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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 2018.01

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Subject: Validation of inductively-coupled plasma mass spectrometer instruments for analysis of trace metals in unfiltered-water and filtered-water samples

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Purpose

This memorandum documents method performance of recently acquired inductively-coupled plasma mass spectrometer (ICP-MS) instrumentation and method quality, including variability, bias, interferences, and detection limits (DLs) for trace metals in unfiltered and filtered-water measured by inductively-coupled plasma mass spectrometry at the National Water Quality Laboratory (NWQL). Out-of-date instruments used to make these measurements have been replaced, and optimized method parameters as well as validation data are reported here.

Summary of Key Findings

Out of date Agilent Technologies 7500ce (referred to as Agilent ICP-MS or Agilent elsewhere) ICP-MS instrumentation was replaced by two PerkinElmer, Inc. Nexion 350D ICP-MS instruments (referred to as Nexion ICP-MS or Nexion elsewhere) for measurement of operationally-defined dissolved (DISS, filtered-water) and whole-water recoverable (WWR, unfiltered digested water) trace elements. On September 30, 2016, production using the Agilent instruments for the methods listed in table 1 was discontinued and transferred to the Nexion instruments on October 1, 2016. Prior to implementation, validation studies were performed on these instruments to characterize DLs, sample matrix effects, bias, variability, and comparability to the superseded instrumentation. Key findings of these validation studies are summarized here:

- Detection limits: For most analytes, the applied DL remains the same as it was with the Agilent ICP-MS or was lowered. The DL was raised for dissolved and WWR chromium (Cr), WWR uranium (U), and dissolved silver (Ag).
- Matrix effects: All samples with specific conductance greater than 2,500 microsiemens per centimeter (µS/cm) will be diluted prior to analysis to reduce matrix effects. Customers who submit samples with specific conductance greater than (>)1,000 µS/cm to the ICP-MS analyses should be aware of potential bias and increased variability that is inherent in the analysis of such samples because of the matrix, and consider the information in this memorandum when interpreting their sample data. Matrix effects are not always predictable and depend on the constituents in the matrix as well as the specific conductance. Therefore, the inclusion of field-requested matrix-spike analyses for environmental samples is an essential aid in interpreting the data.

- Nexion variability and bias: Three reference materials (RM) and reagent-water, groundwater, and surface water spiked with all analytes of interest were analyzed by the Nexion DISS and WWR methods. Measured concentrations of all analytes in the RMs were within 10 percent of most probable values (MPVs) with few exceptions: analytes with concentrations near the DL had greater bias and variability, and zinc (Zn) and beryllium (Be) measured values for one RM were biased and had elevated variability. Spiked reagent-water, groundwater, and surface water showed similar increased bias and variability for some analytes near the DL. At higher concentrations bias was less than 10 percent and variability was less than 5 percent for most analytes. Variability was slightly higher for low mass elements lithium (Li), Be, boron (B), and aluminum (Al).
- Environmental sample data comparison to superseded method: There are primarily high or occasionally low biases and elevated variability for several analytes, most notably for the dissolved analyses when data are compared between the Agilent and Nexion methods. Data users may experience a shift in data trends for many dissolved and some WWR analytes as a result of the implementation of the Nexion ICP-MS instruments based on the data presented in this memorandum. The cause of the biases is unknown, and it is unknown whether they can be attributed to the specific application of the Nexion or Agilent ICP-MS instruments, or both. High bias in environmental data measured on the Agilent relative to the Nexion is sometimes, but not always, accompanied by an observed corresponding high bias in RM samples and laboratory matrix spikes.

Table 1. Method and analyte parameters for analytes covered by this validation study.

[P code, parameter code; NWIS, National Water Information System; DL, detection limit; RL, report limit; RL code, report limit code; µg/L, micrograms per liter]

Analyte abbreviation	Analyte	Source method[1, 2, 3]	Laboratory code	NWIS P code	NWIS method code	DL[4] (µg/L)	RL (µg/L)	NWIS RL code	Source method[1, 5, 6]	Laboratory code	NWIS P code	NWIS method code	DL[4] (µg/L)	RL (µg/L)	NWIS RL code
		Elements, water filtered							Elements, water unfiltered						
Li	Lithium	I-2477-92	2505	01130	PLM40	0.15	0.3	DLBLK	I-4472-97	3418	01132	PLM78	0.15	0.3	DLBLK
Be	Beryllium	I-2477-92	1787	01010	PLM43	0.01	0.02	DLBLK	I-4472-97	3414	01012	PLM78	0.01	0.02	DLBLK
B	Boron	I-2477-92	2504	01020	PLM40	5	10	DLBLK	I-2477-92	3415	01022	PLM78	5	10	DLBLK
Al	Aluminum	I-2477-92	1784	01106	PLM43	3	6	DLBLK	I-4472-97	3411	01105	PLM78	3	6	DLBLK
V	Vanadium	I-2020-05	3134	01085	PLM10	0.1	0.2	DLBLK	I-4020-05	3308	01087	PLM77	0.5	1	DLBLK
Cr	Chromium	I-2020-05	3126	01030	PLM10	0.5	1	DLBLK	I-4020-05	3302	01034	PLM77	0.5	1	DLBLK
Mn	Manganese	I-2477-92	1793	01056	PLM43	0.4	0.8	DLBLK	I-4472-97	3419	01055	PLM78	0.4	0.8	DLBLK
Co	Cobalt	I-2020-05	3124	01035	PLM10	0.03	0.06	DLBLK	I-4020-05	3303	01037	PLM77	0.03	0.06	DLBLK
Ni	Nickel	I-2020-05	3130	01065	PLM10	0.2	0.4	DLBLK	I-4020-05	3305	01067	PLM77	0.2	0.4	DLBLK
Cu	Copper	I-2020-05	3128	01040	PLM10	0.2	0.4	DLBLK	I-4020-05	3304	01042	PLM77	0.2	0.4	DLBLK
Zn	Zinc	I-2020-05	3138	01090	PLM10	2	4	DLBLK	I-4020-05	3309	01091	PLM77	2	4	DLBLK
As	Arsenic	I-2020-05	3122	01000	PLM10	0.05	0.1	DLBLK	I-4020-05	3301	01002	PLM77	0.05	0.1	DLBLK
Se	Selenium	I-2020-05	3132	01145	PLM10	0.05	0.1	DLBLK	I-4020-05	3306	01147	PLM77	0.05	0.1	DLBLK
Sr	Strontium	I-2477-92	2507	01080	PLM40	0.5	1	DLBLK	I-4472-97	3422	01082	PLM78	0.5	1	DLBLK
Mo	Molybdenum	I-2477-92	1794	01060	PLM43	0.05	0.1	DLBLK	I-4472-97	3420	01062	PLM78	0.05	0.1	DLBLK
Ag	Silver	I-2477-92	1796	01075	PLM43	1	2	DLBLK	I-4472-97	3421	01077	PLM78	0.03	0.06	DLBLK
Cd	Cadmium	I-2477-92	1788	01025	PLM43	0.03	0.06	DLBLK	I-4472-97	3416	01027	PLM78	0.03	0.06	DLBLK
Sb	Antimony	I-2477-92	1785	01095	PLM43	0.03	0.06	DLBLK	I-4472-97	3412	01097	PLM78	0.09	0.18	DLBLK
Ba	Barium	I-2477-92	1786	01005	PLM43	0.1	0.2	DLBLK	I-4472-97	3413	01007	PLM78	0.1	0.2	DLBLK
W	Tungsten	I-2477-92	3228	01155	PLM43	0.03	0.06	DLBLK	I-4472-97	3229	01154	PLM78	0.03	0.06	DLBLK
Tl	Thalluim	I-2477-92	2508	01057	PLM40	0.02	0.04	DLBLK	I-4472-97	3423	01059	PLM78	0.02	0.04	DLBLK
Pb	Lead	I-2477-92	1792	01049	PLM43	0.02	0.04	DLBLK	I-4472-97	3417	01051	PLM78	0.02	0.04	DLBLK
U	Uranium	I-2477-92	1797	22703	PLM43	0.01	0.02	DLBLK	I-4472-97	3424	28011	PLM78	0.03	0.06	DLBLK

[1]Faires, 1992.

[2]Garbarino, 1999.

[3]Garbarino and others, 2006;

[4]The DL concentration is reported as the "less than" value to NWIS when an analyte either is not detected or is detected at a concentration below the DL based on the reporting convention changes given in USGS Office of Water Quality Technical Memorandum 2010.07.

[5]Garbarino and Struzeski, 1998;

[6]Garbarino, 2000.

- Variability between two Nexion instruments: A subset of environmental samples was analyzed on both Nexion instruments using the same method on both, and the data were compared. For the low and high mass elements, day-to-day variability in mass spectrometer tuning has an effect on measurement bias, which is manifested as instrument variability in determined concentrations. The biases between Nexion instruments seen for all analytes except silver (Ag) are well within the data quality objectives of both the dissolved and whole-water methods.
- DISS:WWR comparison: Matrix effects could cause suppression or enhancement of analyte signals and could contribute to DISS analyte concentrations being greater than paired WWR analyte concentrations (DISS>WWR) in samples with a specific conductance greater than approximately (~)1,000 µS/cm, especially for cadmium (Cd) and Zn. Paired DISS and WWR environmental sample data was compared to determine the frequency of DISS>WWR when using the Nexion method. The frequency of DISS>WWR varied by analyte and occurred at a frequency similar to or greater than the occurrence of DISS>WWR on the Agilent method. Inclusion of field-requested matrix-spike analyses for environmental samples is an essential aid in interpreting the data where DISS>WWR occurs.

Background

From approximately October 2005 until September 30, 2016, concentrations of operationally-defined dissolved (DISS, filtered-water) and whole-water recoverable (WWR, unfiltered digested water) trace elements were measured by ICP-MS on two Agilent Technologies 7500ce ICP-MS instruments (referred to as Agilent ICP-MS or Agilent elsewhere) at the NWQL (Garbarino and others, 2006). Book 5, section B, chap. These Agilent instruments were replaced by two PerkinElmer, Inc. Nexion 350D ICP-MS instruments (referred to as Nexion ICP-MS or Nexion elsewhere) to continue to meet analytical demands. On September 30, 2016, production using the Agilent instruments for the methods listed in table 1 was discontinued and transferred to the Nexion instruments on October 1, 2016.

Table 1 lists method codes, parameter codes, laboratory codes and source methods for analytes covered by this memorandum. These codes are identical to those previously used except for the method code and laboratory code associated with dissolved and WWR tungsten (W) that were changed as a result of this validation. The parameter codes for W remain the same. All data for W from October 1, 2016, forward will be reported with the new codes. The need for this change is in the following discussion.

Typically, whole-water samples are analyzed on a single instrument and filtered samples are analyzed on a separate instrument. During the 2015 water year, 81,624 analyses for dissolved trace elements and 17,181 analyses for WWR trace elements were performed using the Agilent ICP-MS instruments.

In 2015, two PerkinElmer Nexion 350D ICP-MS instruments were installed at the NWQL. The following year, the trace element methods were optimized on these instruments and a validation study was performed. These ICP-MS instruments were validated for use in analysis of trace elements in unfiltered and filtered-water. Detection limits, variability, and bias were established for the methods on the Nexions. Because of previous concerns, the following studies were also performed:

- evaluation of potential interferences for the methods on the Nexion instruments;
- comparison of results obtained on the Agilent and Nexion ICP-MS instruments for paired environmental samples;
- characterization of Nexion instrument-to-instrument variability; and,
- evaluation of filtered and whole-water bottle pair analyte concentration agreement.

The results of these validation tests are summarized in this memorandum.

Experimental

Each of the Nexion 350D ICP-MS instruments is coupled to an Elemental Scientific Prepfast autosampler. These autosamplers employ flow injection for sample delivery to the nebulizer, which reduces the matrix load entering the sample introduction system, thus reducing analyte carryover and salt build up on the cones. It also allows the autosampler tubing to be rinsed and loaded with the next sample while data are being acquired for a prior sample. This effectively reduces the amount of time the system must be rinsed between samples, which reduces the total per-sample analysis time by nearly 50 percent compared to the Agilent ICP-MS instruments. The Prepfast was also used to perform dilutions of samples and calibrators up to 100×.

The Nexion instruments are equipped with a kinetic energy discrimination (KED) collision cell that is used to help remove molecular ion interferences. Molecular ions are formed in the plasma and in the resulting ion beam from constituents of the matrix and the argon. Molecular ions that have the same mass to charge ratio as an analyte will be measured as that analyte if not removed prior to detection. When the isotopes comprising the molecular ions are of significant abundance, they can contribute a significant positive bias to the analysis. For example, $^{40}Ar^{35}Cl^{+}$ represents a significant interference on $^{75}As^{+}$ when chloride (Cl) is present in the sample matrix. Helium gas in the collision cell collides with the ions and causes a greater loss in kinetic energy for molecules than for ions, essentially removing the molecular ions from the ion beam. A reaction gas in the cell, such as hydrogen, reacts with either the analyte of interest or the interfering molecule to shift it to another mass to charge ratio, removing the interference from the analyte mass. Analytes for which KED mode is used in this method and the cell gas used are listed in table 2. Lists of polyatomic interferences have been published elsewhere (Garbarino and others, 2006; May and Wiedmeyer, 1998).

Instrument settings were optimized for robust plasma conditions, to minimize carryover and matrix effects, and to maximize signal stability and response for each analyte. General instrument operating conditions are summarized in table 3. Instrument parameters that are optimized daily include torch position, nebulizer flow, standard and KED mode quadrupole ion deflector voltages, and the dual detector calibration. The detector voltages, mass calibration, cell entrance and exit voltages (standard mode only), and cell rod offset (standard mode only) are optimized as needed. All these parameters are optimized using the Smart Tune feature of the PerkinElmer Syngistix instrument control software and are not performed manually. A daily performance check must meet minimum criteria (table 4) before initiating calibration and sample analysis. The instrumental operating and calibration parameters specific to analytes are summarized in table 2.

All calibrators and quality control (QC) samples are prepared using 0.4 percent nitric acid (HNO_3) for dissolved analysis and 0.4 percent HNO_3/2 percent hydrochloric acid (HCl) for WWR analysis. Diluent and carrier solutions are 0.4 percent HNO_3 for dissolved analysis and 0.4 percent HNO_3/2 percent HCl for WWR analysis. Rinse/carrier solution delivered directly to the nebulizer between analyses is 5 percent HNO_3 to reduce analyte carryover in the nebulizer and spray chamber. Ultrapure-grade acid is used for all solutions.

Table 2. Nexion ICP-MS instrumental operating and calibration parameters by analyte.

[m/z, mass to charge ratio monitored; L/min, liters per minute; s, seconds; KED, kinetic energy discrimination mode; --, no gas was used; He, helium; H2, hydrogen]

Analyte	m/z	Mode	Gas/flow (L/min)	Dwell time/ integration time (s)	Curve type	
					Dissolved	Whole-water recoverable
Lithium	7	Standard	--	50/750	Weighted linear	Weighted linear
Beryllium	9	Standard	--	50/750	Weighted linear	Weighted linear
Boron	11	Standard	--	50/750	Weighted linear	Weighted linear
Aluminum	27	Standard	--	50/750	Weighted linear	Weighted linear
Vanadium	51	KED	He/4.3	50/750	Weighted linear	Weighted linear
Chromium	52	KED	He/4.3	50/750	Weighted linear	Weighted linear
Manganese	55	Standard	--	50/750	Weighted linear	Weighted linear
Cobalt	59	KED	He/4.3	50/750	Weighted linear	Weighted linear
Nickel	60	KED	He/4.3	50/750	Weighted linear	Weighted linear
Copper	63	KED	He/4.3	50/750	Weighted linear	Weighted linear
Zinc	66	KED	He/4.3	50/750	Weighted linear	Weighted linear
Arsenic	75	KED	He/4.3	100/1,500	Weighted linear	Weighted linear
Selenium	78	KED	H_2+He/1+2.6	100/1,500	Weighted linear	Weighted linear
Strontium	88	Standard	--	50/750	Weighted linear	Weighted linear
Molybdenum	95	Standard	--	50/750	Weighted linear	Weighted linear
Silver	107	Standard	--	50/750	Simple linear	Weighted linear
Cadmium	111	Standard	--	50/750	Weighted linear	Weighted linear
Antimony	121	Standard	--	50/750	Weighted linear	Weighted linear
Barium	137	Standard	--	50/750	Linear through zero	Weighted linear
Tungsten	182	Standard	--	50/750	Weighted linear	Weighted linear
Thallium	205	Standard	--	50/750	Weighted linear	Weighted linear
Lead	206+207+208	Standard	--	50/750	Weighted linear	Weighted linear
Uranium	238	Standard	--	50/750	Weighted linear	Weighted linear

Table 3. Nexion ICP-MS instrumental operating conditions.

[I.D., inner diameter; mm, millimeter; L/min, liters per minute; W, watts]

Component/parameter	Type/value/mode
Nebulizer	ESI PFA-ST 0.25 mm I.D.
Spray chamber	Quartz glass cyclonic w/peltier cooler
Injector	Sapphire, 1.8 mm
Torch	High matrix demountable quartz
Triple cone interface material	Nickel/aluminum
Plasma gas flow	18 L/min
Auxiliary gas flow	1.2 L/min
Nebulizer gas flow	0.85–1.0 L/min
RF power	1,600 W
Sweeps per reading/replicates per sample	15 sweeps/3 replicates

Table 4. Nexion daily performance check minimum criteria for initiating calibration and sample analysis.

[Be, beryllium; In, indium; U, uranium; Bkgd, background; CeO, cerium odixe; Ce, cerium; Ce^{++}, doubly charged cerium; >, greater than; ≤, less than or equal to]

Analyte	Comparator	Target
Be 9	>	2,000 counts
In 114	>	40,000 counts
U 238	>	30,000 counts
Bkgd 220	≤	1 count
CeO 156/Ce 140	≤	0.02
Ce++70/Ce 140	≤	0.03

A minimum of five calibration points are used to construct calibration curves for each analyte. A weighted linear regression curve was selected for most analytes for this validation (table 2). During initial experiments, for certain analytes a linear regression curve forced through zero yielded lesser bias for QC samples in the upper one-third of the curve and comparable bias and variability for QC samples in the lower one-third of the curve, and, therefore, is used. QC samples containing all analytes in both the lower one-third and upper one-third of the calibration curve and a blank sample are analyzed for every 10 environmental samples analyzed.

Since the in-bottle digestion (INBD, Hoffman and others, 1996) procedure used for the WWR analysis introduces a 2 percent dilution of the sample by addition of HCl, a correction is automatically included in the sample concentration calculation to account for this dilution (Stetson and Garbarino, 2017). This correction was applied to all WWR data presented in this report unless specifically noted in the results section.

Initial experiments yielded insufficient sensitivity for arsenic (As) and selenium (Se) to meet existing DL requirements of the NWQL. Also, as the concentration of ions in solution increased, significant matrix effects were observed in some analyte and internal standard (IS) recoveries. Therefore, a matrix modifier of 5 percent HNO_3 and 50 percent glacial acetic acid is added to the acid matrix-matched internal standard solution. When mixed with a sample, this creates a solution of 1 percent HNO_3/10 percent acetic acid (dissolved) or 1 percent HNO_3/10 percent acetic acid/2 percent HCl (WWR) entering the nebulizer. The increased acid content helps reduce matrix effects for environmental samples, calibrators, and QC samples. Acetic acid also serves as a carbon source to increase ionization (and thus sensitivity) in the plasma for elements with high ionization potentials including As and Se (Allain and others, 1991). This solution was effective in providing adequate sensitivity for As and Se.

Interference Studies

Because of design differences of the collision cell and ion path of the Nexion compared with the Agilent ICP-MS, a study was performed to determine removal efficiency of spectral interferences (May and Wiedmeyer, 1998). Some common interferences in ICP-MS analysis include a ClO overlap on vanadium (V) 51 and an ArCl overlap on As 75. A reagent-water solution containing 250 milligram per liter (mg/L) of trace-metal grade HCl was analyzed by the DISS and WWR ICP-MS methods.

Sample conductivity also represents matrix in environmental samples that could be a source of interference in ICP-MS analysis of trace elements. A study of the effect of increasing sample conductivity was performed. The NWQL uses sample conductivity to determine if a sample needs to be diluted prior to analysis by ICP-MS. Samples with conductivity greater than 2,500 microsiemens per centimeter (µS/cm) were routinely diluted prior to analysis on the Agilent instruments. To determine the effect of increasing sample conductivity, samples covering the range of conductivity from 0 to 2,500 µS/cm were spiked with all analytes and recoveries determined on the Nexion. Serial dilutions of filtered groundwater and surface-water samples with high specific conductance were prepared to achieve the range of conductances. Three surface-water samples and three groundwater samples were used to make the dilutions for dissolved analysis. Two surface-water samples and one groundwater sample were used to make the dilutions for the WWR analysis. Specific conductance of each dilution was determined using USGS method I-2781-85 (Fishman and Friedman, 1989). Aliquots of these dilutions were spiked with 10 µg/L of each analyte measured by ICP-MS as a mixed stock standard solution. These diluted unspiked and spiked samples were acidified using 0.4 percent HNO_3 for analysis by the dissolved method and using 0.4 percent HNO_3/2 percent HCl for analysis by the WWR method. Each

unspiked and corresponding spiked sample was analyzed and the analyte's spike recovery was calculated using the determined concentrations in micrograms per liter (µg/L) as:

$$spike\ recovery,\ in\ percent = \frac{[spiked\ sample]-[unspiked\ sample]}{[spike\ sample\ expected]} \times 100$$

where [*spike sample expected*] is the expected or theoretical concentration based on the amount of standard solution fortified into the spiked sample.

Validation Studies

Between May 20, 2016 and July 15, 2016, three analysts collected validation data (table 5). Because of previous questions about instrument-to-instrument variability, validation of the dissolved analysis was performed using both instruments (table 5). All glassware used for sample introduction were soaked in HNO_3 and the cones on the instrument used for the whole-water validation samples were replaced prior to analyzing the filtered-water validation samples in order to minimize the Cl background in the instrument from the WWR matrix.

Table 5. Validation analytical batches for the validation study, analyst, and instrument used to acquire data.

[WF, filtered water; WWR, whole water recoverable]

Validation batch	Analyst	Instrument
WF 1	1	1
WF 2	2	1
WF 3	2	1
WF 4	2	1
WF 5	2	2
WF 6	2	2
WWR 1	2	1
WWR 2	3	1
WWR 3	1	1
WWR 4	1	1
WWR 5	1	1
WWR 6	1	1

Determined concentrations from seven calibrations performed over at least three different days were used to calculate DLs using the ASTM DQCALC software (ASTM International, 2010; Williams and others, 2015). The DL estimated by this program is referred to here as DLDQC. The 99th percentile value from blanks and carryover washes was used as an estimate of the DL (DLBLK) as an additional DL estimation. The number of carryover blanks and QC blanks used for this analysis was >100 for both dissolved and WWR analyses. Carryover washes were included in this DL estimation because carryover cannot be completely eliminated from the analysis for some analytes and therefore should be accounted for in the DL calculation.

National Institute for Standards and Technology (NIST) standard reference material (SRM) 1640a contains ~2 percent nitric acid. No acid matrix matching was attempted for this sample. It was analyzed without filtration or addition of HCl using both the WWR and dissolved analyses, including calibrators in the normal dissolved (0.4 percent nitric acid) and WWR matrices (0.4 percent HNO_3/2 percent HCl). The U.S. Geological Survey (USGS) Branch of Quality Systems' (BQS) standard reference samples (SRS) T-215 and T-219 were processed by INBD in the same manner as whole-water environmental samples prior to WWR analysis and, therefore, were matrix matched.

Spikes near the estimated DL, and in the lower one-third and upper one-third of the curve were prepared in the filtered and whole-water acidified surface water, groundwater, and blank water using stock solution containing certified amounts of all analytes of interest. Groundwater was collected from a domestic well near Elizabeth, Colo. Surface water was provided by Denver Water and was collected from the raw water inlet to the Foothills drinking water treatment plant, which is supplied by the South Platte River at the outlet of Strontia Springs Reservoir (near Roxborough Park, CO). Aliquots of the surface water and groundwater used for the dissolved analysis were filtered using a 0.45 micrometer (µm) filter, then acidified to 0.4 percent HNO_3 and then spiked or diluted. Aliquots used for the WWR analysis were acidified to 0.4 percent HNO_3 and then processed through an INBD. ASTM Type I water (blank water) was acidified to 0.4 percent HNO_3 for preparing dissolved spikes and with 0.4 percent HNO_3/2 percent HCl for WWR spikes. This matrix was not processed though the INBD. In the case of the WWR matrices, the samples were spiked after the HCl was added. The NIST SRM and whole-water matrix surface-water, groundwater, and blank spike mean recovery data was adjusted down by 2 percent since these samples were not subjected to the INBD process and there was no dilution of the samples. The WWR method has a 2 percent correction that is automatically applied to all data to correct for the 2 percent dilution that occurs when HCl is added to WWR samples prior to the INBD processing. All SRM, SRS and spiked groundwater and surface water samples were analyzed in replicate by intermingling with the environmental samples. Where QC did not pass during the analysis for an analyte, the sample was not necessarily re–analyzed resulting in the number of data points (n) used for each analyte ranging from 4 to 26.

About 100 filtered environmental samples and about 100 INBD-processed whole-water environmental samples were selected for analysis on the Nexion ICP-MS. All samples had been previously analyzed on the Agilent ICP-MS as routine production samples. Samples were selected to span a wide range of conductivities and hydrologic conditions. Approximately 60 percent of selected samples were surface water and approximately 40 percent were groundwater. These samples were analyzed over six separate days on the Nexion ICP-MS and the measured concentrations compared to those measured on the Agilent ICP-MS.

Results and Discussion

Detection Limit Determination

Calculated DLs from DLBLK determinations, DLs applied for samples analyzed in water year 2016, and DLs that were selected for use starting October 1, 2016, are summarized in table 6. Calculated DLs from the DQCALC program are presented in attachment 1. Blank and carryover wash data were used to establish the DL, and the RL code is DLBLK. For most analytes, the applied DL will remain the same as it was with the Agilent ICP-MS or be lowered. The DL will be raised for dissolved and WWR Cr, WWR U, and dissolved Ag. WWR lead and barium (Ba) applied DLs are lower than the DLBLK value indicates. A single contamination occurrence led to the elevated DLBLK values that is not expected to be a recurring problem.

