90	<0.088	<0.031	<0.02	17.3	<0.415	8.6	1.5	1.3	4.6	4.7

*Non-Q: concentrations are for informational purposes only, Data Source: DID# 033JB.006

Appendix II

pH Values for Groundwater Wells

Sample Site	SMF Sample ID	Collection Date	pH*
10P Deep	00565144	8/27/2002	7.75
10P Shallow	00565298	8/27/2002	7.75
10P Shallow Dup	00565140	8/27/2002	7.77
10S Zone 2	00565310	9/11/2002	7.94
10S Zone 2 Dup	00565249	9/11/2002	7.89
18P	00565304	8/26/2002	8.19
22PA Deep	00565194	8/28/2002	7.44
22PA Deep Dup	00565286	8/28/2002	7.43
22PA Shallow	00565279	8/28/2002	7.64
22PB Deep	00565186	8/30/2002	7.84
22PB Deep Dup	00565292	8/30/2002	7.87
22PB Shallow	00565312	8/29/2002	8.03
22PB Shallow Dup	00565254	8/29/2002	8.00
22S Zone 1	00565195	9/11/2002	7.68
22S Zone 2	00565135	9/10/2002	7.95
22S Zone 2 Dup	00565259	9/10/2002	7.99
22S Zone 3	00565366	9/10/2002	7.95
22S Zone 4	00565366	9/9/2002	8.22
22S Zone 4 Dup	00565327	9/9/2002	8.20
23P Deep	00576887	10/1/2002	8.75
7SC Zone 1	00565264	9/13/2002	7.38
7SC Zone 1 Dup	00565045	9/13/2002	7.28
7SC Zone 2	00565422	9/13/2002	7.16
7SC Zone 3	00565432	10/3/2002	7.54
7SC Zone 3 Dup	01017517	10/3/2002	7.61
SF1	00556381	2/26/2003	7.63**
SF1 Dup	00556388	2/26/2003	7.65**
SF2	00565030	2/26/2003	7.70**
Travertine #2	01019517	5/23/2003	7.77**
VH-1	00575751	9/18/2002	8.09
Warm Spring	01017557	2/5/2003	7.54**

*Data Source: DID#: 008IF.004
**Data Source: DID#: 008IF.002

Appendix III

Unfiltered Unacidified Sample Concentrations

Sample Site	SMF Sample ID	Filtered/	Collection Date	[As(III)]	[As(V)]	[Cr(III)]	[Cr(VI)]	[Mo(VI)]	[W(VI)]
		Unfiltered		(ppb)*	(ppb)*	(ppb)*	(ppb)*	(ppb)**	(ppb)**
10P Deep	00565387	Unfiltered	8/27/2002	0.036	10.438	<0.015	0.415	15.563	14.724
10P Shallow	00565362	Unfiltered	8/27/2002	0.032	9.681	<0.015	0.51	17.006	1.432
10P Shallow Dup	00565441	Unfiltered	8/27/2002	<0.011	9.654	<0.015	0.511	11.610	1.309
10S Zone 2	00565446	Unfiltered	9/11/2002	1.738	8.741	<0.015	0.588	11.286	2.392
10S Zone 2 Dup	00565396	Unfiltered	9/11/2002	1.795	8.448	<0.015	0.625	14.872	2.578
18P	00565331	Unfiltered	8/26/2002	0.033	7.611	<0.015	0.386	3.638	1.294
22PA Deep	00565336	Unfiltered	8/28/2002	0.104	4.0655	<0.015	1.189	6.169	1.368
22PA Deep Dup	00565381	Unfiltered	8/28/2002	0.031	4.606	<0.015	1.213	11.366	2.408
22PA Shallow	00565350	Unfiltered	8/28/2002	0.088	5.771	<0.015	0.818	12.656	0.534
22PB Deep	00565365	Unfiltered	8/30/2002	0.047	5.305	<0.015	1.609	4.316	0.547
22PB Deep Dup	00565497	Unfiltered	8/30/2002	0.042	5.472	<0.015	1.111	2.589	0.342
22PB Shallow	00565343	Unfiltered	8/29/2002	0.041	4.277	<0.015	0.721	1.849	0.219
22PB Shallow Dup	00565356	Unfiltered	8/29/2002	0.071	4.331	<0.015	1.148	3.245	0.375
22S Zone 1	00565453	Unfiltered	9/11/2002	1.363	2.521	<0.015	0.118	9.784	0.571
22S Zone 2	00565394	Unfiltered	9/10/2002	1.850	2.017	<0.015	<0.023	8.704	0.570
22S Zone 2 Dup	00565345	Unfiltered	9/10/2002	1.835	2.084	<0.015	<0.023	3.426	0.321
22S Zone 3	00565384	Unfiltered	9/10/2002	1.291	2.043	<0.015	0.055	5.098	0.565
22S Zone 4	00565340	Unfiltered	9/9/2002	1.159	2.007	<0.015	0.379	4.911	0.646
22S Zone 4 Dup	00565351	Unfiltered	9/9/2002	1.173	1.936	<0.015	0.383	1.433	0.240
23P Deep	00576891	Unfiltered	10/1/2002	0.082	21.817	<0.015	2.46	40.779	1.761
7SC Zone 1	00565390	Unfiltered	9/13/2002	11.286	0.333	<0.015	<0.023	3.346	0.272
7SC Zone 1 Dup	00565416	Unfiltered	9/13/2002	11.328	0.311	<0.015	<0.023	1.997	0.173
7SC Zone 2	00565426	Unfiltered	9/13/2002	2.013	0.006	<0.015	<0.023	1.626	0.088
7SC Zone 3	00565392	Unfiltered	10/3/2002	0.821	0.128	<0.015	<0.023	2.131	0.330
7SC Zone 3 Dup	01017521	Unfiltered	10/3/2002	0.945	0.127	<0.015	<0.023	2.846	0.406
VH-1	00575752	Unfiltered	9/18/2002	1.735	17.049	<0.015	0.124	8.542	4.562
SF1	00556383	Unfiltered	2/26/2003	0.188	28.043	<0.015	1.138	N/A	N/A
SF2	00565030	Unfiltered	2/26/2003	0.067	30.615	<0.015	2.058	N/A	N/A
SF1 Dup	00556390	Unfiltered	2/26/2003	0.129	27.268	<0.015	1.219	20.232	6.08
Warm Spring	01017555	Unfiltered	2/5/2003	0.183	4.004	<0.015	2.489	13.582	1.202

*Data Source: DID#: 033JB.001

**Non-Q: For corroborative use only: Data Source: DID# 033JB.008

Appendix IV

Filtered Dry Ice Preserved Sample Concentrations

Sample Site	Filtered/ Unfiltered	SMF Sample ID	Collection Date	[As(III)] (ppb)*	[As(V)] (ppb)*	[Cr(III)] (ppb)*	[Cr(VI)] (ppb)*
10S Zone 2	Filtered	00565447	9/11/2002	0.189	9.924	<0.015	0.070
10S Zone 2 Dup	Filtered	00565358	9/11/2002	0.232	9.155	<0.015	0.189
18P	Filtered	00565334	8/26/2002	0.290	7.064	<0.015	<0.023
22PA Deep	Filtered	00565338	8/28/2002	0.085	4.128	<0.015	0.301
22PA Deep Dup	Filtered	00565382	8/28/2002	0.014	4.604	<0.015	0.447
22PA Shallow	Filtered	00565370	8/28/2002	0.085	4.806	<0.015	0.289
22PB Deep	Filtered	00565374	8/30/2002	0.034	4.621	0.029	0.6765
22PB Deep Dup	Filtered	00565498	8/30/2002	0.027	4.724	<0.015	0.060
22PB Shallow	Filtered	00565353	8/29/2002	0.012	4.149	0.0405	0.577
22PB Shallow Dup	Filtered	00565457	8/29/2002	0.073	0.061	0.5505	<0.023
22S Zone 1	Filtered	00565449	9/11/2002	0.048	2.004	<0.015	<0.023
22S Zone 2	Filtered	00565395	9/10/2002	0.036	1.634	<0.015	<0.023
22S Zone 2 Dup	Filtered	00565346	9/10/2002	0.157	2.368	<0.015	<0.023
22S Zone 3	Filtered	00565371	9/10/2002	0.871	2.654	<0.015	<0.023
22S Zone 4	Filtered	00565332	9/9/20002	0.036	1.964	0.052	<0.023
22S Zone 4 Dup	Filtered	00565352	9/9/2002	0.400	2.480	<0.015	<0.023
7SC Zone 1	Filtered	00565377	9/13/2002	0.495	1.464	<0.015	<0.023
7SC Zone 1 Dup	Filtered	00565417	9/13/2002	0.996	1.726	<0.015	<0.023
7SC Zone 2	Filtered	00565427	9/13/2002	0.050	0.803	<0.015	<0.023
7SC Zone 3	Filtered	00556335	10/3/2002	0.668	0.237	<0.015	<0.023
7SC Zone 3 Dup	Filtered	01017522	10/3/2002	0.345	0.138	<0.015	<0.023
VH-1	Filtered	00576882	9/18/2002	0.056	8.771	<0.015	<0.023