There is a molecular interference ($^{40}Ar^{12}C^{+}$) on ^{52}Cr caused by the acetic acid matrix modifier that is not completely eliminated by the KED collision cell. The $^{40}Ar^{12}C^{+}$ increases the background and results in the increased DL for Cr. Blank and carryover wash values for WWR Pb ranged up to 0.04 µg/L, indicating some presence of carryover. Lead is known to be difficult to rinse out after a high calibrator or sample. The DL for dissolved Ag is increasing significantly because of chronic carryover problems observed during the validation study. This carryover is isolated to Ag on the new instrumentation with the 0.4 percent HNO_3 matrix used on the dissolved line. While Ag is stable in the 0.4 percent nitric/2 percent HCl acid matrix used for WWR, it has been found to have high carryover during sample introduction using the Prepfast when in the 0.4 percent nitric acid matrix. Therefore, the applied DL for WWR Ag remains low while it was increased for dissolved Ag.

Table 6. Detection limits, in micrograms per liter, applied for the previous method on the Agilent inductively coupled plasma mass spectrometer (ICP-MS) and method on the Nexion ICP-MS along with detection limits calculated using the 99th percentile of blank values.

[DL, detection limit; DLBLK, detection limit set at the 99th percentile of blank values; µg/L, micrograms per liter]

Analyte	Dissolved			Whole-water recoverable		
	Applied DL		DLBLK (µg/L)	Applied DL		DLBLK (µg/L)
	Agilent DL (µg/L)	Nexion DL[1] (µg/L)		Agilent DL (µg/L)	Nexion DL[1] (µg/L)	
Lithium	0.22	0.15	0.15	0.22	0.15	0.07
Beryllium	0.02	0.01	0.002	0.02	0.01	0.003
Boron	5	5	2.2	5	5	1.8
Aluminum	3	3	0.33	3.8	3	0.72
Vanadium	0.1	0.1	0.015	1	0.5	0.08
Chromium	0.3	0.5	0.23	0.4	0.5	0.09
Manganese	0.4	0.4	0.15	0.4	0.4	0.23
Cobalt	0.05	0.03	0.02	0.05	0.03	0.02
Nickel	0.2	0.2	0.1	0.2	0.2	0.04
Copper	0.8	0.2	0.03	0.8	0.2	0.03
Zinc	2	2	0.8	2	2	0.15
Arsenic	0.1	0.05	0.02	0.2	0.05	0.01
Selenium	0.05	0.05	0.01	0.1	0.05	0.02
Strontium	0.8	0.5	0.3	0.8	0.5	0.52
Molybdenum	0.05	0.05	0.02	0.05	0.05	0.03
Silver	0.02	1	0.5	0.03	0.03	0.01
Cadmium	0.03	0.03	0.005	0.03	0.03	0.02
Antimony	0.027	0.03	0.006	0.18	0.09	0.02
Barium	0.25	0.1	0.04	0.25	0.1	0.24
Tungsten	0.03	0.03	0.004	0.03	0.03	0.006
Thallium	0.03	0.02	0.006	0.06	0.02	0.006
Lead	0.04	0.02	0.008	0.04	0.02	0.04
Uranium	0.01	0.01	0.009	0.014	0.03	0.03

[1]The applied detection limit for the Nexion method has been set higher than the calculated DLBLK in some cases because of known issues with sample contamination (B, Al), because of a known interference (Cr, V), or because an incremental approach to lowering the detection limit from the level on the Agilent to the DLBLK level was preferred.

The DL for WWR V was set conservatively high because interference from the Cl matrix is not completely eliminated by the collision cell, thus reducing the overall sensitivity. For several other analytes, lowering the DL to the DLBLK value would represent a large change in DL. A conservative incremental approach to lowering DLs was preferred by the NWQL. If a year of sample analysis and QC data supports or confirms a lower DL, the DL will be lowered again at the end of the 2017 water year.

In some cases the DLDQC value is much lower than the DLBLK value because the instrument has excellent sensitivity and reproducibility for the analyte with little or no interference, but carryover or contamination during preparation and analysis is a concern. Glassware can contribute to B background and Al is common in the laboratory environment. The DL for Al was set at the same level it was at with the Agilent method, significantly higher than supported by the data presented. The previous year's Al BQS blind blank and blind sample data indicate that an even higher DL might be needed compared to the applied compared DL. The low blank and carryover values observed during validation suggest that careful laboratory practices, especially during pour up of samples, attention to potential carryover situations, and periodic cleaning or replacement of sample carrier lines on the autosampler would allow for a lower DL for Al.

Chloride Interferences

Chlorine-containing molecular ions formed in the plasma can interfere with the ICP-MS analysis of As, Cr, copper (Cu), manganese (Mn), nickel (Ni), and V. With the exception of Mn, these analytes are analyzed using the collision cell, which is generally highly effective at removing molecular ion interferences from the ion beam prior to detection of each analyte (Garbarino, 2006). In the case of Mn, the interfering Cl molecules are from minor isotopes and not expected to be significant. The background counts at ^{51}V are much lower on the dissolved analysis than on the WWR analysis. The HCl from the WWR matrix contributes $^{35}Cl^{16}O$ to the background signal and at the levels in this matrix, the collision cell is not effective at removing all of this interference. This causes lower sensitivity for V and, therefore, a higher DL on the WWR method than on the dissolved method. This was true of the Agilent method and occurs with the Nexion method as well.

Since environmental samples analyzed at the NWQL vary widely in Cl concentration, it was necessary to verify that other Cl interferences were fully removed by the collision cell. No measured analyte concentration in a reagent-water solution containing 250 mg/L of Cl as HCl was above the DL with one exception (table 7). Al was detected at ~3 µg/L in both the dissolved and WWR solutions containing HCl. Since there is no Cl interference on Al, the Al detection is likely because of Al contamination in the concentrated HCl used to make the test solution.

Specific Conductance Related Interference

When samples with a specific conductance greater than 2,500 µS/cm were analyzed on the Nexion ICP-MS, internal standard recoveries in both the filtered and whole-water matrix dropped below an acceptance threshold of 70 percent, confirming the need for dilution of samples having conductivity greater than 2,500 µS/cm for analysis on those instruments. This is the same conductivity threshold for dilution used on the Agilent ICP-MS. High solute content in samples also causes sample viscosity changes that affect conditions in the nebulizer and spray chamber, and matrix loading in the plasma that can lead to interference for some analytes. The interferences can result in negative or positive bias, and represent signal suppression or a positive signal enhancement because of molecular or atomic interference from ions or molecules that are present at concentrations higher than routinely observed for most samples.

As conductivity of dissolved samples increases, the recovery of the 10 µg/L spiked water samples increases for molybdenum (Mo), Se, V, Cr, and As and reaches ~110 percent or higher recovery (Se, V, Cr, As) or ~120 percent (Mo) at a conductivity of ~2,500 µS/cm (figs. 1–5). This trend appears to hold for the WWR spiked water samples as well, but there are fewer data points so the trend is less clear. Cd and Zn show is a 10–20 percent low bias in spike recovery as conductivity approaches 2,500 µS/cm. This appears to occur for both dissolved and WWR analyses, with the suppression appearing to be slightly greater on the WWR analysis (figs. 6 and 7). Depending on the sample matrix composition and Zn and Cd concentrations, this effect could contribute to DISS>WWR concentrations in samples with a specific conductance greater than ~1,000 µS/cm. For example, if a WWR sample has a significant amount of particulate that contributes to the total dissolved solids in the sample upon digestion, then it is expected that there will be greater suppression of the Zn and Cd signals in the WWR sample because of the greater matrix (higher conductivity) than in the dissolved sample.

All the analytes discussed thus far in this section show a distinct pattern of bias with increasing specific conductance. For B there is increased variability in recoveries with increasing conductivity and potentially some bias, but the trend is less clear (fig. 8). This could also ultimately contribute to DISS>WWR.

Table 7. Uncensored blank values measured in reagent-water and reagent-water spiked with 250 milligrams per liter chloride as hydrochloric acid (HCl).

[DL, detection limit; µg/L, micrograms per liter; HCl, hydrochloric acid]

Analyte	Dissolved			Whole-water recoverable		
	DL (µg/L)	Blank (µg/L)	Blank with HCl (µg/L)	DL (µg/L)	Blank (µg/L)	Blank with HCl (µg/L)
Lithium	0.15	0.005	0.034	0.15	0.025	0.011
Beryllium	0.01	0.000	0.000	0.01	0.001	0.001
Boron	5	0.042	1.031	5	1.085	1.275
Aluminum	3	1.219	3.124	3	1.024	3.042
Vanadium	0.1	–0.003	0.017	0.5	–0.014	–0.004
Chromium	0.5	–0.248	0.123	0.5	0.043	0.104
Manganese	0.4	0.008	0.007	0.4	0.017	0.022
Cobalt	0.03	–0.002	0.002	0.03	0.001	0.003
Nickel	0.2	–0.157	0.003	0.2	0.019	0.097
Copper	0.2	0.005	0.031	0.2	–0.002	0.035
Zinc	2	0.260	0.272	2	0.750	0.321
Arsenic	0.05	0.003	0.001	0.05	–0.003	0.000
Selenium	0.05	0.001	0.003	0.05	–0.002	–0.001
Strontium	0.5	0.001	0.017	0.5	0.016	0.015
Molybdenum	0.05	–0.031	0.000	0.05	–0.004	–0.005
Silver	1	0.080	0.263	0.03	0.001	0.004
Cadmium	0.03	0.002	0.002	0.03	0.001	0.002
Antimony	0.03	0.003	0.005	0.09	0.019	0.003
Barium	0.1	–0.005	0.000	0.1	0.002	0.008
Tungsten	0.03	0.017	0.044	0.03	0.058	0.013
Thallium	0.02	0.002	0.005	0.02	0.001	0.001
Lead	0.02	0.002	0.011	0.02	0.003	0.008
Uranium	0.01	0.001	0.001	0.03	0.001	0.001

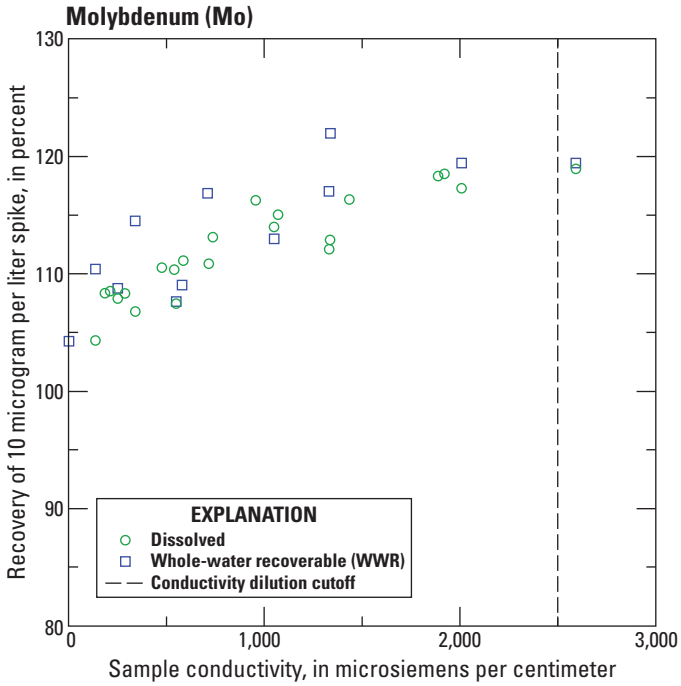

Figure 1. Percent recovery of a 10 microgram molybdenum (Mo) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

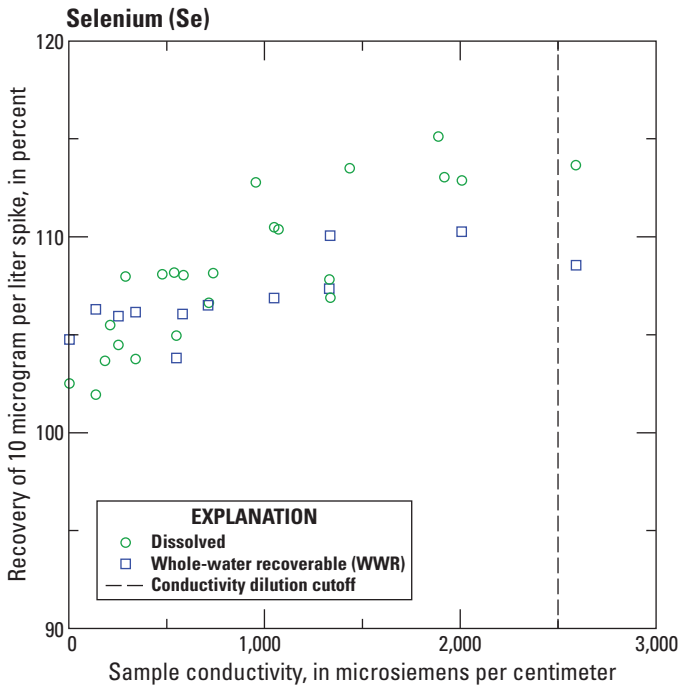

Figure 2. Percent recovery of a 10 microgram selenium (Se) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

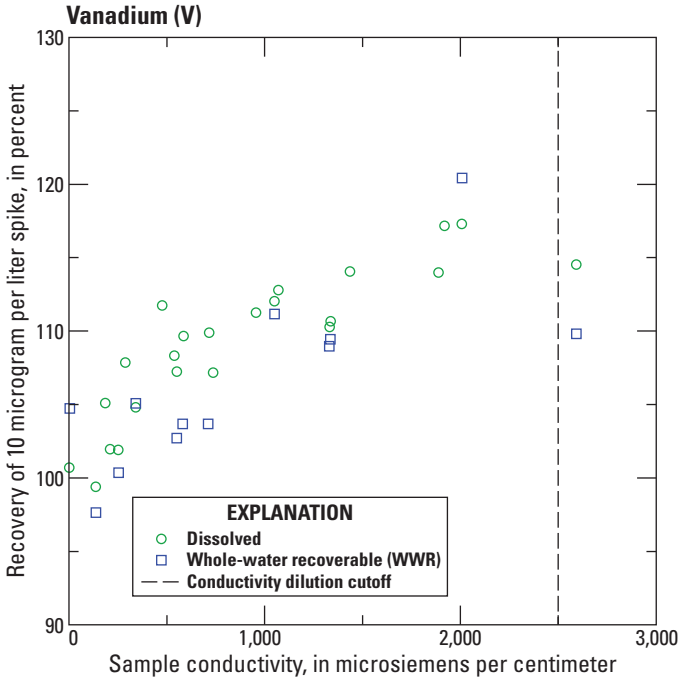

Figure 3. Percent recovery of a 10 microgram vanadium (V) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

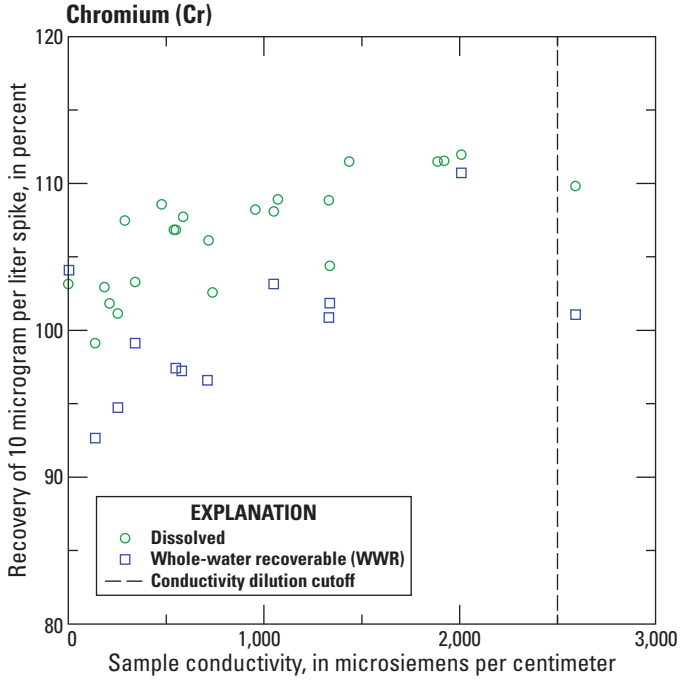

Figure 4. Percent recovery of a 10 microgram chromium (Cr) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

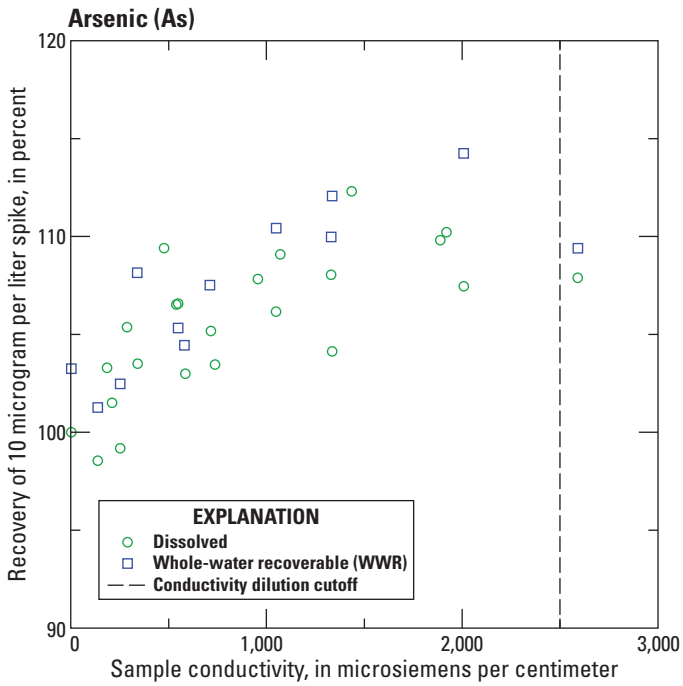

Figure 5. Percent recovery of a 10 microgram arsenic (As) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

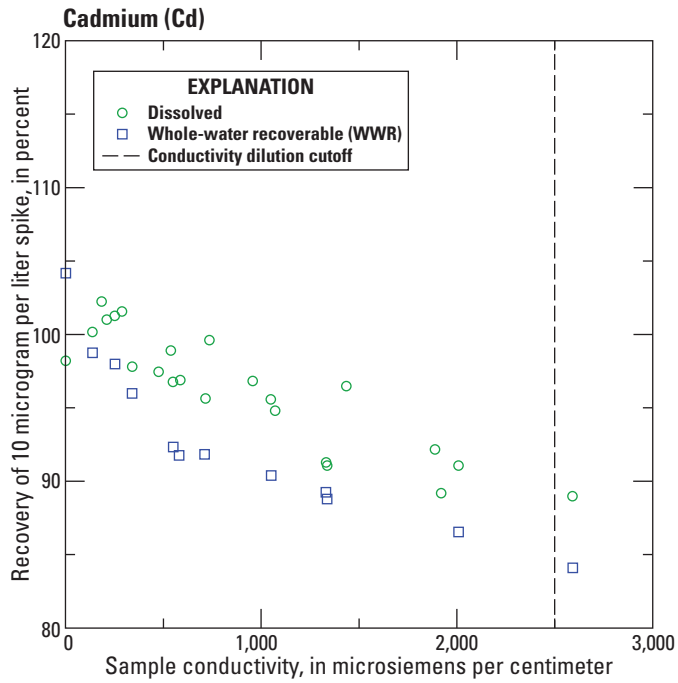

Figure 6. Percent recovery of a 10 microgram cadmium (Cd) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

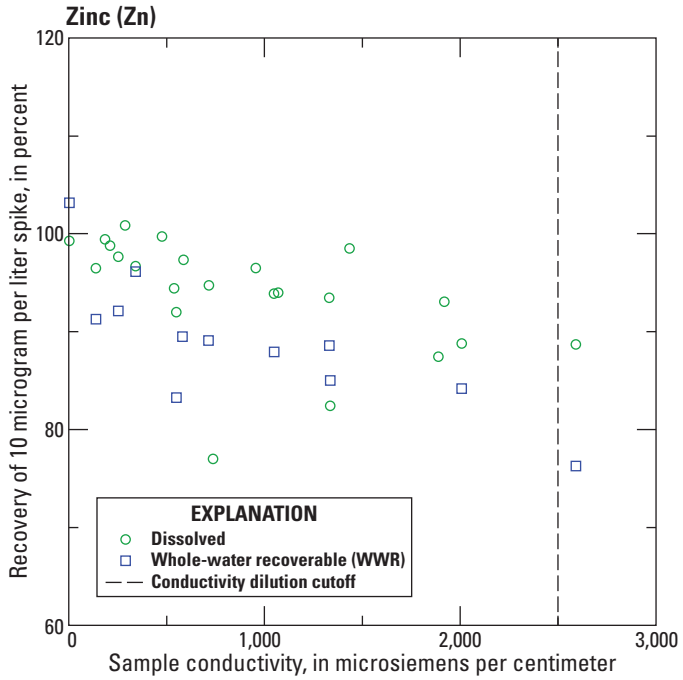

Figure 7. Percent recovery of a 10 microgram zinc (Zn) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

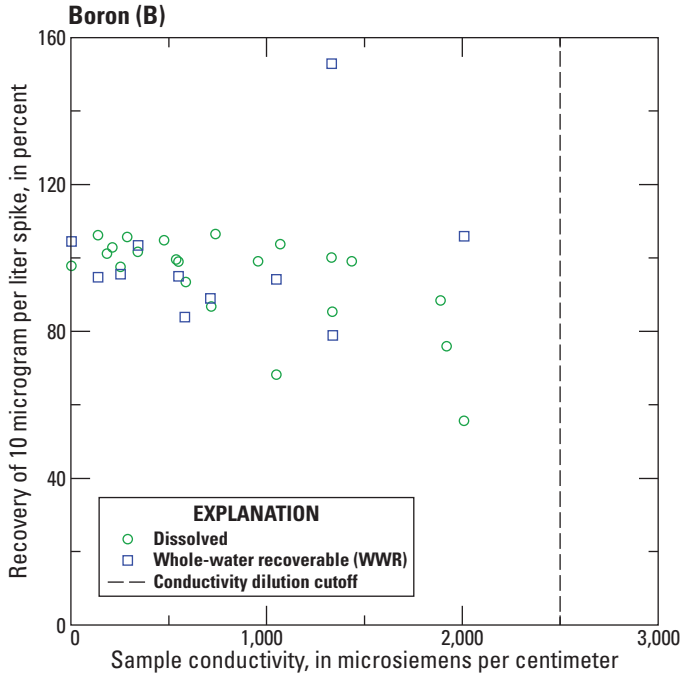

Figure 8. Percent recovery of a 10 microgram boron (B) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

Recovery of Ag dropped as specific conductance increased. The level of suppression depends on the acid matrix, whether filtered or whole water (fig. 9). Some of the decrease in Ag recovery is likely because of sample matrix effects in the plasma that cause signal suppression. Recovery was lower in the filtered matrix and could be because of Cl presence in the matrix at a concentration that causes Ag to fall out (precipitate) of solution as particles. Recovery of QC samples for Ag in the dissolved analysis decreased as analysis of a given batch of samples proceeded with time, suggesting that there is a cumulative effect on the instrument of sample matrix over time. Although Ag is stable (remains dissolved) in reagent-water containing 2 percent HCl, it may not be stable with 0.4 percent nitric acid preservation and the sample matrices used to model increasing specific conductance in the test samples that contain varying concentrations of Cl (attachment 2) since dissolved Ag may not be stable in solutions with lower levels of Cl.

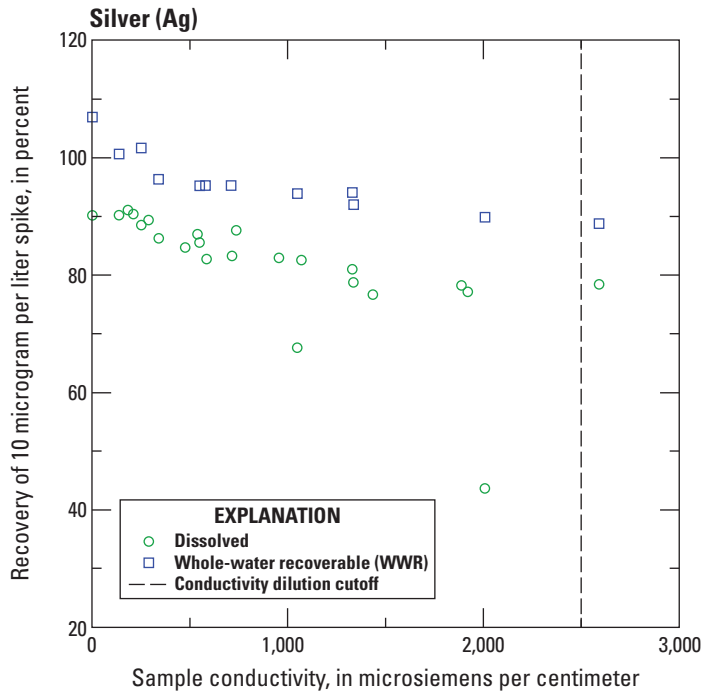

Figure 9. Percent recovery of a 10 microgram silver (Ag) per liter spike in groundwater and surface waters with increasing conductivity compared with sample conductivity. Analyses were performed in both a dissolved and whole-water recoverable (WWR) matrix.

Interference effects associated with these higher conductivity samples could not be entirely attributed to a single major cation or anion. Available data for the major cations for each sample used in the specific conductance study are included in attachment 2. Customers who submit samples to the ICP-MS analyses with specific conductance >1,000 µS/cm should be aware of potential bias and increased variability that will be inherent in the analysis of such samples because of the matrix, and consider the information in this report when interpreting their sample data. Data in attachment 2 also demonstrate that matrix effects do not always follow a linear correlation with specific conductance. Therefore, the inclusion of field-requested matrix-spike analyses for environmental samples is an essential aid in interpreting the data provided the spikes are at the appropriate levels.

Variability and Bias Studies

Mean recoveries in the NIST 1640a SRM by the dissolved analysis were between 95 and 105 percent of the certified value for most analytes (table 8). Dissolved Li, V, strontium (Sr), Ag, Cd, and antimony (Sb) recoveries were between 90 and 110 percent. Dissolved Zn recovery was 88.0 percent. As observed for the dissolved analysis, mean recoveries of most WWR analytes were between 95 and 105 percent. Recoveries of WWR B, Sr, Mo, Cd, thallium (Tl), Pb, and U recoveries were between 90 and 110 percent. Whole-water recoverable Be and Zn had recoveries of 87.7 percent and 84.0 percent, respectively.

The conductivity of NIST 1640a is unknown and cannot be determined because it is supplied in an acid matrix of 2 percent HNO_3. It is suspected that the low Zn recovery by either analysis is because of signal suppression by the SRM matrix. The acid content of NIST 1640a was not adjusted to 2 percent HCl for the WWR analyses although the calibrators contained 2 percent HCl and were not matched to this SRM. During this study, NIST 1640a was run diluted 1:3 for several replicates using the same acid matrix the samples and calibrators have in each method. Diluted and undiluted replicates were used to calculate the averages in table 8 where the data were within the calibration range and diluted values were above the DL. When only diluted data are used to calculate dissolved Zn recovery, the recovery is 94 percent (n=10) and relative standard deviation is 2 percent. The internal standard used to correct Zn data shows greater suppression in the undiluted analysis as well, although to a lesser degree. This supports the hypothesis that low Zn recovery is because of matrix effects whose effects are reduced by dilution of the sample and not completely corrected for by the internal standard. However, it is impossible to decipher whether the acid mismatch or the major ion and cation content of the SRM is the source of the bias.

Recoveries of DISS and WWR analytes in SRS T-215 and T-219 were generally between 90 and 110 percent of the MPV (tables 9 and 10) although there are several exceptions. Recoveries of Se were 76.2–80.2 percent for both dissolved and WWR analyses. This is consistent with Se data obtained for this SRS from the Agilent ICP-MS as summarized by the USGS Branch of Quality Systems Inorganic Blind Sample Program (bqs.usgs.gov/ibsp/; 70–79 percent mean recovery for data collected from

October 1, 2015 to September 26, 2016) and to a lesser extent with the original values reported by the NWQL in the USGS Branch of Quality Systems round robin studies used to determine the most probable values for these samples. The NWQL reported 0.426 µg/L Se (73.5 percent of MPV) for T-215 and 0.58 µg/L Se (93.55 percent of MPV) for T-219.

The MPV for Cr in T-219 is below the DL of the Nexion method, but because the measured values are above the DL and therefore would be reported, the data are included. Recovery of Cr on both DISS and WWR is high (199.6 percent and 241.5 percent respectively) but is consistent with data obtain for this SRS from the Agilent ICP-MS as summarized by the USGS Branch of Quality Systems Inorganic Blind Sample Program (bqs.usgs.gov/ibsp/). Recovery of Cr is slightly greater than 110 percent for T-215 on both DISS and WWR. Recovery of Ni in T-215 by DISS is low (68.8 percent) and by WWR is high (161.3 percent), but the MPV is within 4 times the DL. The high variability in recovery of WWR Ni for T-215 is largely because of measurements made on one day of analysis, and it is suspected the sample was contaminated because no other spike, QC or replicated sample show the same magnitude of variability in precision. The precision of this analyte near the DL will be monitored closely for the first year using a QC sample at the DL and blind submissions of T-215. The high recoveries of Ni for T-215 on WWR and T-219 on both DISS and WWR were somewhat consistent with data obtained for this SRS from the Agilent ICP-MS as summarized by the USGS Branch of Quality Systems Inorganic Blind Sample Program (bqs.usgs.gov/ibsp/). Recovery of B is slightly above 110 percent for both SRS samples, which are both within 4 times the DL. Similar high bias was not observed in the reagent-water spiked at 40 µg/L, suggesting that this high bias is concentration-dependent and limited to data that is less than 8 times the DL.

Table 8. Bias and variability of results from standard reference material NIST 1640a.

[MPV, most probable value; DL, detection level; SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; µg/L, micrograms per liter; %, percent; --, no data available]

Analyte	MPV (µg/L)	Dissolved						Whole-water recoverable					
		DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	0.4066	0.15	0.45	0.03	7.2	109.8	12	0.15	0.40	0.04	10.1	99.3	16
Beryllium	3.026	0.01	2.9	0.2	6.6	95.0	12	0.01	2.7	0.2	8.5	87.7	16
Boron	303.1	5	295	10	3.2	97.3	15	5	272	19	6.9	89.5	16
Aluminum	53	3	55	3	4.7	104.6	22	3	52	2	3.8	97.4	16
Vanadium	15.05	0.1	16	1	3.5	105.9	23	0.5	15	0.3	2.2	100.9	16
Chromium	40.54	0.5	42	1	3.4	102.7	22	0.5	41	1	2.7	100.9	16
Manganese	40.39	0.4	42	2	4.1	104.4	22	0.4	41	2	4.5	100.6	16
Cobalt	20.24	0.03	21	1	3.1	102.2	23	0.03	21	1	2.8	101.6	16
Nickel	25.32	0.2	26	1	2.9	101.2	23	0.2	25	1	3.1	99.1	16
Copper	85.75	0.2	87	2	2.4	101.8	23	0.2	85	3	3.0	98.7	16
Zinc	55.64	2	49	3	6.2	88.0	23	2	47	5	9.8	84.0	16
Arsenic	8.075	0.05	8	0.2	2.5	101.7	22	0.05	8.1	0.3	3.8	100.6	16
Selenium	20.13	0.05	21	0.3	1.4	102.6	10	0.05	20	1	2.8	98.7	10
Strontium	126.03	0.5	136	5	3.7	107.9	23	0.5	132	3	2.2	105.1	16
Molybdenum	45.6	0.05	46	1	2.3	101.0	23	0.05	49	2	4.9	108.1	16
Silver	8.081	1	7.6	0.2	3.0	94.4	20	0.03	8.2	0.2	2.0	100.9	16
Cadmium	3.992	0.03	3.7	0.2	4.1	93.8	23	0.03	3.6	0.2	5.9	90.9	16
Antimony	5.105	0.03	4.8	0.2	4.3	94.8	23	0.09	5.0	0.2	3.3	98.1	16
Barium	151.8	0.1	149	5	3.2	97.9	19	0.1	153	3	2.3	100.5	8
Tungsten	--	0.03	0.01	0.002	12.8	--	13	0.03	0.015	0.002	12.1	--	16
Thallium	1.619	0.02	1.6	0.1	3.2	101.2	23	0.02	1.7	0.03	1.9	105.6	15
Lead	12.101	0.02	12	0.2	2.0	98.8	23	0.02	12	0.3	2.8	102.5	16
Uranium	25.35	0.01	26	0.9	3.3	101.7	23	0.03	26	1	5.5	103.7	12

Table 9. Bias and variability of results from U.S. Geological Survey standard reference sample T-215.

[MPV, most probable value; DL, detection limit; SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; µg/L, micrograms per liter; %, percent; --, no data available]

Analyte	MPV (µg/L)	Dissolved						Whole-water recoverable					
		DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	8.4	0.15	8.8	0.5	5.5	104.2	20	0.15	8.3	0.2	2.5	98.7	7
Beryllium	0.485	0.01	0.51	0.02	3.9	105.4	19	0.01	0.49	0.02	4.1	101.4	7
Boron	15.8	5	18	0.9	4.9	113.5	18	5	17	0.9	5.1	110.1	7
Aluminum	121	3	129	5	4.0	106.5	19	3	127	4	3.2	104.9	7
Vanadium	0.312	0.1	0.34	0.02	5.9	107.9	20	0.5	--	--	--	--	--
Chromium	2.8	0.5	3.1	0.2	5.8	110.5	18	0.5	3.1	0.3	8.0	112.1	7
Manganese	76.9	0.4	83	2	2.9	107.8	20	0.4	82	3	3.1	106.6	7
Cobalt	1.19	0.03	1.2	0.06	5.0	102.5	19	0.03	1.3	0.03	2.4	106.5	7
Nickel	0.54	0.2	0.37	0.06	16	68.8	20	0.2	0.87	0.8	86.2	161.3	7
Copper	0.764	0.2	0.93	0.08	8.6	121.2	20	0.2	0.78	0.02	2.6	102.4	7
Zinc	4.45	2	4.6	0.4	8.0	102.9	17	2	4.3	0.3	7.8	97.5	7
Arsenic	0.51	0.05	0.47	0.03	6.4	93.1	19	0.05	0.48	0.03	6.3	94.3	7
Selenium	0.58	0.05	0.45	0.02	4.4	77.2	20	0.05	0.44	0.02	4.5	76.2	7
Strontium	257	0.5	279	8	2.7	108.5	20	0.5	280	7	2.5	108.8	7
Molybdenum	1.53	0.05	1.7	0.03	1.8	108.6	20	0.05	1.6	0.04	2.5	105.8	7
Silver	5.69	1	5.7	0.3	4.4	99.6	20	0.03	6.1	0.1	2.0	106.9	7
Cadmium	3.85	0.03	4.0	0.09	2.3	103.3	20	0.03	4.0	0.1	3.3	103.7	7
Antimony	1.59	0.03	1.6	0.05	3.1	99.8	20	0.09	1.6	0.02	1.3	98.9	6
Barium	39	0.1	39	1	3.8	100.9	20	0.1	39	0.7	1.9	98.8	7
Tungsten	--	0.03	0.09	0.004	4.4	--	20	0.03	0.10	0.01	10.0	--	7
Thallium	7.03	0.02	7.1	0.3	4.3	100.3	20	0.02	7.3	0.2	2.0	104.3	7
Lead	0.4	0.02	1.7	0.03	1.8	101.9	20	0.02	1.7	0.06	3.4	104.0	6
Uranium	1.67	0.01	0.4	0.03	7.5	100.8	20	0.03	0.42	0.01	2.4	104.1	7

Table 10. Bias and variability of results from U.S. Geological Survey standard reference sample T-219.

[MPV, most probable value; DL, detection limit; SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; µg/L, micrograms per liter; %, percent; --, no data available]

Analyte	MPV (µg/L)	Dissolved						Whole-water recoverable					
		DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	20.7	0.15	23	1	4.4	109.8	24	0.15	22	0.7	3.3	106.1	12
Beryllium	0.22	0.01	0.24	0.01	4.3	110.3	23	0.01	0.24	0.01	2.7	107.3	13
Boron	10.3	5	12	1	6.5	117.3	16	5	11	0.4	3.2	110.9	13
Aluminum	845	3	879	37	4.3	104.0	25	3	882	21	2.4	104.3	12
Vanadium	3.35	0.1	3.6	0.1	2.9	106.0	26	0.5	3.4	0.1	4.2	102.2	13
Chromium[1]	0.341	0.5	0.82	0.20	24.7	241.5	24	0.5	0.7	0.1	10.3	199.6	13
Manganese	219	0.4	238	9	3.8	108.6	25	0.4	235	5	2.0	107.4	13
Cobalt	0.826	0.03	0.9	0.05	5.4	105.3	26	0.03	0.86	0.03	3.1	103.7	13
Nickel	1.78	0.2	2.3	0.3	11.5	128.6	26	0.2	2.1	0.1	3.9	117.1	13
Copper	19.9	0.2	21	1	3.2	107.8	26	0.2	21	1	3.5	104.6	13
Zinc	193	2	201	3	1.5	104.1	9	2	194	8	4.2	100.3	5
Arsenic	3.51	0.05	3.8	0.1	2.8	107.2	26	0.05	3.8	0.1	3.5	107.9	13
Selenium	0.62	0.05	0.50	0.03	6.1	80.0	26	0.05	0.50	0.02	3.4	80.2	13
Strontium	135	0.5	149	5	3.4	110.2	26	0.5	150	5	3.1	111.1	13
Molybdenum	2.67	0.05	2.9	0.1	2.4	109.1	26	0.05	2.8	0.1	3.2	106.4	13
Silver	10.7	1	11	0.5	4.3	101.7	12	0.03	12	0.2	1.7	109.0	6
Cadmium	0.588	0.03	0.63	0.02	2.9	107.7	26	0.03	0.6	0.02	3.0	107.1	13
Antimony	1.26	0.03	1.25	0.04	2.9	99.6	26	0.09	1.3	0.04	3.1	103.3	11
Barium	36.2	0.1	36	1	3.7	99.9	26	0.1	40	1	3.6	109.8	10
Tungsten	--	0.03	0.04	0.01	15.9	--	14	0.03	0.04	0.001	3.7	--	13
Thallium	5.7	0.02	5.6	0.1	1.9	98.1	14	0.02	5.9	0.1	1.7	104.0	13
Lead	2.57	0.02	2.6	0.1	3.2	99.9	26	0.02	2.6	0.1	2.2	102.2	13
Uranium	1.58	0.01	1.6	0.03	2.1	103.0	26	0.03	1.63	0.04	2.7	102.9	11

[1]The most probable value for chromium in T-219 is below the applied detection limit, but is reported because the mean recovery is above the detection limit.

Variability is higher in the reagent-water (blank) spikes when the spike is near or below the DL (table 11) and improves for higher concentration blank spikes (tables 12 and 13). Recoveries were within 10 percent of the spiked amount for the blanks that were spiked at the lower one-third and upper one-third of the calibration range. In general, variability tends to be higher for the low mass dissolved elements Li, Be, and B. The sensitivity of the instrument is lower for these low-mass elements compared to elements with higher masses. Variability of Ag dissolved data are also slightly higher than for all the other higher-mass elements except Zn. This is because of carryover of Ag in the ICP-MS sample introduction system for the dissolved matrix. The Zn blank spike is within 2 times the DL and, therefore, higher variability is expected.

Table 11. Bias and variability of results for a reagent-water (blank) sample spiked near the detection limit.

[DL, detection limit; SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; µg/L, micrograms per liter; %, percent; --, no valid data because spike level was less than 2x lower than DL]

Analyte	Spiked amount (µg/L)	Dissolved						Whole-water recoverable					
		DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	DL	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	0.2	0.15	0.23	0.03	13.7	112.5	10	0.15	0.20	0.07	34.9	99.1	8
Beryllium	0.2	0.01	0.22	0.01	4.3	109.2	8	0.01	0.23	0.01	2.7	112.3	8
Boron1		5	--	--	--	--	--	5	--	--	--	--	--
Aluminum[1]		3	--	--	--	--	--	3	--	--	--	--	--
Vanadium[2]	0.2	0.1	0.21	0.01	5.7	103.0	10	0.5	0.3	0.08	26.9	150.4	8
Chromium[2]	0.2	0.5	0.26	0.06	22.1	130.7	10	0.5	0.27	0.04	16.3	132.7	8
Manganese[2]	0.2	0.4	0.22	0.01	3.1	107.9	10	0.4	0.21	0.02	9.4	107.2	8
Cobalt	0.2	0.03	0.21	0.01	3.3	105.1	10	0.03	0.21	0.01	3.8	106.2	8
Nickel	0.2	0.2	0.22	0.03	14.9	107.9	10	0.2	0.28	0.11	42.7	141.5	8
Copper	0.2	0.2	0.3	0.1	47.7	145.2	10	0.2	0.24	0.02	9.7	120.5	8
Zinc[1]		2	--	--	--	--	--	2	--	--	--	--	--
Arsenic	0.2	0.05	0.21	0.01	3.8	105.4	10	0.05	0.22	0.01	3.4	107.3	8
Selenium	0.2	0.05	0.21	0.01	4.7	104.8	10	0.05	0.22	0.01	4.7	110.5	8
Strontium[2]	0.2	0.5	0.21	0.01	3.3	104.5	10	0.5	0.22	0.01	4.0	112.0	8
Molybdenum	0.2	0.05	0.22	0.01	2.8	109.3	10	0.05	0.25	0.01	3.5	122.9	8
Silver[2]	0.2	1	0.25	0.08	31.5	123.1	10	0.03	0.23	0.003	1.3	113.9	8
Cadmium	0.2	0.03	0.21	0.01	3.7	106.5	10	0.03	0.23	0.01	2.4	113.3	8
Antimony	0.2	0.03	0.20	0.004	2.1	102.2	10	0.09	0.22	0.01	2.3	108.2	6
Barium	0.2	0.1	0.21	0.01	3.1	106.9	10	0.1	0.24	0.04	15.2	122.1	8
Tungsten	0.2	0.03	0.21	0.004	1.9	106.6	10	0.03	0.22	0.003	1.5	109.7	8
Thallium	0.2	0.02	0.21	0.01	2.4	107.3	10	0.02	0.22	0.002	0.8	109.8	8
Lead	0.2	0.02	0.21	0.005	2.2	107.1	10	0.02	0.22	0.01	2.7	108.6	8
Uranium	0.2	0.01	0.21	0.01	2.9	106.8	10	0.03	0.25	0.01	2.5	126.4	8

[1]Spike level was unsuitably low compared to the applied detection limit to report data.

[2]Spike levels for these analytes, except silver WWR are below applied detection limits.

Table 12. Bias and variability of results for a reagent-water (blank) sample spiked in the lower one-third of calibration range and above the detection limit.

[SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; µg/L, micrograms per liter; %, percent]

Analyte	Spiked amount (µg/L)	Dissolved					Whole-water recoverable				
		Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	7.5	7.6	0.4	4.9	101.9	12	7.6	0.2	1.9	101.4	8
Beryllium	0.8	0.83	0.04	5.0	103.8	10	0.83	0.02	2.8	103.3	8
Boron	40	42	2	5.2	104.2	12	41	1	1.8	102.8	8
Aluminum	200	200	8	3.9	100.2	14	202	6	2.5	100.1	8
Vanadium	4	4.0	0.1	2.3	99.8	8	4.0	0.1	2.3	101.0	8
Chromium	7.5	7.6	0.2	2.8	101.2	10	7.5	0.2	2.2	100.2	8
Manganese	75	78	2	2.8	104.0	8	78	1	1.7	103.5	8
Cobalt	4	4.0	0.1	3.1	100.1	6	4.0	0.1	2.3	99.6	8
Nickel	4	4.1	0.1	2.8	102.3	14	4.1	0.1	2.4	101.3	8
Copper	7.5	7.7	0.2	2.4	102.0	13	7.6	0.2	2.0	99.7	8
Zinc	7.5	7.7	0.5	6.2	102.3	11	7.6	0.2	3.2	101.3	8
Arsenic	4	4.1	0.1	3.0	101.3	12	4.1	0.1	3.2	100.1	8
Selenium	0.8	0.82	0.02	2.1	102.1	8	0.80	0.02	2.3	100.5	8
Strontium	200	209	6	3.1	104.6	8	208	4	2.0	103.9	8
Molybdenum	7.5	7.5	0.2	2.6	100.3	14	7.3	0.1	1.4	97.9	8
Silver[1]	0.8	0.8	0.04	4.9	98.8	11	0.84	0.01	1.0	104.3	8
Cadmium	4	4.0	0.1	2.3	101.2	14	4.0	0.1	1.9	100.8	8
Antimony	4	4.0	0.1	3.2	99.8	14	4.1	0.1	3.2	101.3	8
Barium	40	40	1	3.4	100.0	8	41	1	2.9	102.3	8
Tungsten	0.8	0.82	0.02	2.9	102.6	9	0.81	0.01	1.2	102.2	8
Thallium	0.8	0.85	0.02	2.8	106.6	14	0.85	0.02	1.8	106.4	8
Lead	7.5	7.7	0.1	2.0	102.0	9	7.8	0.4	4.9	103.3	8
Uranium	7.5	7.6	0.2	2.9	101.1	9	7.7	0.3	4.5	102.4	8

[1]Spike level for dissolved silver is below applied detection limit.

Table 13. Bias and variability of results for a reagent-water (blank) sample spiked in the upper one-third of calibration range.

[SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; µg/L, micrograms per liter; %, percent]

Analyte	Spiked amount (µg/L)	Dissolved					Whole-water recoverable				
		Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	75	76	4	5.7	100.9	10	80	1	1.7	106.4	8
Beryllium	8	8.4	0.4	4.7	104.7	12	8.4	0.2	1.8	105.4	8
Boron	400	406	17	4.2	101.6	9	416	6	1.4	104.1	6
Aluminum	2,000	2,014	69	3.4	100.7	14	2,052	70	3.4	102.6	7
Vanadium	40	40	1	3.0	101.1	14	42	0.8	1.9	104.0	6
Chromium	75	75	2	3.0	100.5	14	79	1	1.7	105.4	8
Manganese	750	786	20	2.5	104.8	11	790	16	2.0	105.4	8
Cobalt	40	40	1	2.9	100.2	14	41	1	2.3	103.3	8
Nickel	40	41	1	3.4	102.5	14	42	0.6	1.5	104.7	8
Copper	75	76	2	2.1	101.9	14	77	2	2.0	102.4	6
Zinc	75	76	2	3.1	101.2	14	76	2	2.1	101.9	8
Arsenic	40	41	1	2.5	102.6	14	42	1	2.4	104.3	8
Selenium	8	8.2	0.2	2.2	103.1	14	8.6	0.1	1.1	108.0	8
Strontium	2,000	2,156	48	2.2	107.8	12	2,065	85	4.1	103.2	8
Molybdenum	75	74	1	1.0	98.4	14	76	1	1.3	101.0	8
Silver	8	7.7	0.3	3.5	96.4	14	8.4	0.1	1.3	104.8	8
Cadmium	40	39	1	3.0	98.5	14	41	1	2.4	101.5	8
Antimony	40	40	1	2.2	98.9	14	41	2	4.7	102.7	7
Barium	400	419	18	4.3	104.7	11	414	12	2.9	103.6	4
Tungsten	8	8.2	0.2	2.9	102.2	8	8.4	0.2	1.8	104.9	8
Thallium	8	8.4	0.2	1.8	104.5	8	8.6	0.2	2.2	107.3	7
Lead	75	79	2	3.2	104.9	10	78	3	4.4	103.8	8
Uranium	75	79	3	3.2	105.5	8	79	4	4.5	104.7	7

Recoveries of spikes in groundwater and surface water were within 10 percent of the spiked amount for all analytes at all levels spiked except for DISS Ni. Recoveries for DISS Ni in surface water at all 3 levels were elevated and ranged from 105.0 to 121.0 percent. Variability of measured analyte concentrations in spiked groundwater and surface water generally follow the same pattern as the blank-water spikes (tables 14–19). Variability tends to be higher near the DL and for low mass elements. Dissolved Ag and dissolved and WWR Cr variability tend to be elevated near the DL.

Table 14. Bias and variability of results from a groundwater sample spiked near the detection limit or diluted to a concentration near the detection limit.

[DL, detection level; SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; --, no valid data available; µg/L, micrograms per liter; %, percent]

Analyte	Spiked amount (µg/L)/ dilution	Dissolved						Whole-water recoverable					
		DL	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	DL	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	25 fold dilution	0.15	0.44	0.06	14.2	--	11	0.15	0.42	0.07	16.2	--	8
Beryllium	0.2	0.01	0.22	0.01	6.4	97.6	11	0.01	0.25	0.01	3.1	104.1	8
Boron	no dilution	5	23.7	0.9	3.8	--	6	5	23.8	0.4	1.5	--	8
Aluminum	--	3	--	--	--	--	11	3	--	--	--	--	--
Vanadium	no dilution	0.1	4.1	0.2	4.5	--	14	0.5	4.4	0.2	3.8	--	8
Chromium	--	0.5	--	--	--	--	--	0.5	--	--	--	--	--
Manganese[1]	0.2	0.4	0.37	0.01	3.6	95.2	12	0.4	0.27	0.03	11.0	102.2	8
Cobalt	0.2	0.03	0.21	0.004	1.9	96.6	11	0.03	0.21	0.01	4.5	98.0	8
Nickel	0.2	0.2	0.49	0.04	7.9	102.1	12	0.2	0.45	0.02	4.1	101.1	8
Copper	100 fold dilution	0.2	3.6	0.1	2.2	--	14	0.2	1.33	0.04	2.9	--	8
Zinc	no dilution	2	11	0.4	3.5	--	13	2	6.9	0.1	2.0	--	8
Arsenic	25 fold dilution	0.05	0.22	0.01	4.6	--	10	0.05	0.24	0.01	4.5	--	9
Selenium	0.2	0.05	1.5	0.04	2.6	107.7	12	0.05	1.5	0.02	3.7	92.0	8
Strontium	100 fold dilution	0.5	2.9	0.1	3.0	--	13	0.5	2.9	0.06	2.2	--	8
Molybdenum	0.2	0.05	1.0	0.02	2.4	99.2	12	0.05	1.0	0.02	1.7	100.5	8
Silver[1]	--	1	--	--	--	--	--	0.03	0.2	0.002	1.0	100.7	8
Cadmium	0.2	0.03	0.21	0.01	5.8	97.3	12	0.03	0.2	0.005	2.2	100.0	8
Antimony	0.2	0.03	0.23	0.01	2.9	96.8	12	0.09	0.24	0.01	3.0	98.9	8
Barium	100 fold dilution	0.1	0.37	0.01	2.4	--	14	0.1	1.53	0.04	2.8	--	7
Tungsten	0.2	0.03	0.21	0.01	3.4	99.2	12	0.03	0.22	0.003	1.3	106.6	8
Thallium	0.2	0.02	0.19	0.01	3.0	93.4	12	0.02	0.20	0.003	1.5	99.0	8
Lead	0.2	0.02	0.86	0.03	3.2	91.6	12	0.02	0.87	0.01	1.6	95.7	8
Uranium	25 fold dilution	0.01	0.08	0.01	13.2	--	12	0.03	0.09	0.004	4.4	91.7	10

[1]Spiked amounts are below the applied detection limit but data is reported since measured amounts are close to the detection limit.

Table 15. Bias and variability of results from a groundwater sample spiked in the lower one-third of the calibration range.

[SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; --, no valid data; µg/L, micrograms per liter; %, percent]

Analyte	Spiked amount (µg/L)	Dissolved					Whole-water recoverable				
		Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	7.5	19	1	6.4	93.4	12	19	0.4	2.1	102.6	8
Beryllium	0.8	0.85	0.05	5.5	102.6	10	0.88	0.02	2.0	104.3	10
Boron	40	65	3.4	5.2	103.3	14	64	1	1.5	101.1	9
Aluminum	200	198	11	5.5	98.4	14	205	5	2.4	102.2	10
Vanadium	4	8.3	0.3	3.0	105.0	14	8.5	0.2	2.8	101.5	10
Chromium	7.5	7.7	0.2	2.7	101.0	13	7.7	0.2	2.8	101.6	10
Manganese	75	78	3	3.6	103.3	13	79	2	2.4	105.8	10
Cobalt	4	4.0	0.1	2.5	100.4	13	4.0	0.1	2.8	99.5	10
Nickel	4	4.4	0.2	4.0	102.0	14	4.3	0.1	2.0	100.4	10
Copper	7.5	--	--	--	--	--	--	--	--	--	--
Zinc	7.5	19	1	4.2	105.2	13	14.1	0.5	3.6	96.8	10
Arsenic	4	9.8	0.3	3.3	104.1	13	10.1	0.5	4.8	104.7	10
Selenium	0.8	2.1	0.04	1.9	102.5	14	2.1	0.1	3.6	103.2	10
Strontium	200	516	8.5	1.6	106.8	13	530	15	2.8	106.2	10
Molybdenum	7.5	8.4	0.1	1.4	101.4	14	8.5	0.2	2.6	102.0	10
Silver[1]	0.8	0.8	0.1	7.8	77.6	14	0.83	0.01	1.3	103.5	10
Cadmium	4	4.0	0.1	1.9	99.0	14	4.0	0.1	2.7	100.4	10
Antimony	4	4.0	0.1	2.8	98.6	14	4.2	0.2	3.9	102.8	10
Barium	40	77	3	3.4	97.7	14	80	3	3.6	105.6	6
Tungsten	0.8	0.83	0.03	4.0	102.8	14	0.87	0.01	1.1	107.5	10
Thallium	0.8	0.80	0.05	5.6	100.4	14	0.84	0.01	1.5	104.6	10
Lead	7.5	7.9	0.3	3.7	95.7	14	8.3	0.2	2.6	99.1	10
Uranium	7.5	9.4	0.2	2.2	98.9	14	9.6	0.3	3.6	99.8	9

[1]Spiked amount is below the applied detection limit for dissolved silver (Ag).