*Data source: DID#: 033JB.005

Appendix V

Unfiltered Dry Ice Preserved Sample Concentrations

Sample Site	Filtered/ Unfiltered	SMF Sample ID	Collection Date	[As(III)] (ppb)*	[As(V)] (ppb)*	[Cr(III)] (ppb)*	[Cr(VI)] (ppb)*
10P Shallow	Unfiltered	00565369	8/27/2002	0.046	5.573	<0.015	0.165
10P Shallow Dup	Unfiltered	00565437	8/27/2002	0.047	6.814	<0.015	0.236
10S Zone 2	Unfiltered	00565444	9/11/2002	0.021	6.046	0.1415	0.0085
10S Zone 2 Dup	Unfiltered	00565499	9/11/2002	0.073	9.542	<0.015	0.1815
18P	Unfiltered	00565335	8/26/2002	0.340	5.771	<0.015	<0.023
22PA Deep	Unfiltered	00565341	8/28/2002	<0.011	4.297	0.049	0.2785
22PA Deep Dup	Unfiltered	00565385	8/28/2002	0.044	3.349	<0.015	0.443
22PA Shallow	Unfiltered	00565373	8/28/2002	0.082	4.887	0.031	0.1355
22PB Deep	Unfiltered	00565376	8/30/2002	0.033	4.157	<0.015	0.5395
22PB Deep Dup	Unfiltered	00565378	8/30/2002	0.053	2.674	<0.015	0.3915
22PB Shallow	Unfiltered	00565354	8/29/2002	0.064	3.287	0.047	0.433
22PB Shallow Dup	Unfiltered	00565458	8/29/2002	0.046	2.839	<0.015	0.286
22S Zone 1	Unfiltered	00565450	9/11/2002	0.031	1.966	<0.015	<0.023
22S Zone 2	Unfiltered	00565397	9/10/2002	0.163	2.417	<0.015	<0.023
22S Zone 2 Dup	Unfiltered	00565348	9/10/2002	0.083	1.907	0.0215	<0.023
22S Zone 3	Unfiltered	00565372	9/10/2002	0.086	1.203	<0.015	<0.023
22S Zone 4	Unfiltered	00565333	9/9/2002	0.101	0.690	0.041	<0.023
22S Zone 4 Dup	Unfiltered	00565357	9/9/2002	0.078	1.989	<0.015	<0.023
7SC Zone 1	Unfiltered	00565375	9/13/2002	0.660	1.644	<0.015	<0.023
7SC Zone 1 Dup	Unfiltered	00565418	9/13/2002	0.488	1.122	<0.015	<0.023
7SC Zone 2	Unfiltered	00565428	9/13/2002	0.037	1.308	<0.015	<0.023
7SC Zone 3	Unfiltered	00565483	10/3/2002	1.454	0.219	<0.015	<0.023
7SC Zone 3 Dup	Unfiltered	01017523	10/3/2002	0.272	0.104	N/A	N/A
VH-1	Unfiltered	00576883	9/18/2002	0.182	15.686	<0.015	<0.023
23P Deep	Unfiltered	00576893	10/1/2002	0.036	5.256	0.052	1.085

*Data Source: DID# 033JB.004

Appendix V

Eh Calculated Values for Select Wells

$H_3AsO_4 \leftrightarrow H^+ + H_2AsO_4^-$ $\quad K_1 = 0.055$
$H_2AsO_4^- \leftrightarrow H^+ + HAsO_4^{2-}$ $\quad K_2 = 1.7 * 10^{-7}$
$HAsO_4^{2-} \leftrightarrow H^+ + AsO_4^{3-}$ $\quad K_3 = 5.1 * 10^{-12}$
$H_3AsO_3 \leftrightarrow H^+ + H_2AsO_3^-$ $\quad K_1 = 5.8888 * 10^{-10}$
$H_2AsO_3^- \leftrightarrow H^+ + HAsO_3^{2-}$ $\quad K_2 = 7.413 * 10^{-13}$
$HAsO_3^{2-} \leftrightarrow H^+ + AsO_3^{2-}$ $\quad K_3 = 3.981 * 10^{-14}$

10P Deep					
[As(V)] ppb*	10.4	[As(III)] ppb*	0.06		
[[As(V)]]	1.38667E-07	[[As(III)]]	8E-10		
pH**	**7.75**				
[H+]	1.77828E-08	[H+]	1.77828E-08		
K1	0.0055	K1	5.888E-10		
K2	0.00000017	K2	7.413E-13		
K3	5.1E-12	K3	3.981E-14		
				pE	**0.104855**
[H3AsO4]	4.24464E-14	**[H3AsO3]**	**7.74359E-10**	**Eh*****	**0.01**
[HAsO42-]	**1.25502E-07**	**[H2AsO3-]**	2.56395E-11		
[H2AsO4-]	1.31281E-08	**[HAsO32-]**	1.06882E-15		
[AsO43-]	3.59934E-11	**[AsO33-]**	2.39275E-21		

10P Shallow					
[As(V)] ppb*	9.7	[As(III)] ppb*	0.02		
[[As(V)]]	1.29333E-07	[[As(III)]]	2.667E-10		
pH**	**7.75**				
[H+]	1.77828E-08	[H+]	1.778E-08		
K1	0.0055	K1	5.888E-10		
K2	0.00000017	K2	7.413E-13		
K3	5.1E-12	K3	3.981E-14		
				pE	**0.328285**
[H3AsO4]	3.95894E-14	**[H3AsO3]**	**2.581E-10**	**Eh*****	**0.02**
[HAsO42-]	**1.17055E-07**	**[H2AsO3-]**	8.547E-12		
[H2AsO4-]	1.22445E-08	**[HAsO32-]**	3.563E-16		
[AsO43-]	3.35707E-11	**[AsO33-]**	7.976E-22		

*Data Source: DID# 033JB.003
**Data Source: DID# 008IF.004
***Data Source: DID# 033JB.007

Appendix VII

Publications, Presentations, and Posters

1. Farnham, I.M.; Johanneson, K.H.; Singh, A.K.; Hodge, V.F.; Stetzenbach, K.J.; 2003. Factor analytical approaches for evaluating groundwater trace element chemistry data. Analytical Chimica Acta, 490, 123-138. (Referred Publication)
2. Perkin Elmer User's Meeting: *Determination of the Oxidation State Speciation of Metals in Groundwater by IC-ICP-MS*: Southern Nevada Water District, Boulder City, NV- April 2002 (Presentation)
3. Perkin Elmer User's Meeting: *Arsenic and Chromium in Nevada Groundwater*: Desert Research Institute, Las Vegas, NV- July 2002 (Presentation)
4. Pittcon Conference: *Arsenic and Chromium Oxidation State Measurements in Nevada Groundwater by IC-ICPMS* - Orlando, FL- March 2003 (Presentation)
5. Devil's Hole Meeting: *Arsenic and Chromium Oxidation State Measurements in Southern Nevada Groundwater using Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry*: Death Valley National Park, CA- May 2003 (Poster)
6. Perkin Elmer User's Meeting: *Multi-Element Speciation of Groundwater by IC-ICPMS* : Desert Research Institute, Las Vegas, NV - July 2003 (Presentation)