Table 16. Bias and variability of results from a groundwater sample spiked in the upper one-third of the calibration range.

[SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; --, no valid data; µg/L, micrograms per liter; %, percent]

Analyte	Spiked amount (µg/L)	Dissolved					Whole-water recoverable				
		Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	75	83	6	6.8	95.9	8	94	2	2.1	110.4	10
Beryllium	8	8.2	0.5	6.6	101.9	11	8.5	0.2	2.4	105.8	10
Boron	400	420	20	4.9	99.0	7	449	14	3.1	106.4	9
Aluminum	2,000	1,968	127	6.4	98.4	13	2,101	56	2.7	105.0	10
Vanadium	40	45	1	2.1	102.4	13	46	1	3.2	105.0	9
Chromium	75	75	2	2.4	100.4	13	79	3	3.6	105.8	10
Manganese	750	779	29	3.8	103.8	9	811	15	1.8	108.2	10
Cobalt	40	40	1	3.0	99.2	13	41	1	2.7	102.5	10
Nickel	40	41	1	3.0	101.3	13	41	1	2.1	101.9	10
Copper	75	--	--	--	--	--	--	--	--	--	--
Zinc	75	83	1	1.3	94.7	13	79	2	2.3	95.6	10
Arsenic	40	47.3	0.8	1.8	104.1	13	48	1	2.1	105.4	10
Selenium	8	9.6	0.2	2.0	104.2	11	9.8	0.3	2.7	106.2	8
Strontium	2,000	2,460	24	1.0	105.9	7	2,467	81	3.3	107.5	7
Molybdenum	75	76.4	1.2	1.6	100.8	13	79	1	1.6	104.2	10
Silver	8	7.3	0.2	2.3	90.1	13	8.3	0.1	1.7	103.8	10
Cadmium	40	39	1	2.0	97.7	13	40	1	2.5	101.2	10
Antimony	40	39	1	2.8	98.3	13	41	2	4.2	103.1	9
Barium	400	456	16	3.4	104.7	10	457	27	5.9	104.7	4
Tungsten	8	8.1	0.3	3.1	101.2	7	8.8	0.1	1.5	109.4	10
Thallium	8	7.8	0.2	2.0	97.6	7	8.6	0.1	1.6	107.7	9
Lead	75	73	3	4.5	96.3	8	79	1	1.8	104.7	10
Uranium	75	80	2	2.1	103.7	7	82	2	2.9	106.9	8

Table 17. Bias and variability of results from a surface water sample spiked near the detection limit or diluted to a concentration near the detection limit.

[DL, detection limit; SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; --, no valid data; µg/L, micrograms per liter; %, percent]

Analyte	Spiked amount (µg/L)/ dilution	Dissolved						Whole-water recoverable					
		DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	DL (µg/L)	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	25 fold dilution	0.15	0.33	0.02	5.4	--	10	0.15	0.30	0.07	21.8		8
Beryllium	0.2	0.01	0.22	0.01	6.0	101.0	12	0.01	0.23	0.01	2.7	103.6	8
Boron	no dilution	5	14	0.5	3.9	--	12	5	13	0.5	3.5	--	8
Aluminum	25 fold dilution	3	1.8	0.1	6.1	--	10	3	5.2	0.6	11.3	--	8
Vanadium	0.2	0.1	0.42	0.01	3.3	99.2	13	0.5	--	--	--	--	--
Chromium	--	0.5	--	--	--	--	--	0.5	--	--	--	--	--
Manganese	100 fold dilution	0.4	0.39	0.01	2.6	--	13	0.4	0.45	0.03	6.7	--	8
Cobalt	0.2	0.03	0.30	0.01	4.1	95.9	13	0.03	0.33	0.01	2.5	--	8
Nickel	0.2	0.2	1.2	0.03	2.7	121.0	13	0.2	1.1	0.03	3.1	95.1	8
Copper	25 fold dilution	0.2	0.53	0.03	6.2	--	13	0.2	1.3	0.05	3.7	98.7	8
Zinc	no dilution	2	5.8	0.2	3.8	--	12	2	7.5	0.5	7.0	--	8
Arsenic	0.2	0.05	0.47	0.02	3.3	102.3	13	0.05	0.51	0.01	2.8	99.7	8
Selenium	0.2	0.05	0.32	0.01	3.9	106.5	13	0.05	0.31	0.01	4.6	102.3	8
Strontium	100 fold dilution	0.5	1.9	0.03	1.7	--	12	0.5	1.9	0.05	2.6	--	8
Molybdenum	25 fold dilution	0.05	0.31	0.01	2.7	--	11	0.05	0.30	0.01	2.6	--	8
Silver	0.2	1	--	--	--	--	--	0.03	0.20	0.003	1.6	96.6	8
Cadmium	0.2	0.03	0.27	0.01	5.4	99.8	13	0.03	0.25	0.01	3.9	96.2	8
Antimony	0.2	0.03	0.24	0.01	2.4	99.3	13	0.09	0.23	0.01	3.0	91.1	6
Barium	25 fold dilution	0.1	1.5	0.05	3.6	--	11	0.1	1.5	0.03	1.7	--	8
Tungsten	0.2	0.03	0.24	0.01	3.4	101.4	13	0.03	0.24	0.01	3.2	101.9	8
Thallium	0.2	0.02	0.19	0.01	2.8	94.8	13	0.02	0.20	0.01	2.4	96.8	8
Lead	0.2	0.02	0.21	0.01	2.4	94.2	13	0.02	0.28	0.01	3.6	94.0	8
Uranium	0.2	0.01	1.5	0.03	1.9	100.7	13	0.03	1.5	0.04	2.5	84.1	8

Table 18. Bias and variability of results from surface water spiked in the lower one-third of the calibration range.

[SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; --, no valid data; µg/L, micrograms per liter; %, percent]

Analyte	Spiked amount (µg/L)	Dissolved					Whole-water recoverable				
		Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	7.5	15.8	0.7	4.5	100.3	11	15	0.4	2.7	98.4	8
Beryllium	0.8	0.86	0.05	5.6	105.8	12	0.84	0.03	3.2	101.0	8
Boron	40	55	2	4.4	102.5	12	52	1	1.8	98.0	8
Aluminum	200	235	10	4.4	99.1	12	328	11	3.5	100.3	8
Vanadium	4	4.5	0.1	3.3	106.2	13	4.3	0.1	2.8	102.4	8
Chromium	7.5	7.8	0.2	2.9	100.7	13	8.0	0.2	2.3	104.4	8
Manganese	75	116	4	3.0	102.5	13	128	3	2.2	105.5	8
Cobalt	4	4.2	0.1	2.4	101.4	13	4.2	0.1	1.6	100.7	8
Nickel	4	5.2	0.1	2.4	105.0	13	5.0	0.1	2.3	100.8	8
Copper	7.5	35	1	2.9	107.2	13	38	1	1.7	98.8	8
Zinc	7.5	13	0.4	2.9	100.4	13	15	1	3.4	95.9	8
Arsenic	4	4.5	0.1	2.7	106.7	13	4.5	0.1	2.2	104.1	8
Selenium	0.8	0.95	0.03	2.7	106.3	13	0.94	0.02	1.7	105.0	8
Strontium	200	413	14	3.4	105.6	13	422	8	1.8	107.7	8
Molybdenum	7.5	16	0.3	1.8	103.8	13	15.2	0.4	2.8	100.7	8
Silver[1]	0.8	0.80	0.03	4.3	82.0	13	0.82	0.01	1.3	101.6	8
Cadmium	4	4.1	0.1	2.4	100.8	13	4.0	0.1	2.9	98.8	8
Antimony	4	4.0	0.1	2.9	100.0	13	3.9	0.1	3.2	97.1	8
Barium	40	76	2	2.9	97.6	13	76	1	1.3	98.5	8
Tungsten	0.8	0.87	0.03	3.0	104.4	13	0.88	0.01	0.8	105.4	8
Thallium	0.8	0.81	0.03	3.8	101.2	13	0.83	0.01	1.8	103.3	8
Lead	7.5	7.1	0.2	3.0	94.0	13	7.6	0.2	3.2	99.7	8
Uranium	7.5	8.7	0.2	1.7	98.7	13	8.9	0.3	3.3	101.2	8

[1]Spiked amount is below the applied detection limit for dissolved silver (Ag). The mean recovery is not 100% because the measured amount in the unspiked sample was subtracted from the measured spiked concentration.

Table 19. Bias and variability of results from a surface water sample spiked in the upper one-third of the calibration range.

[SD, one standard deviation; RSD, relative standard deviation; n, number of replicates measured; --, no valid data; µg/L, micrograms per liter; %, percent]

Analyte	Spiked amount (µg/L)	Dissolved					Whole-water recoverable				
		Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n	Mean (µg/L)	SD (µg/L)	RSD (%)	Mean recovery (%)	n
Lithium	75	86	4	5.2	103.3	8	88	3	2.9	107.1	8
Beryllium	8	8.3	0.5	5.6	103.2	9	8.3	0.3	3.4	103.6	8
Boron	400	433	25	5.8	104.7	7	431	16	3.7	104.5	8
Aluminum	2,000	2,064	104	5.0	101.3	10	2,177	57	2.6	102.5	7
Vanadium	40	42.0	0.9	2.1	104.4	10	42	1	2.4	105.0	8
Chromium	75	77	1	1.9	102.3	10	79	2	2.6	105.6	8
Manganese	750	843	20	2.4	107.1	9	856	14	1.6	107.6	8
Cobalt	40	40	2	3.8	99.1	10	41	1	2.4	102.1	8
Nickel	40	45	1	3.1	111.2	10	41	0.9	2.2	101.2	8
Copper	--	--	--	--	--	--	--	--	--	--	--
Zinc	75	80	2	2.2	98.9	10	78	2.6	3.3	93.2	8
Arsenic	40	42	1	2.6	104.3	10	43.5	1.5	3.6	107.9	8
Selenium	8	8.5	0.2	2.0	105.1	10	8.6	0.2	2.7	106.7	8
Strontium	2,000	2,407	50	2.1	107.0	8	2,365	101	4.3	107.9	8
Molybdenum	75	84	1	1.4	101.2	10	88	3	2.9	107.1	8
Silver	8	7.3	0.2	3.1	89.7	10	8.3	0.2	2.2	103.4	8
Cadmium	40	39	0.7	1.8	97.4	10	40	1	2.4	99.9	8
Antimony	40	39	1	3.5	98.5	10	40	1	2.5	99.8	7
Barium	400	462	9	1.8	106.2	9	458	27	5.9	105.5	8
Tungsten	8	8.2	0.2	2.8	102.7	6	8.8	0.1	1.3	109.5	8
Thallium	8	7.8	0.1	1.4	97.2	6	8.6	0.2	1.9	107.1	7
Lead	75	74	2	2.9	98.5	7	77	3	3.8	103.0	8
Uranium	75	80	1	1.8	105.5	6	83	3	3.8	108.5	8

Sample Comparison Data

For comparison, 108 dissolved and 140 WWR environmental samples were analyzed on both the Nexion and Agilent ICP-MS instruments. Linear regression analysis was performed to compare results from each instrument (table 20, attachment 3 figs. A3.1–56). A Wilcoxon signed-rank test was performed ($\alpha = 0.05$) to determine if measurements made on each instrument are significantly different from each other (table 20). Where QC did not pass during the analysis for an analyte, the sample was not necessarily reanalyzed resulting in the number of data points (n) used for each analyte ranging from 57 to 138.

Differences between the two dissolved methods are significant (P value less than [<]0.05) for all analytes except V, As, Cd, W, and Tl. Slopes ranged from 0.71 to 1.83 in the dissolved analyte data. The analytes Mo, Ag, Cd, Sb, Ba, and Tl had slopes between 0.950 and 1.050, indicating no or minimal bias between the two instruments. Slopes were between 0.900 and 1.100 for B, V, Cobalt (Co), Ni, Cu, Zn, As, W, and Pb. Coefficients of determination (R^2) ranged from 0.609 to 1.000 for all analytes. Coefficients of determination for B, Mn, Zn, As, Se, Sr, Mo, Cd, Sb, Ba, W, Tl, and Pb were greater than or equal to 0.995 indicating minimal variability. Higher variability for Be, Al, and Ag is partly because of the poor agreement near the DL. V, Ni, and Cr are affected by molecular interferences, copper potentially by contamination. The source of the higher variability for Li and Co is unknown.

Table 20. Linear regression results for dissolved and whole-water recoverable environmental sample data analyzed using a Nexion inductively coupled plasma mass spectrometer (ICP-MS) and an Agilent ICP-MS.

[Linear regression model MS2 = a x MS1 + b, where analyte concentrations from MS1 and MS2 are in micrograms per liter; DL, detection limit; R^2 coefficient of determination; Prob>|S|, the observed significance probability calculated using a Wilcoxon signed rank test where the null hypothesis is that the difference in data from the Agilent ICP-MS and Nexion ICP-MS = 0; n, number of environmental sample analyses used in regression]

Analyte	Dissolved						Whole-water recoverable					
	DL	Slope	y-intercept[1]	R^2	Prob>|S|[2]	n	DL	Slope	y-intercept	R^2	Prob>|S|[2]	n
Lithium	0.15	1.21	–2.42	0.991	<0.0001*	96	0.15	1.01	–0.39	0.998	0.0928	115
Beryllium	0.01	0.71	–0.01	0.609	<0.0001*	98	0.01	1.01	0.01	0.996	0.059	57
Boron	5	1.08	–1.36	0.996	0.0123*	94	5	0.98	–0.10	0.997	0.0112*	132
Aluminum	3	1.83	–20.46	0.966	0.0259*	99	3	1.00	0.99	0.995	0.2936	137
Vanadium	0.1	1.10	–0.17	0.985	0.6802	108	0.5	0.99	–0.51	0.957	<0.0001*	83
Chromium	0.5	1.16	0.19	0.932	<0.0001*	105	0.5	1.03	0.09	0.997	<0.0001*	135
Manganese	0.4	1.11	–3.31	0.999	<0.0001*	108	0.4	1.06	0.59	0.995	<0.0001*	137
Cobalt	0.03	1.10	–0.03	0.985	0.0007*	105	0.03	1.01	–0.01	0.997	0.0562	138
Nickel	0.2	1.06	–0.12	0.957	0.0003*	102	0.2	1.02	–0.05	0.994	0.0848	135
Copper	0.2	1.06	0.03	0.983	<0.0001*	106	0.2	1.01	0.04	0.995	<0.0001*	135
Zinc	2	1.07	0.21	0.999	<0.0001*	103	2	1.00	1.23	0.998	0.1507	133
Arsenic	0.05	1.08	–0.13	0.999	0.0712	99	0.05	0.99	–0.11	0.996	0.0002*	133
Selenium	0.05	1.21	–0.09	0.997	<0.0001*	108	0.05	1.09	0.00	0.995	<0.0001*	125
Strontium	0.5	1.09	4.83	0.987	<0.0001*	107	0.5	1.04	8.60	0.997	<0.0001*	137
Molybdenum	0.05	1.04	–0.04	0.999	<0.0001*	108	0.05	1.02	0.05	0.999	<0.0001*	132
Silver	1	1.03	0.18	0.920	<0.0001*	85	0.03	1.06	0.01	1.000	<0.0001*	126
Cadmium	0.03	0.99	0.00	0.995	0.2922	108	0.03	1.02	0.00	0.996	<0.0001*	138
Antimony	0.03	0.99	–0.01	0.997	0.0030*	107	0.09	1.00	–0.03	0.999	<0.0001*	122
Barium	0.1	1.00	–1.84	0.998	0.0003*	108	0.1	1.08	–1.79	0.995	<0.0001*	133
Tungsten	0.03	1.07	–0.02	0.995	0.6366	107	0.03	0.99	–0.01	1.000	0.6714	119
Thallium	0.02	1.00	0.00	0.999	0.0686	105	0.02	1.02	0.02	0.998	<0.0001*	125
Lead	0.02	1.06	–0.01	1.000	0.0223*	108	0.02	0.96	0.27	0.998	0.075	138
Uranium	0.01	0.85	0.28	0.991	0.0092*	108	0.03	0.98	–0.03	0.996	<0.0001*	132

[1]Where the y-intercept is more than 3x the detection limit, a separate regression was performed using only the lower concentration data (Appendix 2). In all cases except for dissolved aluminum these regressions yielded y-intercepts within 2 times the detection limit demonstrating good agreement between the two methods near the detection limit.

[2]Statistical significance at $\alpha = 0.05$ is indicated by an *.

The analtyes Li, Al, Cr, Mn, Se, and Sr have greater than 10 percent high bias for DISS analysis on the Nexion relative to the Agilent when sample data are compared. Both Be and U have greater than 10 percent low bias on the Nexion relative to the Agilent. The specific source of bias for each of these eight analytes is unknown. There are at least five calibration points per analyte used for the Nexion analyses, and a weighted linear regression calibration model is used. Previously on the Agilent, there were up to three calibration points and the calibration model used was a linear regression force through zero. These changes in number of calibrants and calibration model used may be contributing to some of the differences observed between the methods applied on the Nexion and Agilent ICP-MS instruments.

The Al data must be considered carefully because the level and direction of bias is highly concentration dependent (fig. A3.8–A3.10). Below about 30 µg/L (fig. A3.9), Al data from analysis on the Nexion appears to be mostly low biased relative to data from the method applied on the Agilent ICP-MS, suggesting that contamination might be high biasing the data from the Agilent ICP-MS method. This observation is further supported by results for data from the USGS BQS Inorganic Blind Sample Program (bqs.usgs.gov/ibsp/) that shows false positives in blind blank samples. The Al data from the Nexion appear to be high biased relative to the Agilent above about 30 µg/L.

The slopes for nearly all analytes were between 0.95 and 1.05 in the WWR analyte data, indicating minimal bias of data from the Nexion relative to Agilent ICP-MS analyses (table 20). Slopes observed for Mn, Se, and Ba were between 1.05 and 1.1, indicating a positive bias of results from the Nexion relative to Agilent ICP-MS analyses. Coefficients of determination for all WWR analytes were greater than or equal to 0.995 except for Al, V, and Ni. Both V and Ni may have higher variability because of molecular interferences. The variability of Al increases with increasing concentration, which could be related to the use of a weighted linear curve for the Nexion analysis. Differences between the two WWR methods are significant (P value <0.05) for all analytes except Li, Be, Al, Co, Ni, Zn, W, and Pb (table 20).

Some analytes appear to have some false positives on the Agilent dissolved analysis (Al and Be; figs. A3.4 and A3.9), on the Nexion dissolved analysis (Cr and Ag; fig. A3.14 and A3.37), or on the Agilent WWR analysis (V; fig. A3.13). Al false positives were discussed previously in this section. The Be false positives might instead be from false negatives (not detected) on the Nexion analysis. Both sets of values are valid by all QC measures and Be dissolved blind blanks determined had a 0 percent false positive rate for water year 2016 on the Agilent ICP-MS. The apparent Cr and Ag false positives on the Nexion could be in part because of a lack of sensitivity or carryover at the low end of the calibration range. The DL for these two analytes has been raised as a result. The V WWR had an 18 percent false positive rate for water year 2016 for blind blanks submitted by the USGS BQS Inorganic Blind Sample Program (bqs.usgs.gov/ibsp/) with the Agilent ICP-MS that are likely because of carryover or inadequate spectral interference removal during analysis.

There are several indicators that one or more spectral interferences on DISS Cr are not being removed as effectively by the Nexion KED cell as they were on the Agilent analysis. In addition to the high bias of Nexion data for environmental samples on the DISS analysis, T-215 (table 9) and T-219 (table 10) had high recovery on the Nexion. Since both T-215 and T-219 are near or below the DL additional blind sample data collected after implementation will help constrain this.

Instrument-to-Instrument Comparison

Data from dissolved samples analyzed on both Nexion ICP–MS instruments were compared to determine if there is instrument-to-instrument bias (attachment 4). Slope, intercept, and coefficient of variation for a simple linear regression of concentration for each analyte on both instruments, as well as P value, are summarized in table 21. A Wilcoxon signed-rank test was performed ($\alpha = 0.05$) to determine if measurements made on each instrument are significantly different from each other (table 21). Differences are significant (P value <0.05) for 12 analytes. However, for all those except Be and Ag, the slope of the regression line is between 0.900 and 1.100 indicating acceptable agreement between the 2 instruments. Sixteen analytes have slopes between 0.950 and 1.050. See plots in attachment 4 for details on the direction of bias relative to concentration.

For most of the analytes showing bias between instruments, the comparison is affected by only a few data points. For the low mass elements Li, Be, B, and Al, there is greater variability in the analysis inherently because of their low mass. The sample-introduction carryover observed for Ag was worse on instrument one than on instrument two, which is reflected in the instrument comparison samples (attachment 2). As of March 1, 2017, changes were made to the sample introduction system to reduce the carryover of Ag on both instruments. All settings controlling plasma conditions were set equal on the two instruments. Although robust plasma conditions are being used to minimize matrix effects in the plasma, matrix effects cannot be eliminated completely and vary slightly from day to day. Calibrators and QC samples are analyzed frequently to ensure that method performance is continually being met.

Instrument differences were compared because of concerns that instrumental bias could lead to cases of DISS>WWR concentrations, particularly for Al, As, Cd, Pb, Mo, Se, and Zn. Al, As, and Mo had intercepts that were greater in magnitude than the DL, indicating that there may be bias near the DL between the instruments. Se and Mo data from one instrument (designated MS 2) tended to be higher than that from MS 1; for Pb, lower (attachment 4). MS 1 will typically be used for dissolved analysis and MS 2 for WWR analysis.

WWR/Dissolved Pair Comparison

There were 19 sample pairs comprised of a filtered and whole-water sample analyzed in the validation study. Whole-water recoverable and dissolved data were collected on separate instruments for both the Agilent and Nexion analyses. These sample pairs were evaluated to determine the rate of occurrence of the value measured for DISS being 110 percent or more than the value measured for WWR (DISS>WWR). Data from the Agilent ICP-MS analyses for the same pairs also were evaluated so that the rate of occurrence of DISS> WWR could be compared for results from both the Nexion and Agilent ICP-MS methods. Where the measured concentration in the sample pair of either dissolved or WWR analytes were <10 times the DL, DISS>WWR was not evaluated. For 1 sampling event, all analyte concentrations were two to three times higher in the filtered-water sample

Table 21. Linear regression and statistical analysis results comparing the same filtered environmental samples measured on two independent Nexion 350D instruments.

[Linear regression model MS2 = a x MS1 + b, where analyte concentrations from MS1 and MS2 are in micrograms per liter; R^2, coefficient of determination; n, number of environmental sample analyses used in regression; Prob>|S|, the observed significance probability calculated using a Wilcoxon signed rank test where the null hypothesis is that the difference in data from MS1 and MS2 = 0; --, no valid data]

Analyte	DL (µg/L)	Slope [a]	y-Intercept [b]	R^2	n	Prob>|S|[1]
Lithium	0.15	0.967	0.470	0.995	33	0.5226
Beryllium	0.01	0.882	0.003	0.996	32	0.0018*
Boron	5	0.936	1.868	0.993	35	0.9872
Aluminum	3	0.985	4.260	0.888	38	0.3343
Vanadium	0.1	1.008	0.389	0.91	41	0.0243*
Chromium	0.5	0.937	0.078	0.853	36	0.0001*
Manganese	0.4	0.962	0.006	0.998	41	<0.0001*
Cobalt	0.03	0.988	–0.004	0.999	34	0.4969
Nickel	0.2	0.942	–0.018	0.995	38	0.00001*
Copper	0.2	0.991	–0.062	0.985	37	0.00009*
Zinc	2	1.017	–0.041	1.000	30	0.1688
Arsenic	0.05	1.046	0.108	0.990	37	0.0708
Selenium	0.05	1.020	0.008	0.999	40	0.0002*
Strontium	0.5	0.984	5.779	0.997	40	0.3533
Molybdenum	0.05	1.079	–0.150	0.997	41	0.0062*
Silver	1	--	--	--	--	--
Cadmium	0.03	0.998	0.001	0.999	41	0.1919
Antimony	0.03	0.957	0.005	0.998	40	0.6251
Barium	0.1	0.959	1.825	0.998	39	0.4095
Tungsten	0.03	0.952	0.003	0.998	40	0.0627
Thallium	0.02	0.961	–0.001	1.000	38	<0.0001*
Lead	0.02	0.928	0.001	0.997	41	0.0002*
Uranium	0.01	0.961	0.010	0.999	40	<0.0001*

[1]Statistical significance at α = 0.05 is indicated by an *.

than in the whole-water sample from both the Nexion and Agilent ICP-MS analyses, suggesting that the sample pair was mismatched rather than the differences being an instrumental effect that was causing some analyte to have higher DISS to WRR concentrations. Therefore, this pairing was not included in the analysis.

Of the 18 remaining pairs, there were 21 occurrences across all 23 analytes of DISS>WWR resulting from measurement on the Nexion and 14 occurrences resulting from measurement on the Agilent instrument (table 22). Some of the difference is because of differences in the DL between the Nexion and Agilent methods. There is no clear pattern of occurrence by analyte although the rate of occurrence is higher for the low mass elements using the Nexion method than with the Agilent method. Since the Nexion instrument is more sensitive to matrix effects than the Agilent, it is not surprising that there are more occurrences of DISS>WWR in the Nexion data.

The specific conductance of a sample is used to estimate an appropriate dilution to minimize matrix effects. However, the calculated dilution factor based on specific conductance may not be high enough for the WWR sample if there is a large amount of particulate matter present in the initial samples that is dissolved during the INBD, which would increase the total dissolved solids and conductance when the sample is digested. It would be difficult to quantify “large amount” both theoretically and in practical application. However, where there is an occurrence of DISS>WWR that causes NWQL QC checks to flag the

samples for reanalysis, it may be useful for a larger dilution on the WWR sample to be initiated if the dilution is unlikely to affect results of the analyte of interest. Where a customer has an occurrence of DISS>WWR, they may contact the NWQL (labhelp@usgs.gov) to discuss whether this approach would be useful. Also, customers should request laboratory matrix spikes for samples where there is a potential for this to be a concern since suppressed or enhanced spike recoveries are indicative of matrix effects.

Table 22. Frequency of occurrence of analyte concentrations being greater than or equal to 10 percent higher in the dissolved sample than in the paired whole-water recoverable sample. The same 18 pairs were analyzed on both the Nexion inductively coupled plasma mass spectrometer (ICP-MS) and the Agilent ICP-MS. Whole-water recoverable and dissolved data were collected on separate instruments for both the Agilent and Nexion analyses.

[DISS>WWR, number of occurrences where the measured values were greater than 10 times the applied DL and the analyte concentrations were greater than or equal to 10 percent higher in the dissolved sample than in the paired whole-water recoverable sample; Samples>10x DL, number of sample pairs out of the 18 analyzed where both the dissolved and whole-water recoverable measured values were more than ten times the applied detection limit; Occurrence, percentage of samples >10xDL that had DISS>WWR; %, percent]

Analyte	Nexion			Agilent		
	DISS> WWR	Samples >10xDL	Occurrence (%)	DISS> WWR	Samples >10xDL	Occurrence (%)
Lithium	2	11	18	0	12	0
Beryllium	2	5	40	0	2	0
Boron	0	5	0	0	5	0
Aluminum	1	7	14	0	6	0
Vanadium	0	0	0	0	0	0
Chromium	0	0	0	0	3	0
Manganese	2	15	13	2	15	13
Cobalt	3	10	30	1	6	17
Nickel	1	5	20	1	5	20
Copper	2	5	40	0	0	0
Zinc	0	4	0	0	5	0
Arsenic	2	12	17	0	6	0
Selenium	0	8	0	0	3	0
Strontium	0	18	0	1	18	6
Molybdenum	1	18	6	3	18	17
Silver	0	0	0	0	8	0
Cadmium	2	5	40	3	5	60
Antimony	0	4	0	0	3	0
Barium	1	17	6	1	18	6
Tungsten	1	3	33	1	3	33
Thallium	0	5	0	0	5	0
Lead	0	10	0	0	5	0
Uranium	1	17	6	1	17	6

Recommendations

This validation study documents effects of sample matrix on the analysis as well as comparability of data produced by the Nexion instruments to the superseded Agilent instruments. Some explanation of the potential interferences present in ICP-MS analysis in general and specifically on the Nexions may help the data user to understand anomalies in their data such as DISS>WWR. Analytes Cr and Ag are discussed in more detail in section 6.1 Interferences, because the new methods have caused a significant shift in DLs for these two analytes and potentially a shift in bias for Ag of which the data user should be aware. DISS Al has poor agreement between the two methods for sample data and all other data indicate acceptable bias and precision potential sources of the disagreement between methods and discussed to help the data used understand why there may be shifts in their data.

Interferences

There is evidence of matrix-induced signal suppression or enhancement for some analytes, especially when the specific conductance of a sample is greater than or equal to 1,000 µS/cm. Where matrix is of concern, laboratory matrix spikes should be requested by the customer and (or) data user and recovery of the spikes used when interpreting the data. In fact, any sample or sampling area with a substantial amount or an abnormal type of matrix should request laboratory matrix spikes to help inform the effects of the matrix (including dilution of the matrix) on analyte recoveries. While much information is available regarding matrix interferences in ICP-MS (Allain and others, 1991; Larsen and Stürup, 1994; Stewart and Olesik, 1998b; Stewart and Olesik, 1998a; Agatemor and Beauchemin, 2011), effects vary by sample. Laboratory matrix spikes at appropriate analyte concentrations for the sample are the most cost effective and straightforward method of understanding analyte recoveries for a given environmental sample matrix.

When matrix suppression is suspected by the analyst, one appropriate response may be to reanalyze the sample with a higher dilution, if possible and practical. This is especially needed for the WWR analysis when the total dissolved solids in solution after digestion can be greater than what was in the corresponding dissolved pair, which would therefore be greater than what is indicated by the specific conductance of the undigested sample. The present dilution protocol that is based on the specific conductance of the sample might still be resulting in greater signal suppression for the whole-water sample than for the corresponding filtered-water sample pair. Suppression of the internal standard signal in the WWR sample compared to the DISS sample is a possible indicator that matrix suppression in the WWR analysis has occurred.

Matrix suppression might be contributing to DISS>WWR for some analytes. The recovery of the analyte associated internal standard in both the WWR and DISS matrix can be compared by the analyst to determine if there is more signal suppression in the whole-water analysis. Analyte concentration is adjusted for internal standard recovery, but if the internal standard and its associated analyte do not behave exactly the same in the plasma, the correction might not be sufficient and lead to either positive or negative bias in the determined analyte concentration. This has been demonstrated for several analytes where a reduction in spike recoveries occurs as conductivity increases (figs. 1–11, attachment 2). Analytes were paired with internal standards of similar mass or ionization potential to ensure that analytes were matched in performance as closely as possible to the associated internal standards, but each analyte and internal standard still behaves slightly different in the plasma. Recoveries of customer-requested laboratory matrix spikes will indicate whether matrix suppression is responsible for the difference in internal standard recoveries between the two analyses, or if the difference is related to another instrument condition that could be causing internal standard drift.

As conductivity increases, the low bias observed in Cd and Zn and the high bias observed in As and Se increases. Where samples have conductivity >1,000 µS/cm and Se, As, Cd, and (or) Zn are of concern, a higher dilution should be requested by the customer if the concentration of the analyte in the sample is high enough to not dilute them to a concentration that is below the DL.

Sample Comparison Data

There are primarily high or occasionally low biases and elevated variability for several analytes, most notably for the dissolved analyses when data are compared between the Agilent and Nexion methods. Data users may experience a shift in data trends for many dissolved analytes as a result of the implementation of the Nexion ICP-MS instruments based on the data presented in this report. The cause of the biases is unknown and it is unknown whether they can be attributed to the specific application of the Nexion or Agilent ICP-MS instruments, or both. High bias in environmental data measured on the Agilent relative to the Nexion is sometimes, but not always, accompanied by an observed corresponding high bias in SRS samples and laboratory matrix spikes.

The use of the Nexion autosampler dilutor system for diluting samples, enforcement of good laboratory practices mandated by the standard operating procedures of the methods, the recent replacement of clean benches used for reagent and calibrator preparation, and the increased application of instrument maintenance protocols should help reduce variability in sample data.

The Nexion Prepfast autosampler can automatically dilute samples by a factor of 2 to 100. This feature was used throughout the validations study whenever sample dilution was required. The highly accurate (less than plus or minus 0.2 percent) and precise (less than 0.05 percent) syringe-driven dilutor system is checked every time a calibration is performed since the calibration standards are prepared using the dilutor system. This represents an improvement from the previous method where dilutions were performed manually using a single pipette, two pipettes, or a pipette and volumetric flask, depending on the amount of dilution required. Some of the variability and bias contributed by the dilution should be eliminated with the Nexion methods.

Chromium

There is a molecular interference ($^{40}Ar^{12}C^{+}$) on ^{52}Cr caused by the acetic acid matrix modifier that is not completely eliminated by the KED collision cell. The ArC molecules are not completely removed in the Nexion collision cell and cause an increase in the background signal. It is expected that this will lead to increased variability and possibly some bias near the DL in Cr data on the Nexion ICP-MS compared to the Agilent ICP-MS. Data near the DL are more affected by this interference; consequently, the DL for dissolved and WWR Cr has been raised to 0.5 µg/L compared with use of the Agilent ICP-MS (table 6).

Silver

U.S. Environmental Protection Agency method 200.8 states:

> "Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L."

Observations at the NWQL support the assertion that Ag is, at times, unstable in a 0.4 percent HNO_3 matrix and the variability in environmental sample data could be caused by the presence of low concentrations of Cl. The stability of Ag in a sample depends not only on acid level, but also on the chemical components of the sample. All WWR data in this report support the assertion that Ag is stable in a 0.4 percent HNO_3/2 percent HCl matrix.

Because of the instability of Ag in the dissolved acid matrix and carryover in the sample introduction system on the Nexion, the DL has been raised from 0.02 µg/L on the Agilent for the DISS method to 1 µg/L on the Nexion. The DL for the WWR method remains at 0.03 µg/L. If a DL less than 1.0 µg/L is needed for Ag, it is recommended that the user submit an unfiltered sample and request the whole-water method for determining Ag in the samples. The SRS and blank water spike recoveries for dissolved Ag suggest that measurements well above the DL are accurate and precise (tables 8–13). However, the recoveries of Ag in the spiked groundwater and surface water are low biased (tables 15–16 and 18–19; the lower one-third of range spike was 0.8 µg/L Ag).

When sample data (fig. A3.37) are compared, there is poor agreement between the Agilent and the Nexion data below 1 µg/L. There are two possible reasons for this: either the Agilent method was insufficiently sensitive for the selected DL and therefore yielded low-biased data or the Nexion method is yielding high-biased data and false positives. The QC samples that are currently analyzed at the limit of quantitation (set at 2 times the DL of 0.02 µg/L) on the Agilent have an 11 percent rate of the measured value being less than or equal to half the limit of quantitation concentration. Therefore, it is likely that the concentration measured for at least one sample and possibly more on the Nexion is a false positive.

To address this, all dissolved Ag detections above the DL beginning October 1, 2016, were reanalyzed on the Nexion to confirm the detection. The rerun data was accumulated for six months and used to determine if the false positive rate by the Nexion method is acceptably low or unacceptably high. It was determined that the rate is acceptably low, and automatic reruns of detections has been discontinued. The NWQL is also investigating techniques to stabilize the dissolved Ag analysis including new rinsing protocols for the autosampler.

Aluminum

The Al data that appear to be false positives in the DISS Agilent data (fig. A3.8) are likely because of contamination during pour-up and analysis. This is supported by the USGS BQS blind blank data for Al. During water year 2016 when filtered samples were analyzed on the Agilent ICP-MS, the false positive rate was 12 percent compared to 5 percent on the Agilent whole-water line. Between October 1, 2016 and February 1, 2017, the BQS blind blank false positive rate for DISS on the Nexion was 0 percent.

Al is present in many common materials, including deodorant and potentially many fixtures in the laboratory, and these represent potential sources of contamination during the pour-up and analysis of samples. During this validation, potential sources of contamination were identified and steps have been taken to minimize these risks in the laboratory in order to achieve the lowest possible rates of sample and QC contamination. Practices that apply to both field and laboratory operations for minimizing sample contamination include wearing gloves while pouring samples and minimizing sample contact with the outside environment.

Biases observed in DISS Al (Section 5.5 Sample Comparison Data, fig. A3.8 and A3.9) could be caused by high bias on the Nexion instruments, low bias on the Agilent instrument, or by contamination of the samples. The bias is accompanied by high variability in recovery between the two analyses. In all cases, the analysis on the Nexion occurred after analysis on the Agilent, so if the sample bottle was contaminated with Al it would appear to be a high bias on the Nexion. The variability of replicate measurements of SRM, SRS, and laboratory matrix spikes on the Nexion are not higher than those of other analytes (tables 8–19), suggesting that the elevated variability in environmental sample measurements likely occurred on the Agilent or is caused by the sample matrix on both instrument types. The average measured values for the SRS samples (tables 8–10) are slightly high-biased, but are within ±10 percent of the MPV. Nonetheless, data users might see a shift in Al data based on the instrument platform change that will depend on the concentration level.

Sample Pair Agreement

It is unlikely that the occurrence of DISS>WWR will decrease with implementation of the Nexion ICP-MS instruments. In fact, there were more occurrences of DISS>WWR on the Nexion than on the Agilent platforms during this study. It is possible that this is at least in part because of matrix suppression effects that are greater for the whole-water sample than for the filtered sample. Increasing the dilution factor for the whole–water sample may help reduce the occurrence of DISS>WWR, but may also increase the occurrence of reported non–detection of the analyte in the WWR sample because of dilution to a concentration that is below the DL. Analysis of duplicates and spikes may help with the interpretation of paired DISS and WWR comparison data. For sites with known DISS>WWR occurrences, requesting analysis of spikes of both the filtered and unfiltered sample would be prudent.

Instrument Comparison

There were some statistically significant differences in measured concentrations between the two Nexion instruments (P value <0.05) for V, Mn, Cu, Se, Tl and U; however, the magnitude of the difference was small as indicated by the slope of the regression lines being between 0.95 and 1.05 (table 21). Several other analytes had a statistically significant difference between instruments and the slope indicates >5 percent bias (Be, Cr, Ni, Mo, Ag, and Pb). For the low and high mass elements, day-to-day variability in mass spectrometer tuning has an effect on measurement bias, which is manifested as instrument variability in determined concentrations. The bias seen for all analytes except Ag are well within the data quality objectives of both the dissolved and whole-water methods.

Summary

This memorandum documents the data quality expected to be obtained using the PerkinElmer Nexion inductively-coupled plasma mass spectrometer (ICP–MS) instruments that were implemented at the National Water Quality Laboratory on October 1, 2016, for analysis of trace elements in unfiltered (whole) and filtered-water. Some potential sources of bias and variability in the analysis have been investigated. It is likely that there will be shifts in bias and variability for some analytes by moving the analyses from the Agilent ICP-MS to Nexion ICP-MS instruments. The National Water Quality Laboratory will continue to work toward resolving the difficulties in measurement of dissolved Ag that have been documented in this report.

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Attachments

Attachment 1. Detection limits, in micrograms per liter, calculated using the DQCALC software for the method on the Nexion ICP-MS in accordance with Williams and others, 2015.

Attachment 2. Recovery, in percent, of 10 µg/L of each trace element spiked into increasing dilutions of surface-water or groundwater. Relevant major ion composition, specific conductance, and residue on evaporation are included for undiluted samples where available. Specific conductance of each dilution was measured and is reported. Major ion compositions were calculated for all dilutions from the undiluted value. All sample data below DISS blank are from filtered samples (DISS) and all data below WWR blank are from unfiltered samples processed through the in-bottle digestion procedure (WWR), except where noted.

Attachment 3. Linear regressions of each analyte in dissolved and whole-water recoverable matrix measured on the Agilent 7500ce inductively coupled plasma mass spectrometer (ICP–MS) and on the Nexion 350D ICP–MS. The solid line represents the 1:1 correlation and the dashed line represents the linear fit of the data. Where the y-intercept of the regression line was more than 3 times greater in magnitude than the detection limit for the analyte, a regression of data near the detection limit was performed to determine if there is agreement between the methods near the detection limit.

Attachment 4. Linear regression plots of each analyte comparing data, in micrograms per liter, obtained on two Nexion inductively coupled plasma mass spectrometers, MS2 versus MS1.

/signed/

Jeff McCoy, Chief

National Water Quality Laboratory

Laboratory and Analytical Services Division

Supersedes: N/A

Key words: Agilent, Nexion, ICP-MS, inductively coupled plasma-mass spectrometer, trace elements, trace metals, INBD, in-bottle digestion, WWR, DISS

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Attachment 1. Detection limits, in micrograms per liter, calculated using the DQCALC software for the method on the Nexion inductively-coupled plasma mass spectrometer in accordance with Williams and others, 2015.

[WWR, whole water recoverable; DL, detection limit; DLDQC, detection limit calculated using ASTM DQCALC program]

Analyte	Dissolved DLDQC	WWR DLDQC
Li	0.004	0.004
Be	0.002	0.0001
B	0.146	0.13
Al	0.188	0.181
V	0.013	0.045
Cr	0.045	0.049
Mn	0.019	0.007
Co	0.0008	0.003
Ni	0.02	0.03
Cu	0.004	0.005
Zn	0.033	0.136
As	0.002	0.011
Se	0.003	0.007
Sr	0.001	0.011
Mo	0.004	0.004
Ag	0.062	0.0002
Cd	0.002	0.0009
Sb	0.002	0.001
Ba	0.003	0.005
W	0.003	0.003
Tl	0.0006	0.0002
Pb	0.0008	0.0001
U	0.001	0.0008

Attachment 2. Recovery, in percent, of 10 micrograms per liter of each trace element spiked into increasing dilutions of surface-water or ground water. Relevant major ion composition, specific conductance, and residue on evaporation are included for undiluted samples where available. Specific conductance of each dilution was measured and is reported. Major ion compositions were calculated for all dilutions from the undiluted value. All sample data below DISS blank are from filtered samples (DISS) and all data below WWR blank are from unfiltered samples processed through the in-bottle digestion procedure (WWR), except where noted. [DISS, dissolved matrix; WWR, whole-water recoverable matrix; ROE, residue on evaporation; µS/cm, microsiemens per centimeter at 25 degrees Celsius, mg/L, milligrams per liter; IS, internal standard; IS PASS, internal standards IS FAIL, internal standard recovery was outside of established limits (70–130%) and data would not routinely be reported, this is indicative of matrix induced effects on recovery; GSL, water from Great Salt Lake; %, percent, NA, no data available either because parameter was not measured or measured value was outside of calibration range; >, greater than]

Dissolved sample identification[1,2,4,5,6]	Conduct-ance (µS/cm)	Residue on evaporation (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Alkalinity (mg/L)	Potassium (mg/L)	Bromide (mg/L)	Lithium	Beryllium	Boron	Aluminum	Manganese	Strontium	Molybdenum	Silver	Cadmium	Antimony	Barium	Tungsten	Thallium	Lead	Uranium	Selenium	Vanadium	Chromium	Cobalt	Nickel	Copper	Zinc	Arsenic	IS Status
DISS blank	<5	NA	NA	NA	NA	NA	NA	NA	NA	NA	105%	101%	98%	102%	98%	85%	101%	90%	98%	97%	97%	98%	100%	98%	100%	103%	101%	103%	103%	108%	100%	99%	100%	IS PASS
20153280043 x50	139	71.2	3.88	1.32	19.56	31.4	2.14	NA	0.2054	0.005	107%	106%	106%	101%	101%	101%	104%	90%	100%	103%	101%	104%	99%	96%	100%	102%	99%	99%	100%	94%	94%	97%	99%	IS PASS
20151680110 x50	185	96.4	1.94	1.34	29	45.8	3.48	NA	1.1404	0.0336	105%	103%	101%	102%	98%	133%	108%	91%	102%	106%	105%	108%	101%	98%	102%	104%	105%	103%	102%	97%	96%	99%	103%	IS PASS
20151170154 x50	212	NA	2.6	1.4	35.4	48.4	10.58	7.54	0.1898	0	104%	106%	103%	100%	100%	110%	108%	90%	101%	106%	78%	107%	100%	97%	101%	105%	102%	102%	102%	98%	96%	99%	102%	IS PASS
20153370036 x50	250	150.6	5.72	6.14	29.8	2.18	82.2	9.56	0.262	0	104%	99%	98%	104%	99%	165%	108%	89%	101%	104%	101%	103%	98%	95%	101%	105%	102%	101%	101%	96%	95%	98%	99%	IS PASS
20151390060 x50	290	157.6	7.68	4.8	34.4	58.6	21.2	NA	1.208	NA	111%	108%	106%	104%	103%	56%	108%	89%	102%	106%	104%	108%	101%	97%	102%	108%	108%	107%	108%	102%	101%	101%	105%	IS PASS
20153280043 x20	341	178	9.7	3.3	48.9	78.5	5.35	NA	0.5135	NA	102%	102%	102%	99%	98%	131%	107%	86%	98%	105%	103%	109%	98%	95%	99%	104%	105%	103%	101%	95%	95%	97%	103%	IS PASS
20151680110 x20	478	241	4.85	3.35	72.5	114.5	8.7	NA	2.851	NA	104%	98%	105%	98%	95%	122%	110%	85%	97%	105%	112%	109%	98%	95%	100%	108%	112%	109%	106%	99%	97%	100%	109%	IS PASS
20151170154 x20	538	NA	6.5	3.5	88.5	121	26.45	18.85	0.4745	NA	103%	102%	100%	103%	97%	123%	110%	87%	99%	108%	116%	113%	99%	96%	102%	108%	108%	107%	104%	98%	96%	94%	107%	IS PASS
GSL x50	549	NA	NA	NA	NA	NA	NA	NA	NA	NA	92%	102%	99%	102%	95%	102%	107%	85%	97%	106%	102%	107%	96%	93%	99%	105%	107%	107%	103%	99%	96%	92%	107%	IS PASS
20153370036 x20	584	376.5	14.3	15.35	74.5	5.45	205.5	23.9	0.655	NA	101%	92%	93%	102%	95%	171%	111%	83%	97%	104%	101%	104%	96%	92%	101%	108%	110%	108%	105%	100%	96%	97%	103%	IS PASS
20153280043 x10	714	356	19.4	6.6	97.8	157	10.7	NA	1.027	NA	101%	97%	87%	98%	95%	152%	111%	83%	96%	105%	104%	111%	96%	93%	98%	107%	110%	106%	102%	96%	93%	95%	105%	IS PASS
20151390060 x20	738	394	19.2	12	86	146.5	53	NA	3.02	NA	110%	105%	107%	100%	100%	205%	113%	88%	100%	110%	108%	116%	101%	96%	104%	108%	107%	103%	102%	97%	94%	77%	103%	IS PASS
20151680110 x10	958	482	9.7	6.7	145	229	17.4	NA	5.702	NA	NA	93%	99%	101%	93%	147%	116%	83%	97%	107%	100%	111%	99%	94%	102%	113%	111%	108%	104%	96%	94%	97%	108%	IS PASS
20153370036 x10	1,050	753	28.6	30.7	149	10.9	411	47.8	1.31	NA	94%	86%	68%	105%	93%	190%	114%	68%	96%	105%	104%	107%	95%	90%	100%	110%	112%	108%	104%	97%	94%	94%	106%	IS PASS
20151170154 x10	1,070	NA	13	7	177	242	52.9	37.7	0.949	NA	99%	98%	104%	111%	94%	125%	115%	83%	95%	107%	103%	115%	98%	94%	101%	110%	113%	109%	104%	97%	94%	94%	109%	IS PASS
GSL x20	1,331	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	97%	100%	101%	96%	108%	112%	81%	91%	104%	101%	110%	96%	92%	99%	108%	110%	109%	103%	96%	92%	94%	108%	IS PASS
20153280043 x5	1,337	712	38.8	13.2	195.6	314	21.4	NA	2.054	NA	98%	90%	85%	91%	76%	68%	113%	79%	91%	104%	101%	112%	95%	90%	99%	107%	111%	104%	99%	89%	62%	82%	104%	IS PASS
20151390060 x10	1,435	788	38.4	24	172	293	106	NA	6.04	NA	108%	100%	99%	102%	99%	187%	116%	77%	97%	111%	111%	126%	103%	97%	110%	114%	114%	112%	106%	100%	96%	98%	112%	IS PASS
20151680110 x5	1,890	964	19.4	13.4	290	458	34.8	NA	11.404	NA	NA	87%	88%	100%	92%	112%	118%	78%	92%	108%	102%	111%	96%	90%	101%	115%	114%	111%	104%	97%	92%	87%	110%	IS PASS
20151170154 x5	1,922	NA	26	14	354	484	105.8	75.4	1.898	NA	93%	89%	76%	100%	133%	152%	119%	77%	89%	108%	107%	116%	96%	90%	102%	113%	117%	112%	105%	97%	92%	93%	110%	IS PASS
20153370036 x5	2,007	1,506	57.2	61.4	298	21.8	822	95.6	2.62	NA	85%	79%	56%	104%	89%	307%	117%	44%	91%	107%	107%	114%	94%	87%	101%	113%	117%	112%	104%	97%	92%	89%	107%	IS FAIL
GSL x10	2,594	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	89%	95%	106%	96%	183%	119%	78%	89%	106%	104%	111%	96%	90%	100%	114%	115%	110%	103%	97%	92%	89%	108%	IS FAIL
20151390060 x5	2,641	1,576	76.8	48	344	586	212	NA	12.08	NA	105%	92%	96%	107%	95%	541%	121%	78%	92%	112%	114%	140%	104%	96%	117%	118%	122%	119%	109%	100%	96%	NA	117%	IS FAIL
20153280043 x2	3,140	1,780	97	33	489	785	53.5	NA	5.135	NA	129%	111%	NA	130%	90%	130%	116%	73%	85%	106%	100%	120%	95%	86%	101%	112%	114%	109%	100%	90%	88%	80%	108%	IS FAIL
20151680110 x2	4,491	2,410	48.5	33.5	725	1145	87	NA	28.51	NA	NA	115%	359%	155%	122%	177%	124%	73%	86%	110%	113%	117%	94%	85%	102%	117%	124%	117%	104%	96%	89%	83%	114%	IS FAIL
20153370036 x2	4,560	3,765	143	153.5	745	54.5	2055	239	6.55	NA	100%	93%	45%	154%	127%	931%	121%	34%	85%	108%	116%	124%	94%	83%	196%	118%	126%	119%	107%	99%	91%	84%	112%	IS FAIL
201511700154 x2	5,108	NA	65	35	885	1210	264.5	188.5	4.745	NA	NA	111%	118%	155%	149%	254%	122%	71%	84%	109%	114%	127%	97%	86%	107%	117%	122%	115%	104%	96%	89%	83%	114%	IS FAIL
GSL x5	5,330	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	111%	256%	137%	121%	161%	123%	73%	84%	107%	108%	115%	96%	87%	100%	118%	124%	120%	107%	98%	93%	81%	115%	IS FAIL
20151390060 x2	6,604	3,940	192	120	860	1465	530	0	30.2	NA	128%	109%	72%	130%	215%	-12%	122%	69%	86%	112%	111%	156%	103%	90%	125%	121%	128%	121%	110%	101%	93%	NA	119%	IS FAIL

Whole-water recoverable sample ID[1,2,4,5]	Conductance (µS/cm)	ROE (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	SO_4 (mg/L)	Alkalinity (mg/L)	K (mg/L)	Br (mg/L)	Li	Be	B	Al	Mn	Sr	Mo	Ag	Cd	Sb	Ba	W	Tl	Pb	U	Se	V	Cr	Co	Ni	Cu	Zn	As	IS Status
WWR blank	<5	NA	NA	NA	NA	NA	NA	NA	NA	NA	107%	109%	105%	105%	108%	106%	104%	107%	104%	104%	105%	107%	109%	101%	107%	105%	105%	104%	103%	104%	105%	103%	103%	IS PASS
20153280043 x50	139	71	4	1	20	31	2	NA	NA	NA	95%	98%	95%	104%	101%	103%	110%	101%	99%	107%	102%	101%	96%	96%	104%	106%	98%	93%	97%	95%	95%	91%	101%	IS PASS
20153370036 x50	250	151	6	6	30	2	82	10	NA	NA	98%	100%	96%	99%	104%	116%	109%	102%	98%	105%	101%	100%	97%	99%	108%	106%	100%	95%	97%	96%	95%	92%	102%	IS PASS
20153280043 x20	341	178	10	3	49	79	5	NA	NA	NA	93%	94%	104%	98%	110%	113%	115%	96%	96%	108%	101%	96%	91%	96%	107%	106%	105%	99%	102%	100%	99%	96%	108%	IS PASS
GSL x50	549	NA	NA	NA	NA	NA	NA	NA	NA	NA	102%	97%	95%	99%	98%	110%	108%	95%	92%	101%	102%	96%	92%	96%	107%	104%	103%	97%	98%	97%	93%	83%	105%	IS PASS
20153370036 x20	584	377	14	15	75	5	206	24	NA	NA	94%	95%	84%	101%	102%	48%	109%	95%	92%	104%	98%	98%	92%	95%	103%	106%	104%	97%	97%	96%	94%	90%	104%	IS PASS
20153280043 x10	714	356	19	7	98	157	11	NA	NA	NA	93%	94%	89%	94%	100%	124%	117%	95%	92%	108%	98%	93%	87%	96%	108%	107%	104%	97%	99%	96%	94%	89%	108%	IS PASS
20153370036 x10	1,050	753	29	31	149	11	411	48	NA	NA	101%	97%	94%	97%	107%	109%	113%	94%	90%	106%	101%	99%	93%	97%	112%	107%	111%	103%	103%	99%	96%	88%	110%	IS PASS
GSL x20	1,331	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	103%	153%	106%	108%	116%	117%	94%	89%	107%	104%	99%	95%	99%	113%	107%	109%	101%	101%	97%	89%	89%	110%	IS PASS
20153280043 x5	1,337	712	39	13	196	314	21	NA	NA	NA	98%	96%	79%	103%	136%	143%	122%	92%	89%	112%	104%	94%	87%	97%	110%	110%	109%	102%	100%	97%	95%	85%	112%	IS PASS
20153370036 x5	2,007	1,506	57	61	298	22	822	96	NA	NA	124%	100%	106%	106%	116%	250%	119%	90%	87%	112%	108%	102%	95%	98%	107%	110%	120%	111%	106%	101%	97%	84%	114%	IS PASS
GSL x10	2,594	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	103%	108%	118%	110%	120%	119%	89%	84%	109%	136%	99%	97%	98%	111%	109%	110%	101%	99%	95%	90%	76%	109%	IS PASS
20153280043 x2	3,140	1,780	97	33	489	785	54	NA	NA	NA	112%	96%	NA	106%	199%	187%	128%	85%	81%	118%	111%	94%	90%	98%	110%	112%	117%	106%	103%	97%	92%	76%	117%	IS FAIL
20153370036 x2	4,560	3,765	143	154	745	55	2,055	239	NA	NA	119%	95%	70%	107%	115%	-365%	123%	80%	78%	115%	114%	99%	97%	98%	82%	115%	129%	115%	108%	101%	94%	76%	115%	IS FAIL
GSL x5	5,330	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	101%	-47%	121%	112%	102%	124%	83%	78%	113%	88%	97%	97%	97%	112%	113%	129%	118%	113%	106%	99%	77%	123%	IS FAIL
20153280043	5,946	3,560	194	66	978	1,570	107	NA	NA	NA	126%	98%	NA	114%	NA	494%	135%	79%	76%	124%	147%	94%	93%	98%	107%	113%	121%	110%	102%	94%	89%	68%	117%	IS FAIL
20153370036	8,115	7,530	286	307	1,490	109	4,110	478	NA	NA	94%	86%	14%	111%	109%	494%	125%	75%	73%	117%	127%	98%	102%	101%	NA	111%	135%	118%	106%	99%	90%	71%	112%	IS FAIL
GSL x2	11,809	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	101%	NA	143%	119%	83%	132%	76%	73%	122%	112%	99%	107%	97%	110%	113%	126%	116%	104%	95%	88%	68%	113%	IS FAIL

[1]The dilution used for each sample is indicated by the suffix xNN (for example x50) on the sample identification.

[2]A filtered sample with 2 percent hydrocloric acid added was used in the whole water recoverable study for samples 20153280043 and 20153370036.

[3]Cells are highlighted pink where the spike level was too low to accurately measure spike recovery (ambient sample concentration was greater than 5 times the spike concentration).

[4]Where bracketing quality control were outside of established limits, data are highlighted yellow.

[5]Where bracketing quality control were outside of established limits and the ambient sample concentration was greater than 5 times the spike concentration, cells are highlighted orange.

[6]The recovery of internal standards dropped below the 70 percent recovery limit for acceptable data for higher conductivity samples. This is noted in the final column where it occurred.

Attachment 3.

Linear regressions of each analyte in dissolved and whole-water recoverable matrix measured on the Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. The solid line represents the 1:1 correlation and the dashed line represents the linear fit of the data. Where the y-intercept of the regression line was more than 3 times greater in magnitude than the detection limit for the analyte, a regression of data near the detection limit was performed to determine if there is agreement between the methods near the detection limit.

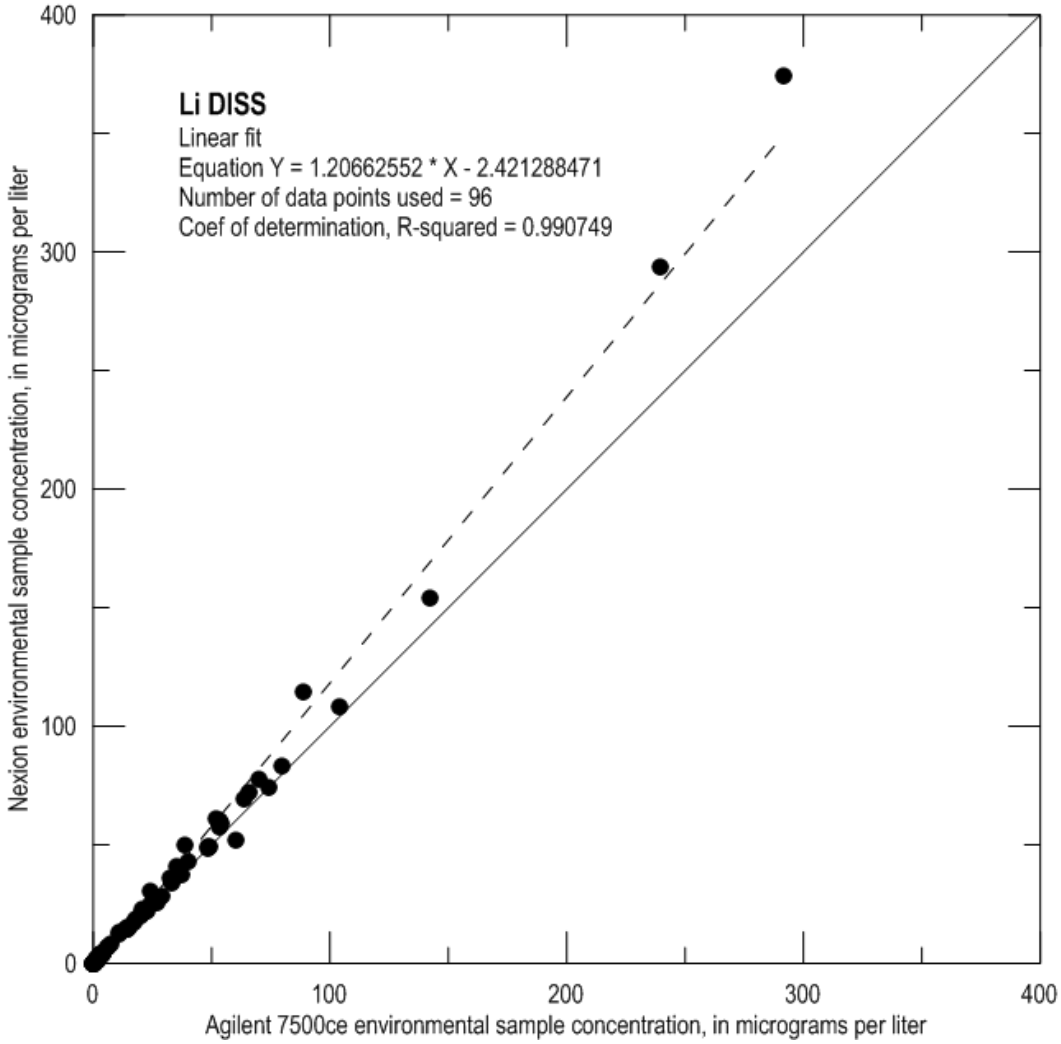


Figure A3.1. Linear regression of lithium dissolved (Li DISS) environmental sample data analyzed on the Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

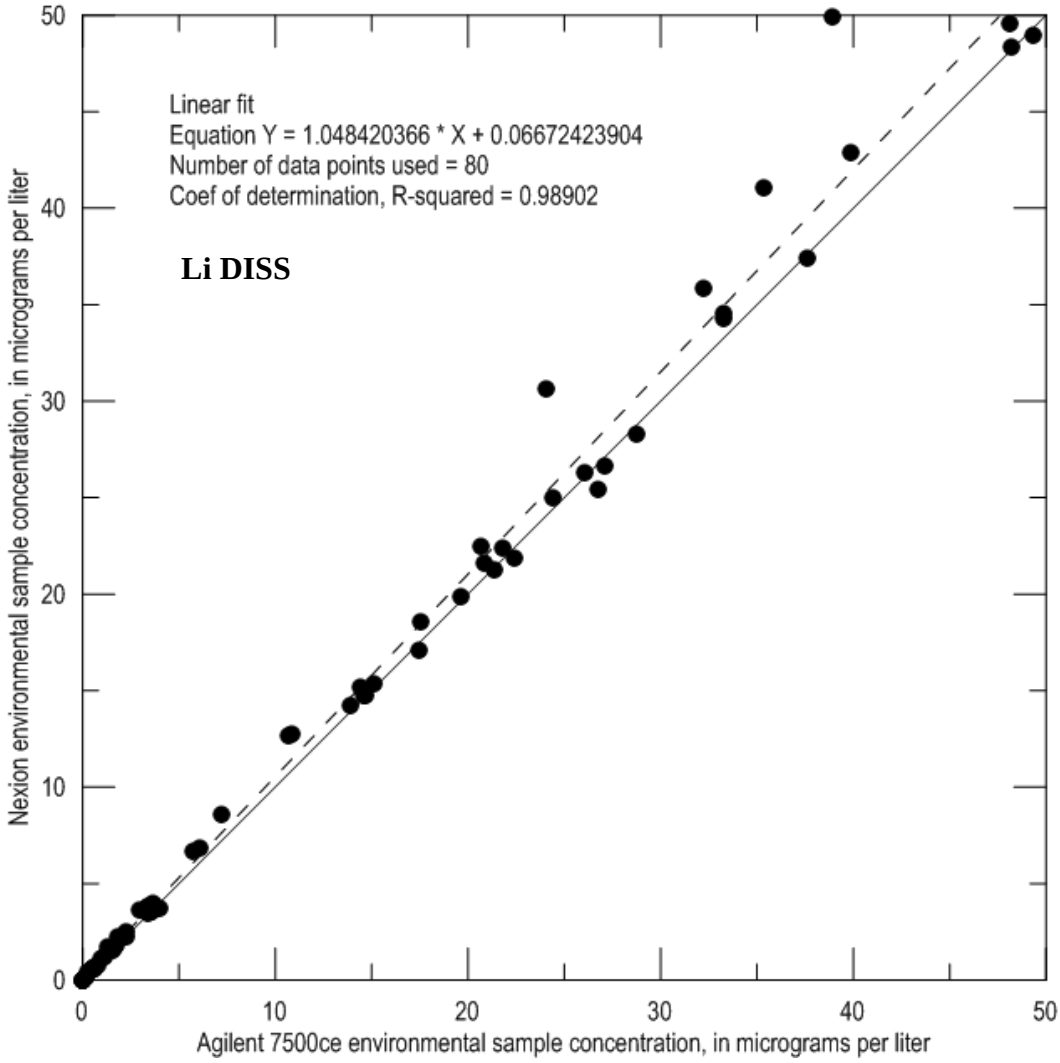


Figure A3.2. Linear regression of a subset of lithium dissolved (Li DISS) environmental sample data to 50 micrograms per liter analyzed on the Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. There is good agreement between the two methods near the detection limit.

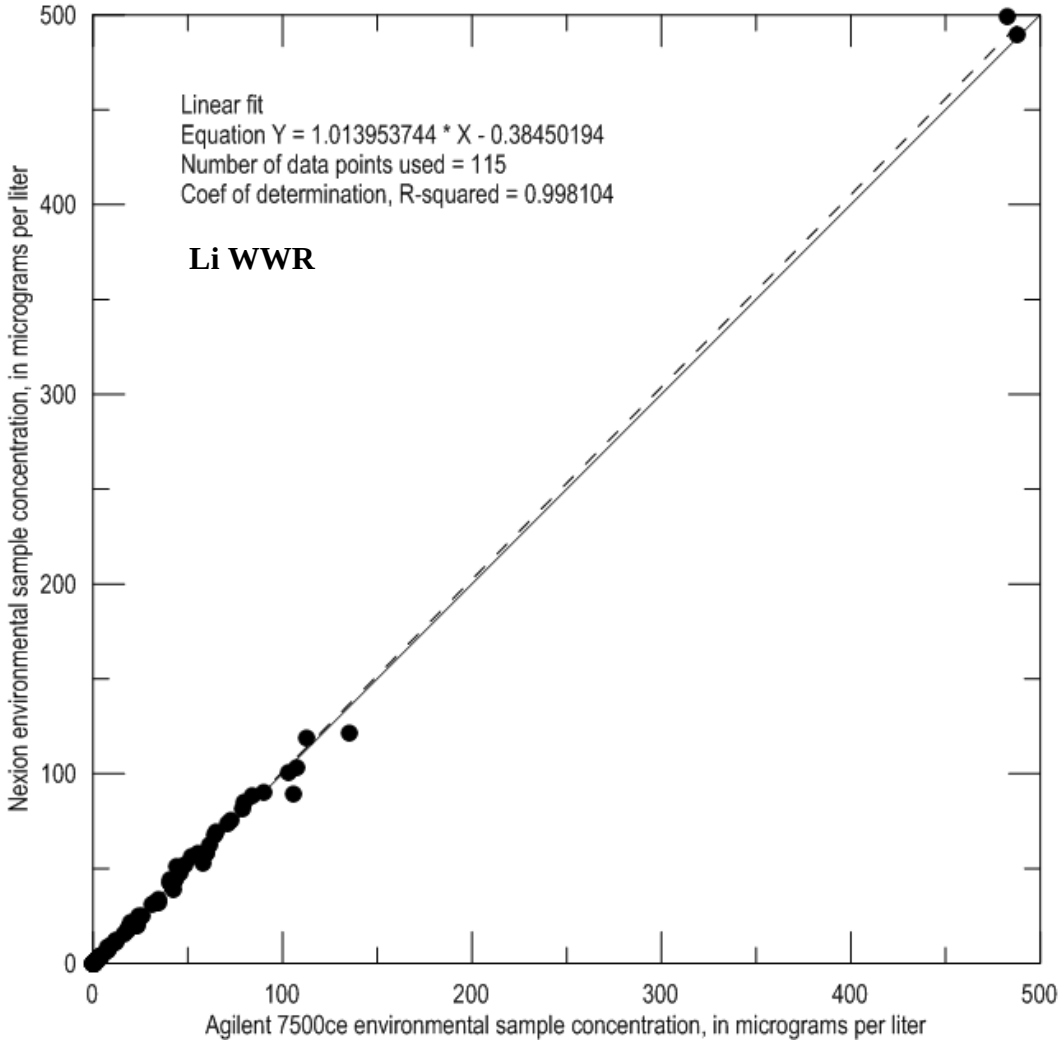


Figure A3.3. Linear regression of lithium whole-water (Li WWR) recoverable environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

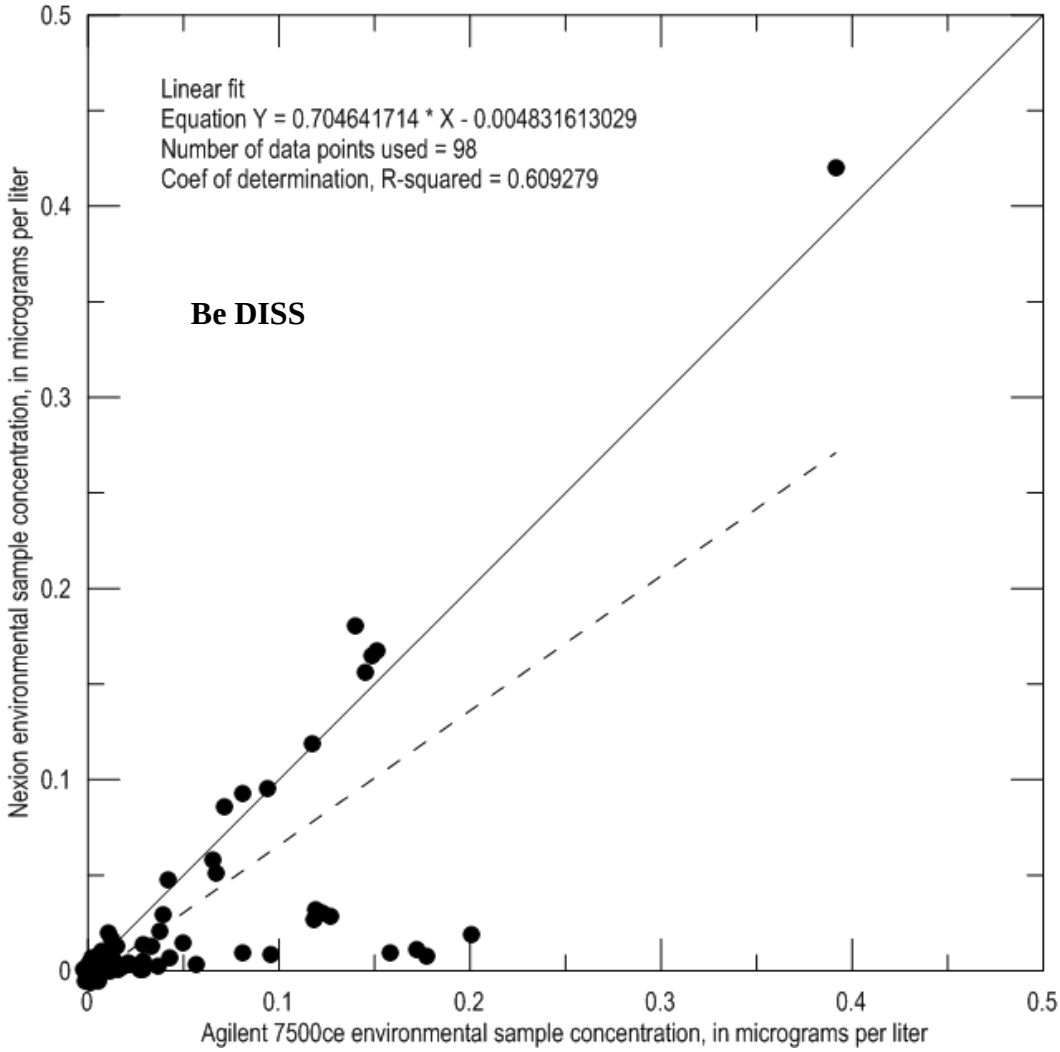


Figure A3.4. Linear regression of beryllium dissolved (Be DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

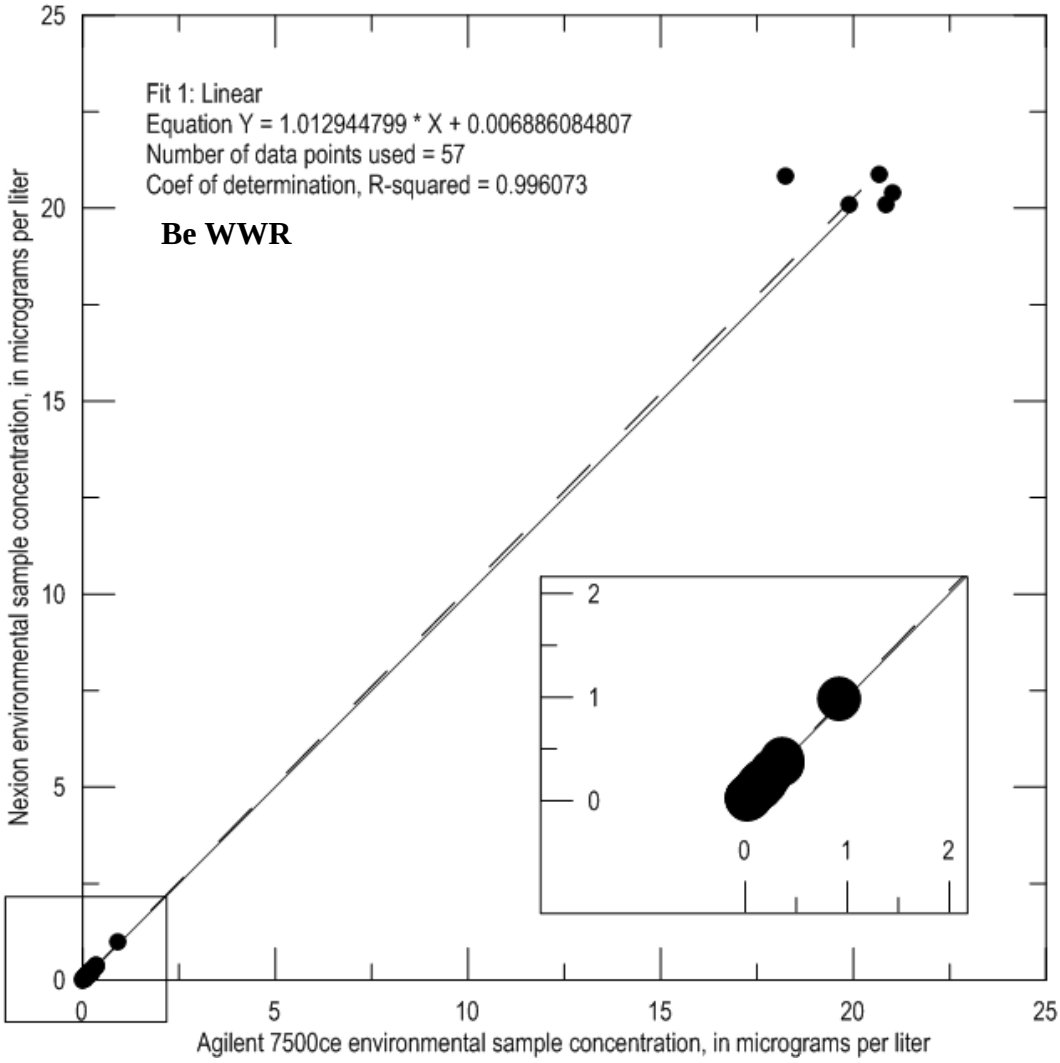


Figure A3.5. Linear regression of beryllium whole-water recoverable (Be WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

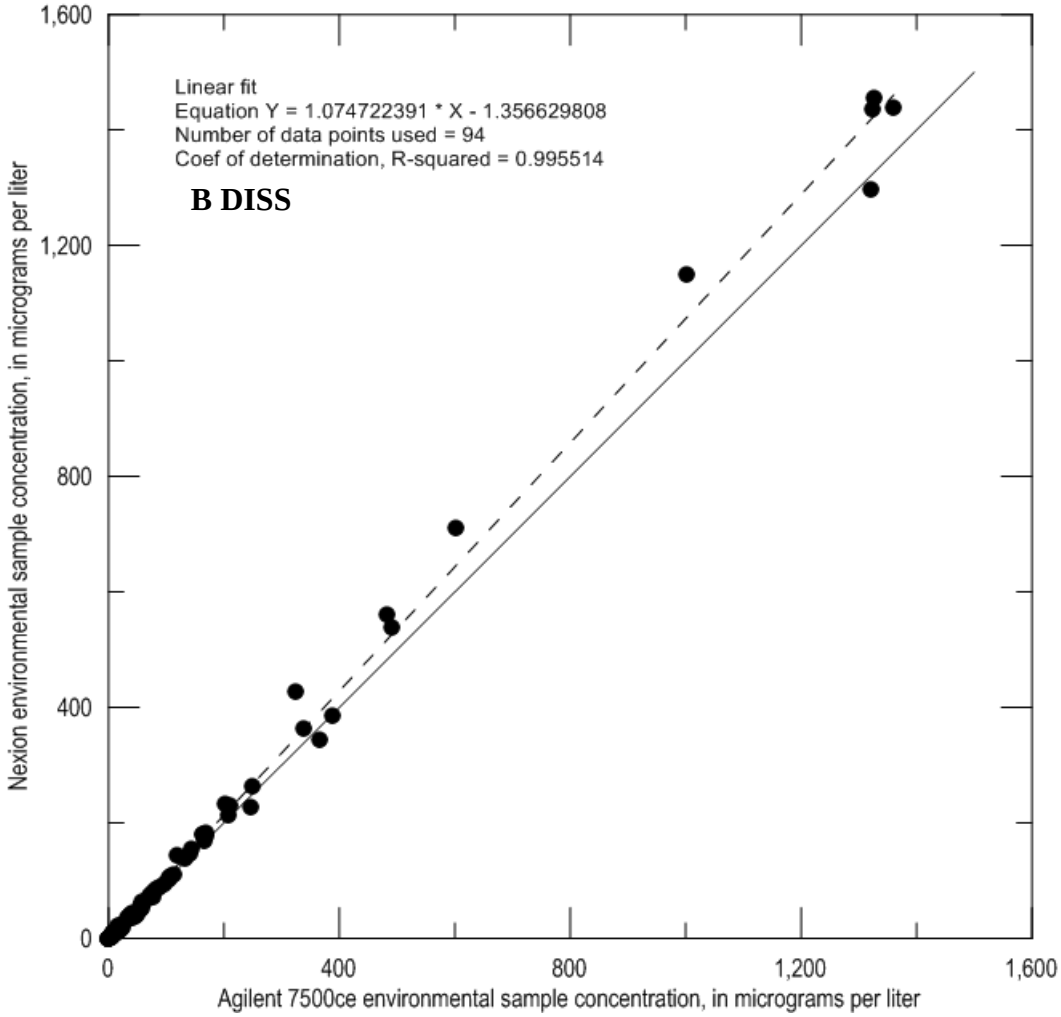


Figure A3.6. Linear regression of boron dissolved (B DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

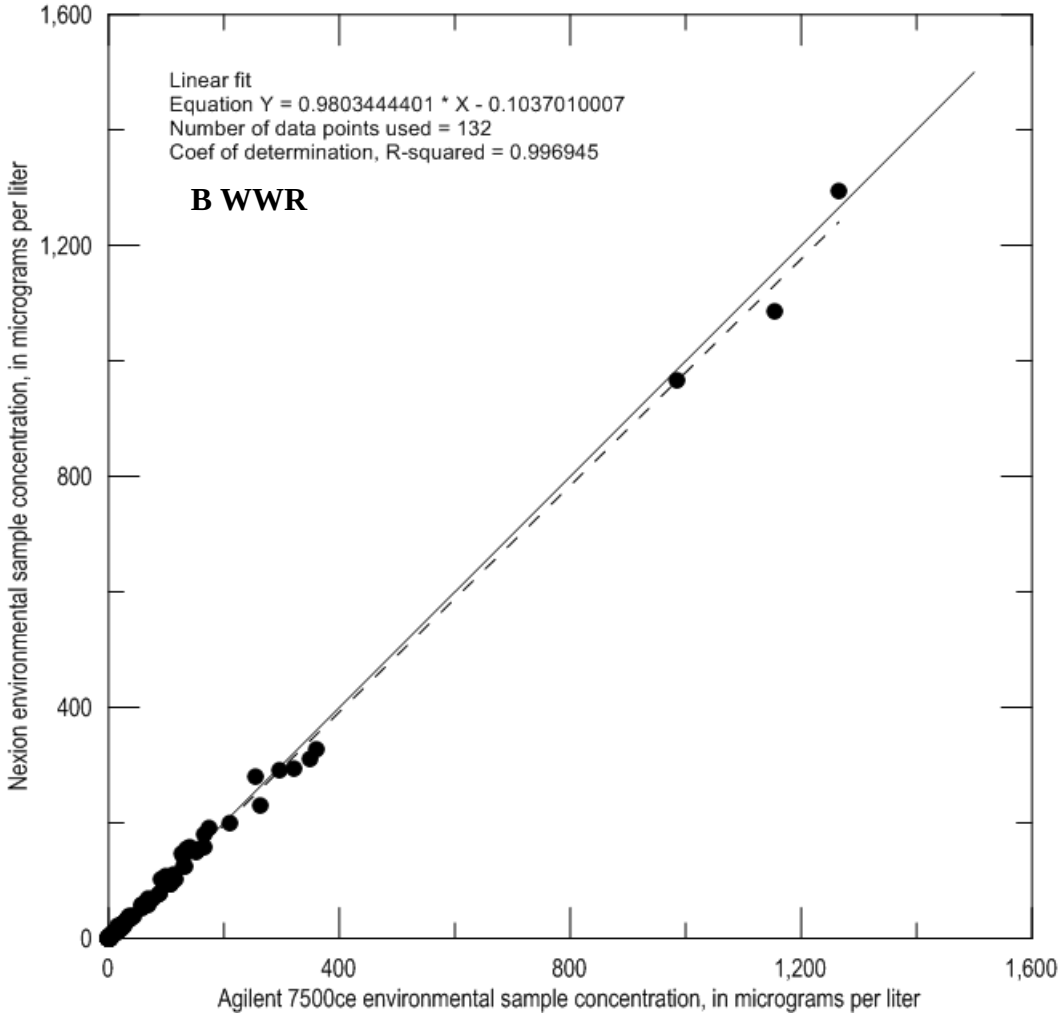


Figure A3.7. Linear regression of boron whole-water recoverable (B WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

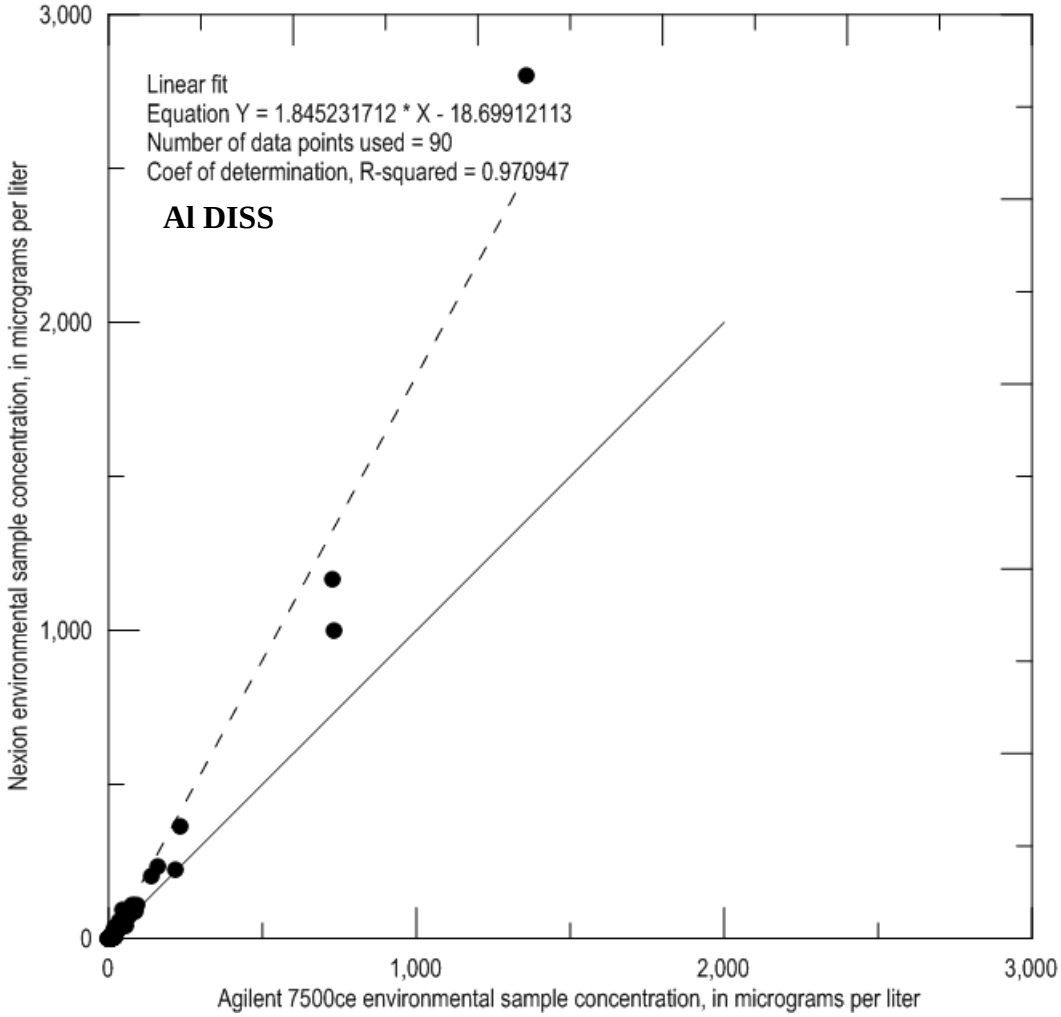


Figure A3.8. Linear regression of aluminum dissolved (Al DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

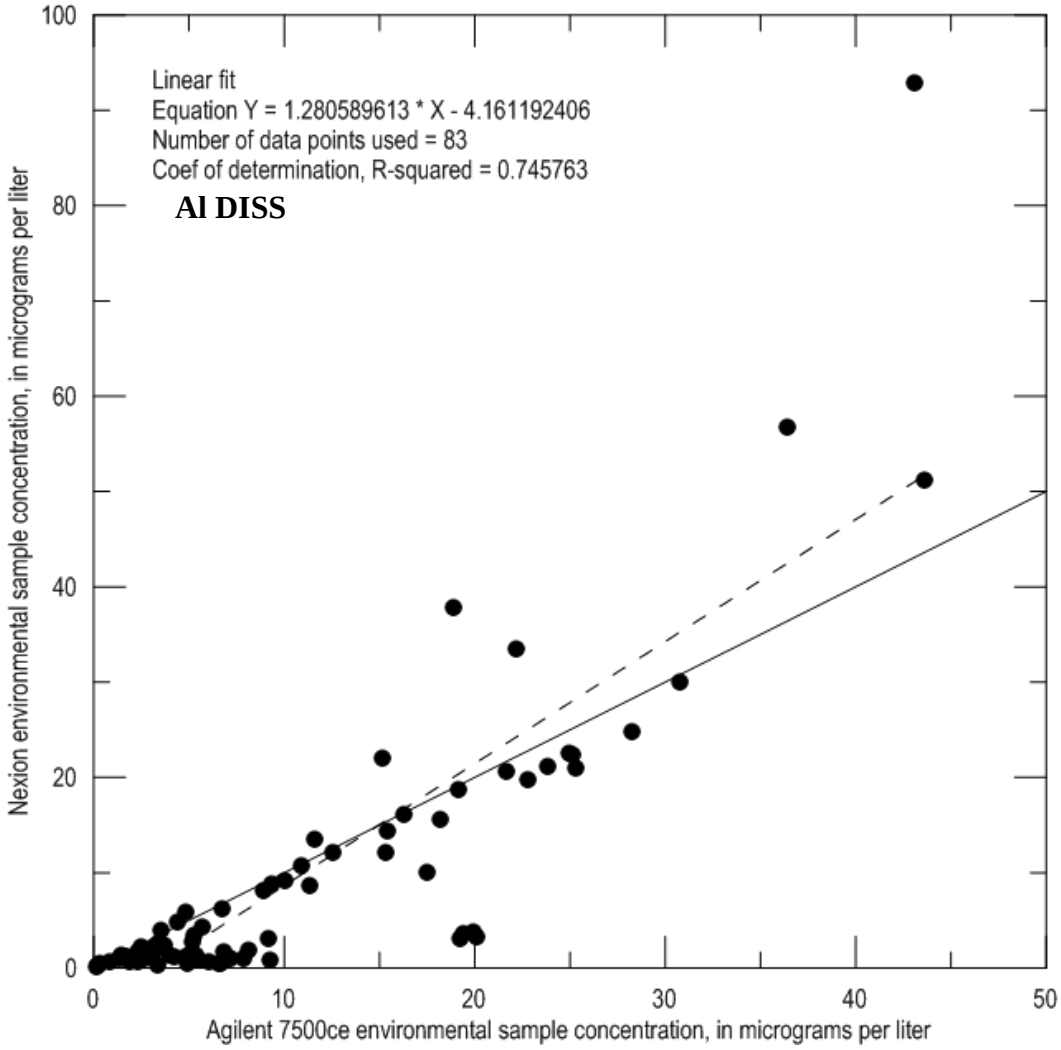


Figure A3.9. Linear regression of a subset of aluminum dissolved (Al DISS) environmental sample data to 50 micrograms per liter analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

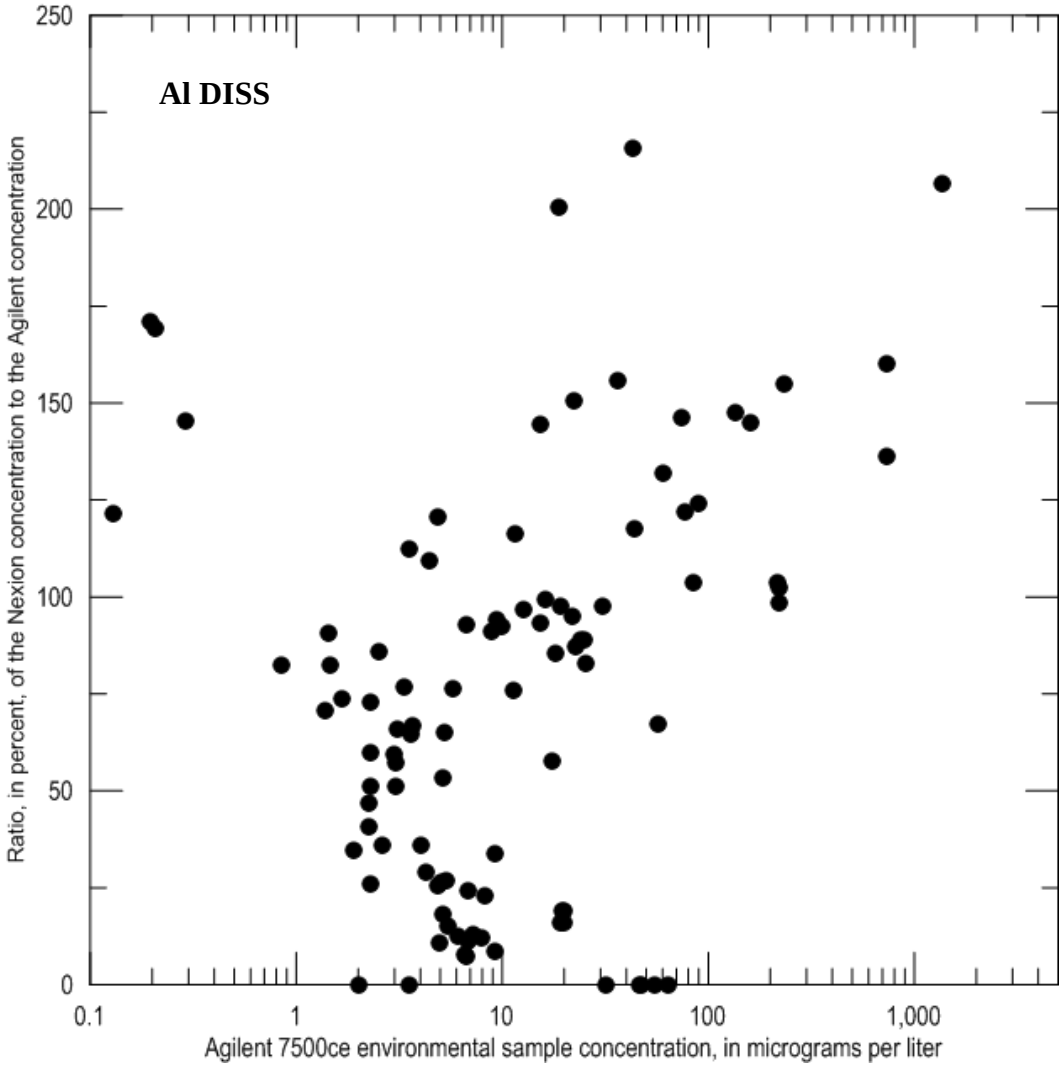


Figure A3.10. Ratio, in percent, of the aluminum dissolved (Al DISS) environmental-sample concentration determined on the Nexion 350D inductively coupled plasma mass spectrometer (ICP-MS) to the corresponding sample data on the Agilent ICP-MS compared with the Agilent ICP-MS concentration data in micrograms per liter. Note that up to 50 µg/L on the Agilent ICP-MS, that the ratios of Nexion to Agilent ICP-MS determined concentration often are less than or equal to 100 percent, whereas the ratio typically exceeds 100 percent above 50 µg/L (see also figs. A3.7 and A3.8).

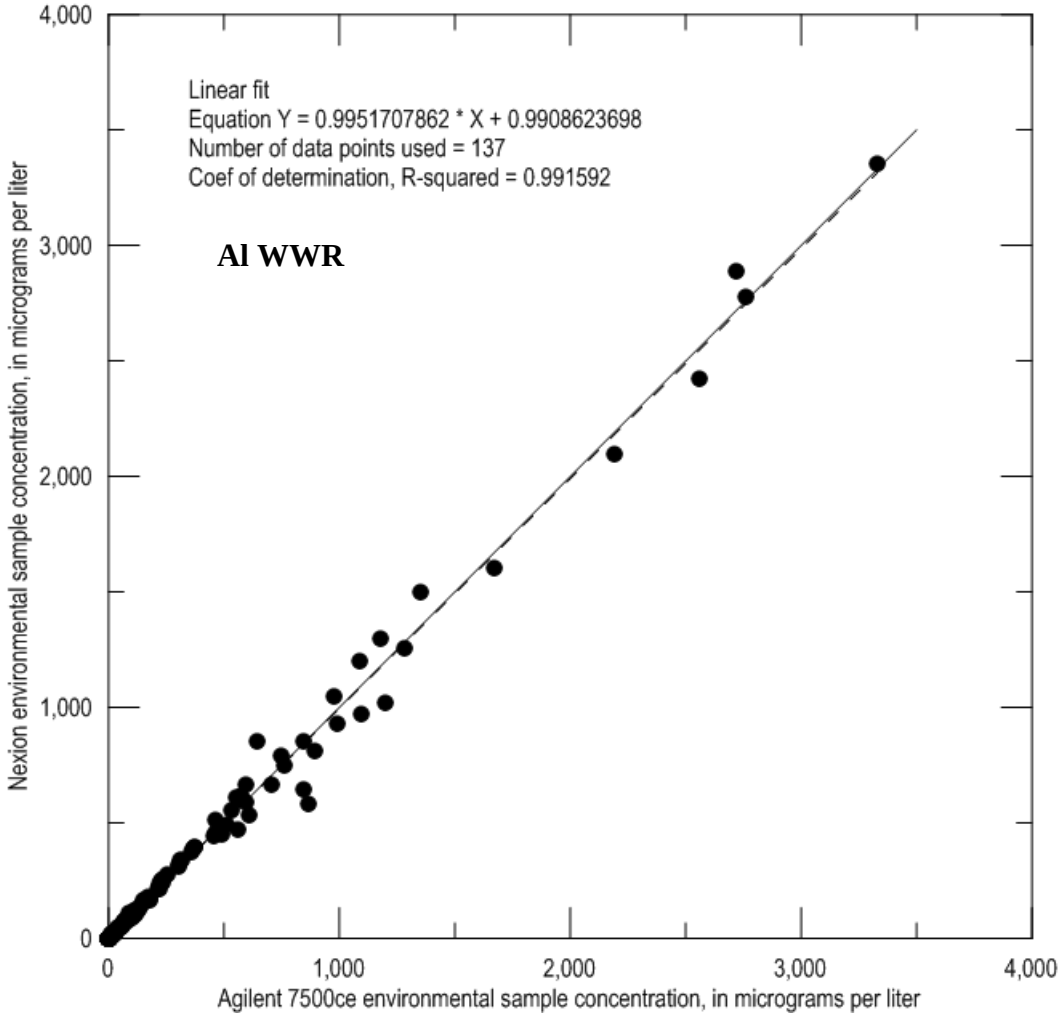


Figure A3.11. Linear regression of aluminum whole-water recoverable (Al WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

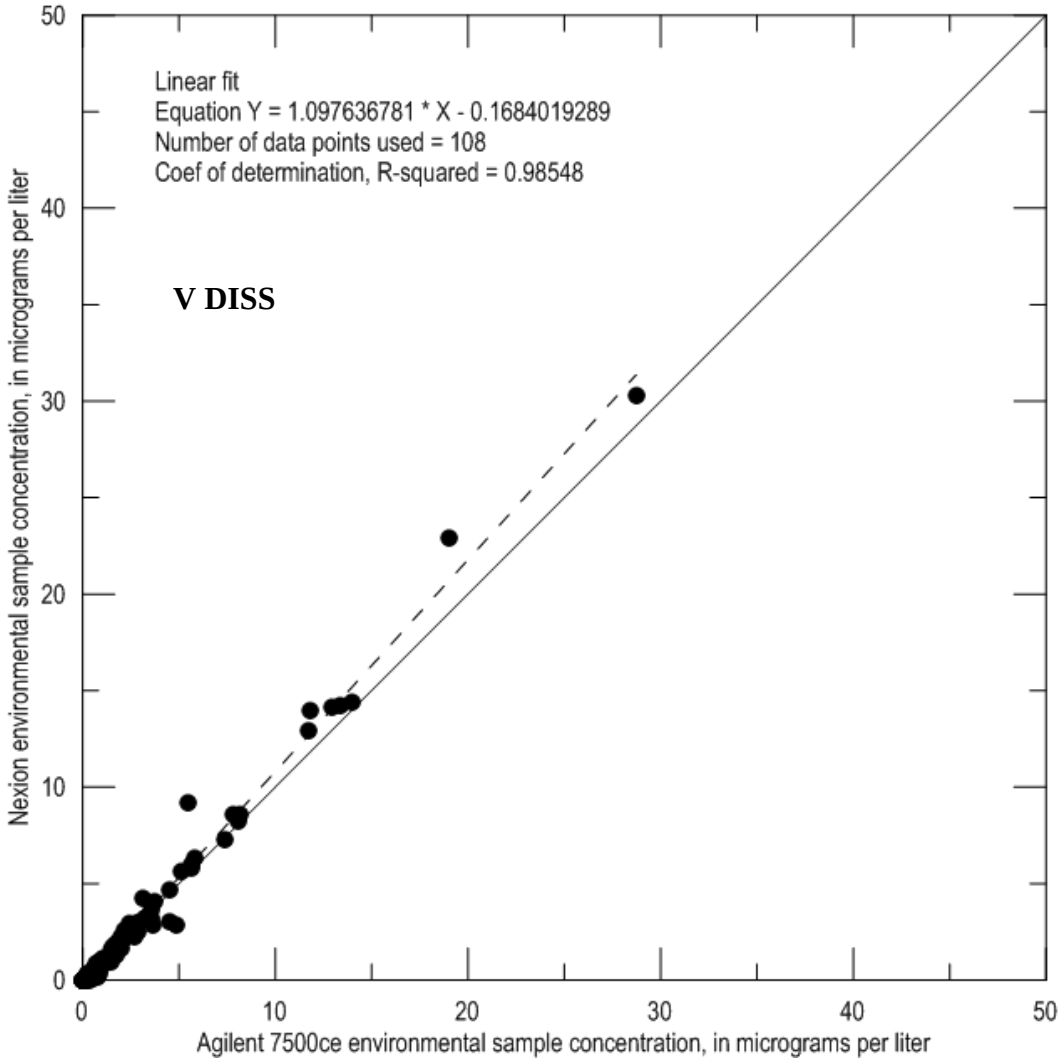


Figure A3.12. Linear regression of vanadium dissolved (V DISS) sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

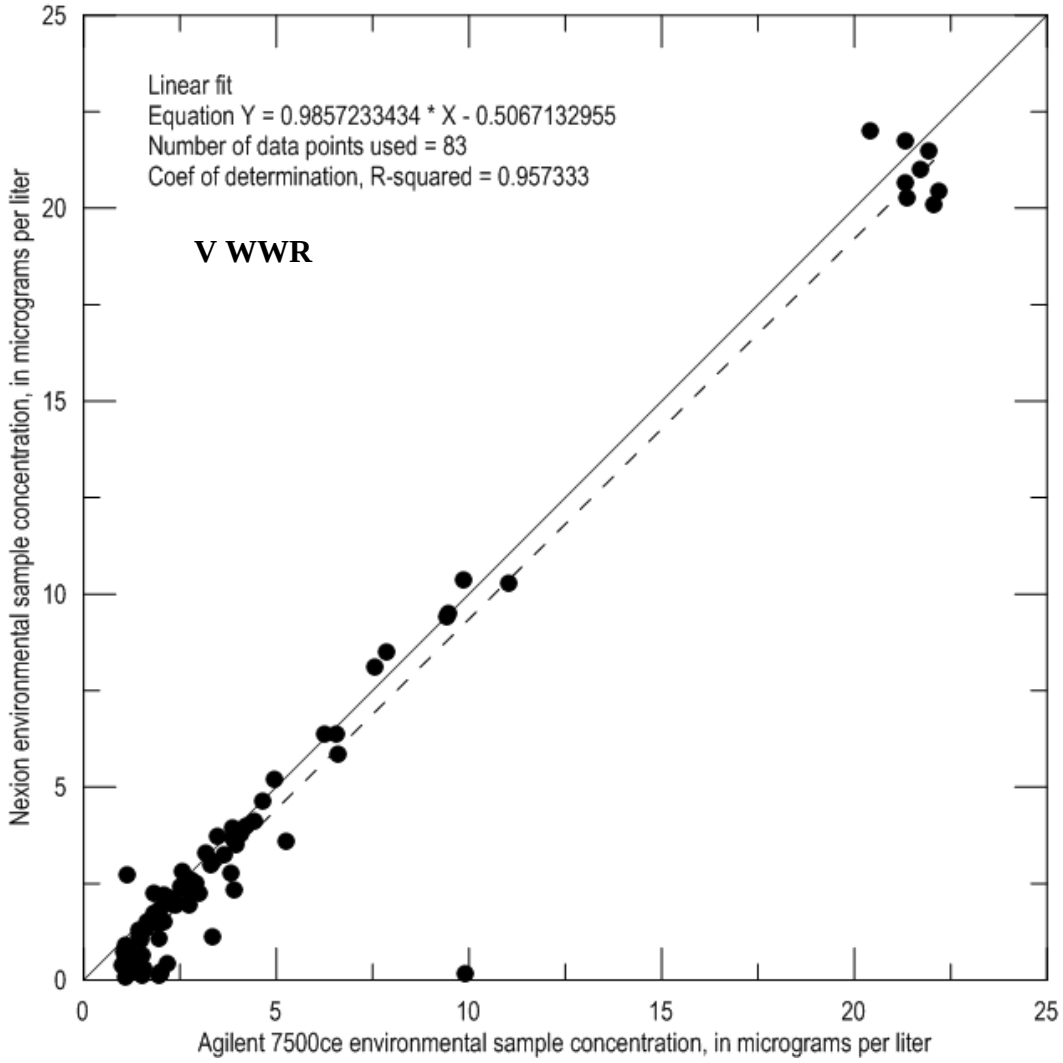


Figure A3.13. Linear regression of vanadium whole-water recoverable (V WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

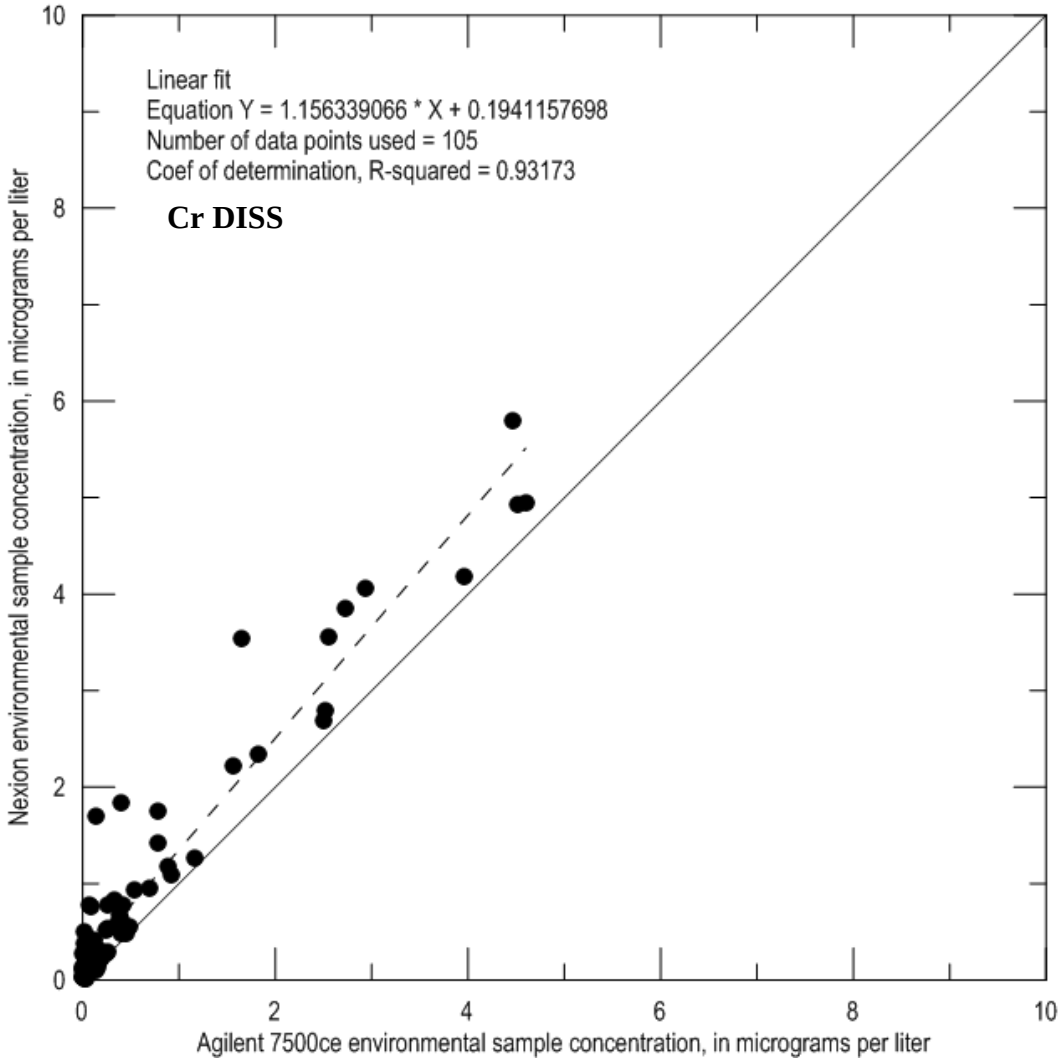


Figure A3.14. Linear regression of chromium dissolved (Cr DISS) sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

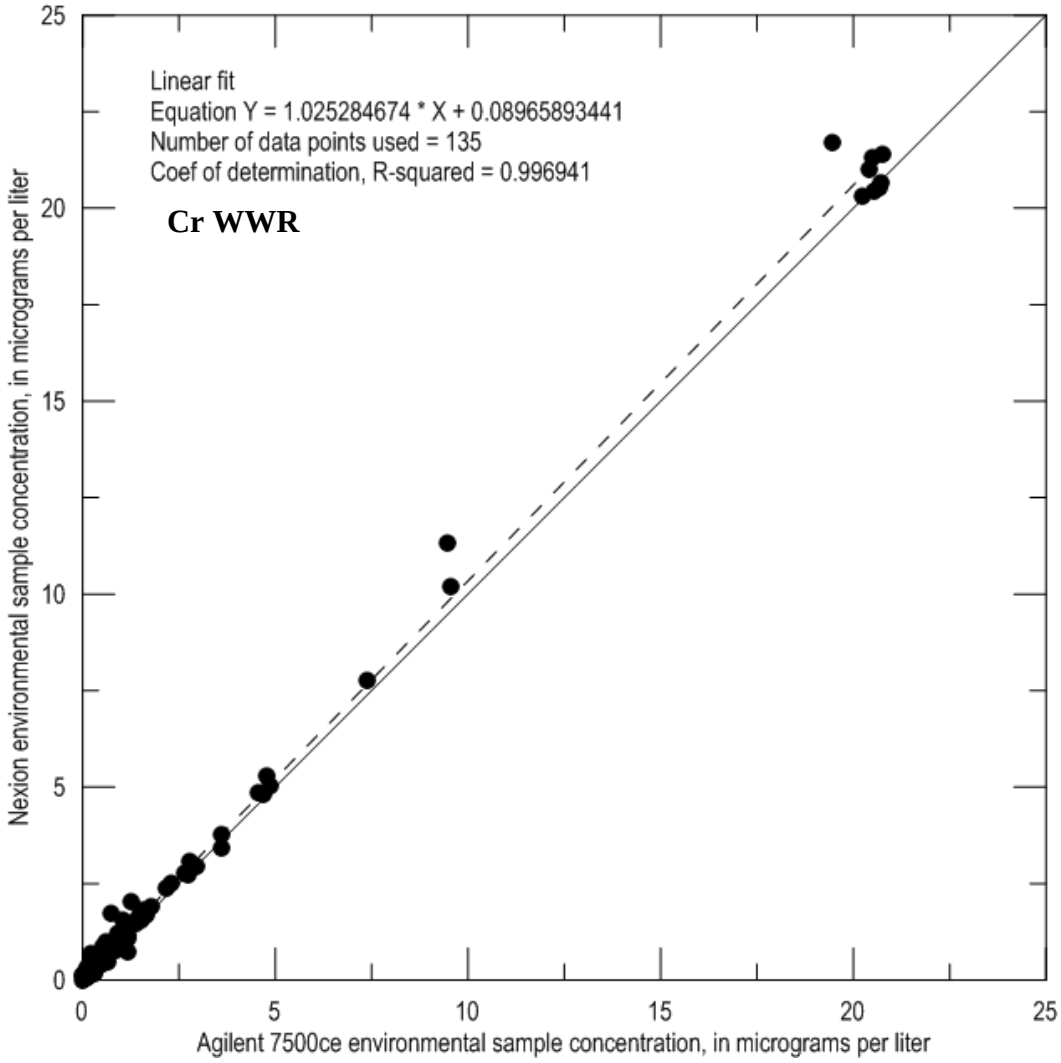


Figure A3.15. Linear regression of chromium whole-water recoverable (Cr WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

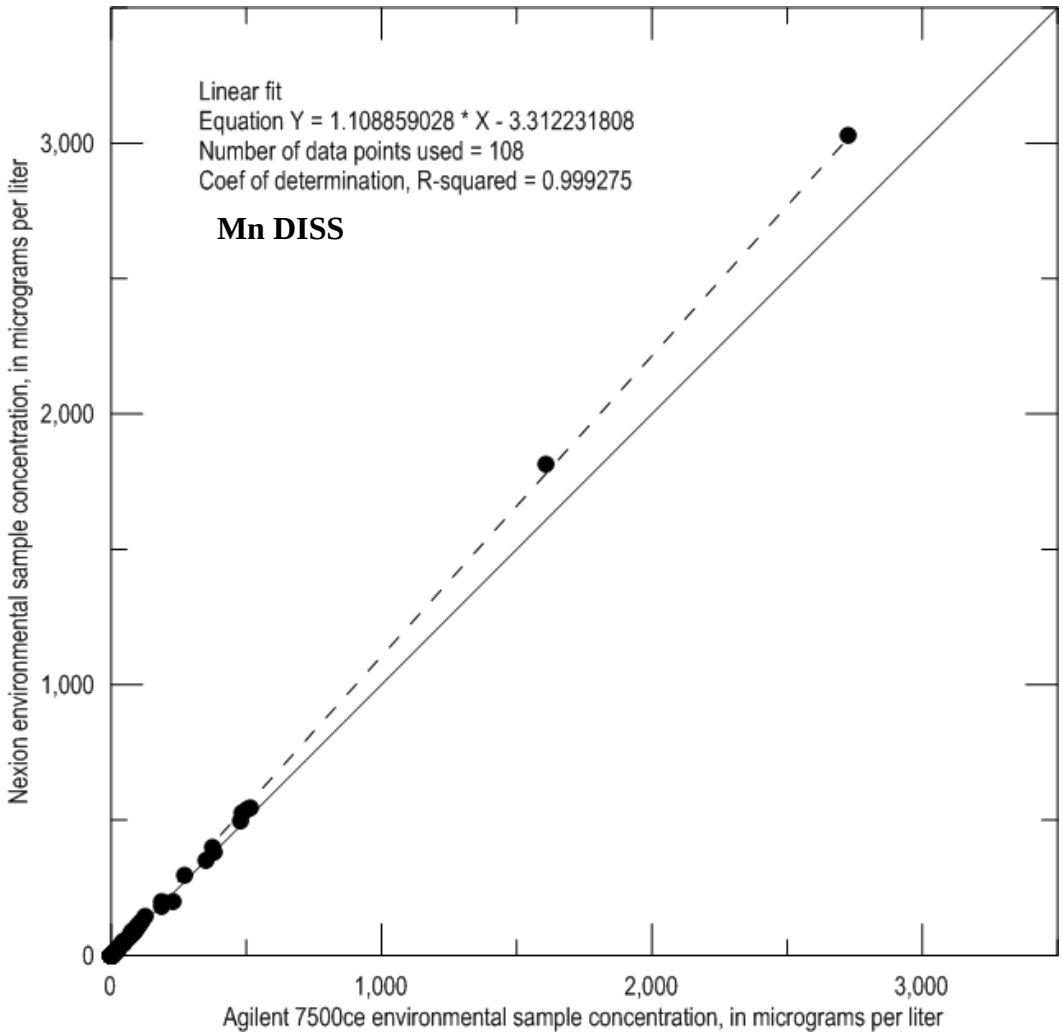


Figure A3.16. Linear regression of manganese dissolved (Mn DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

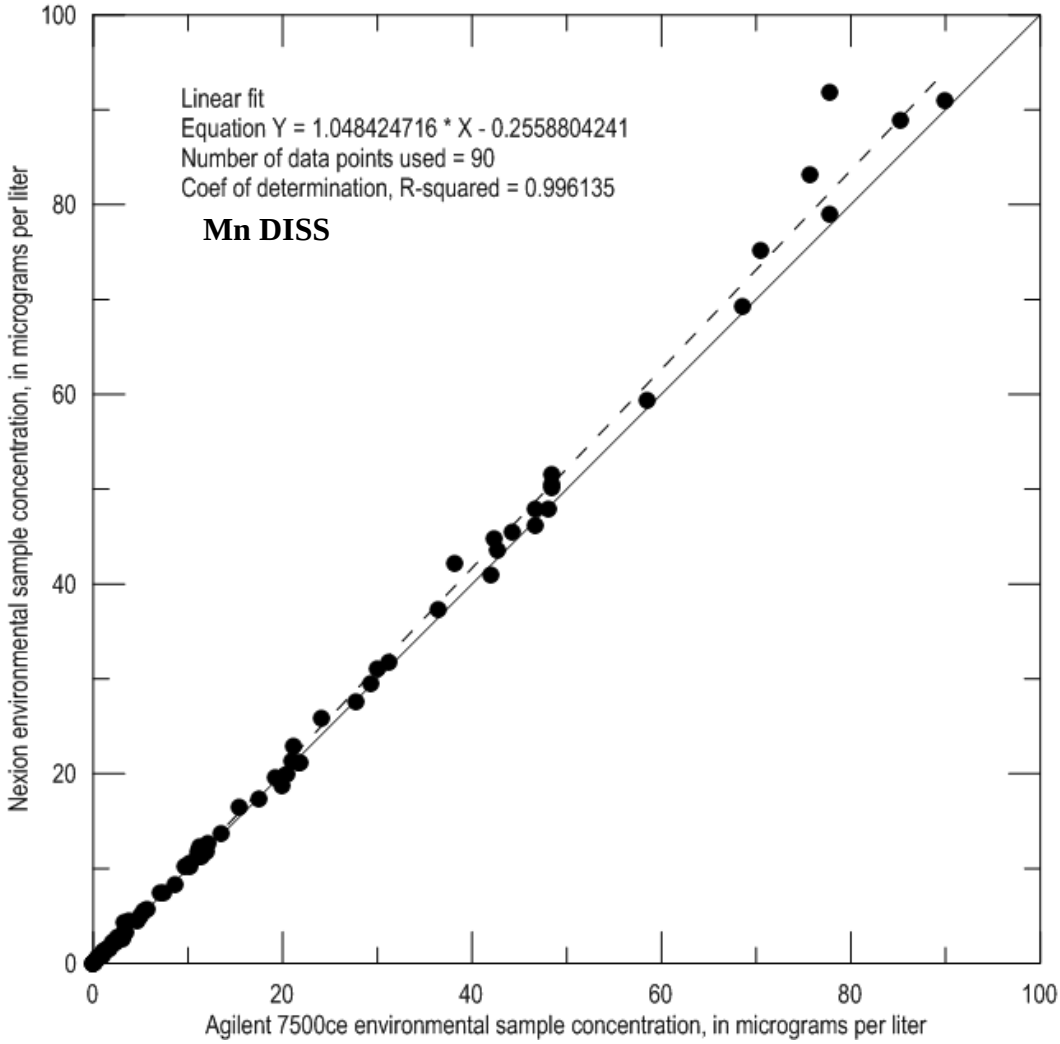


Figure A3.17. Linear regression of a subset of manganese dissolved (Mn DISS) environmental sample data to 100 micrograms per liter analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. There is good agreement between the methods near the detection limit.

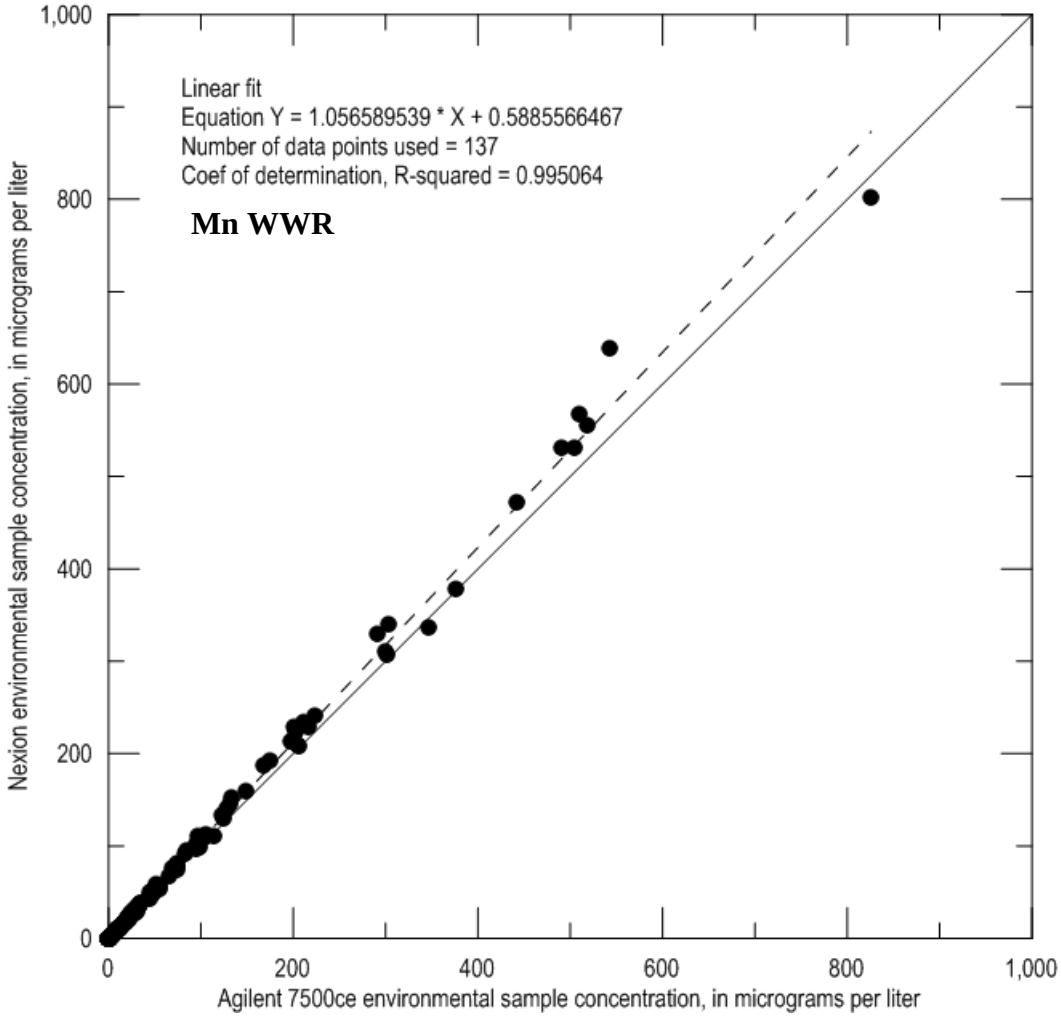


Figure A3.18. Linear regression of manganese whole-water recoverable (Mn WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

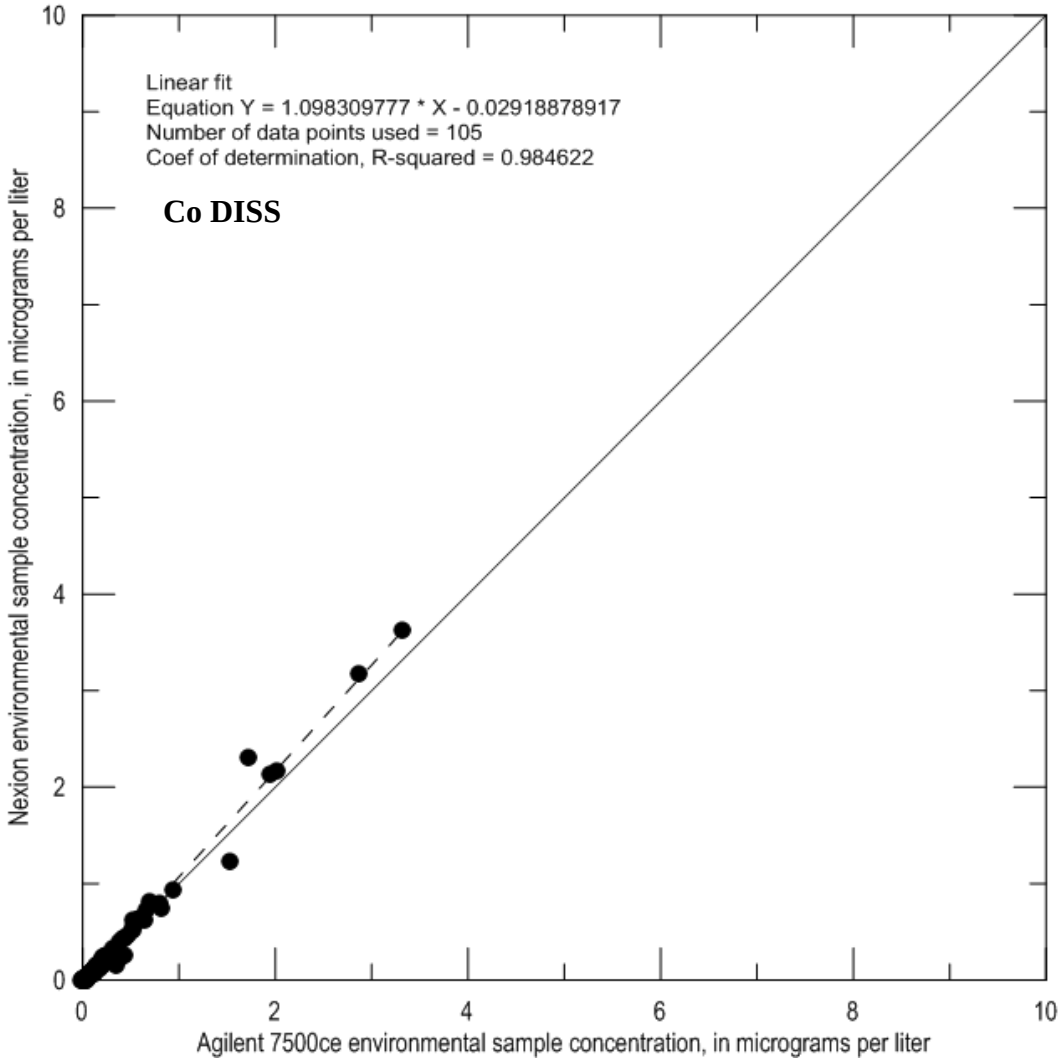


Figure A3.19. Linear regression of cobalt dissolved (Co DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

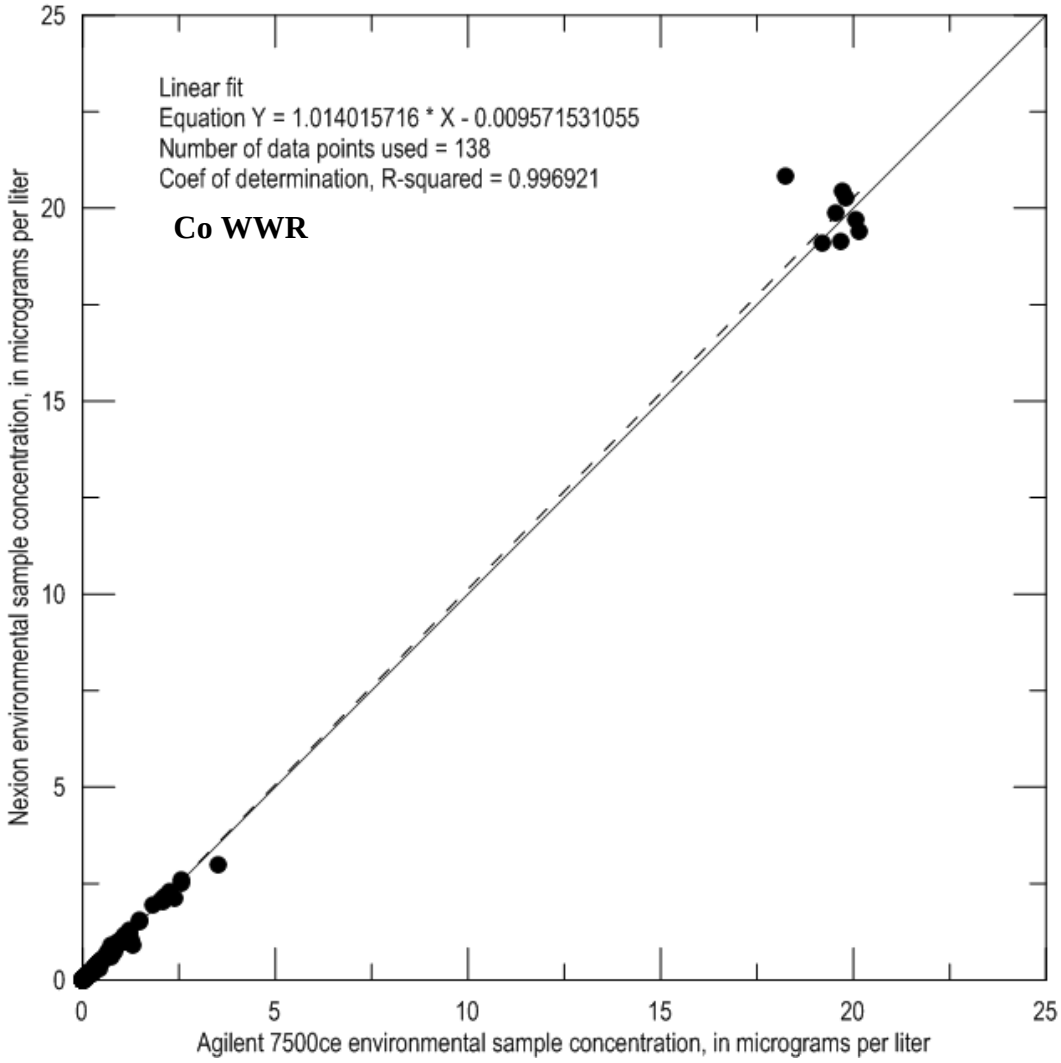


Figure A3.20. Linear regression of cobalt whole-water recoverable (Co WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

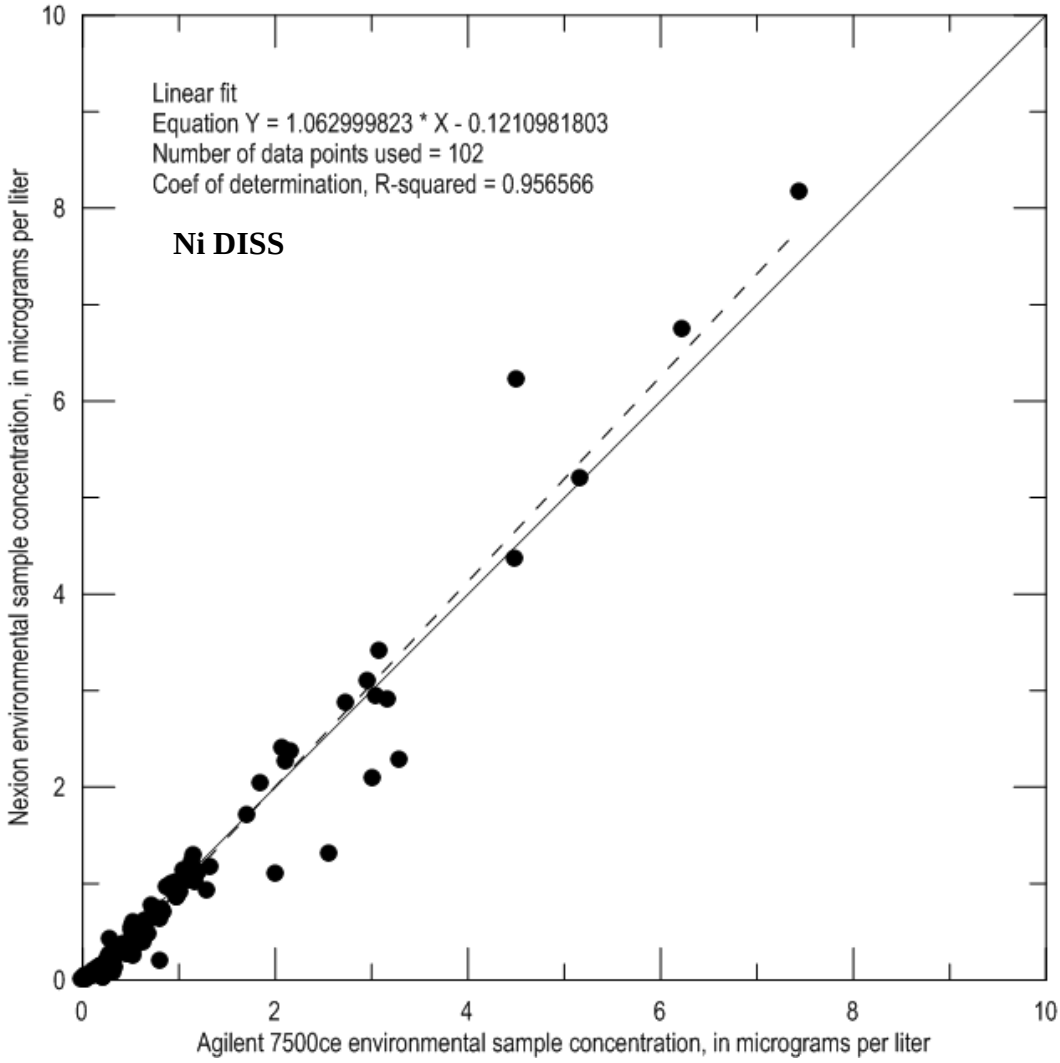


Figure A3.21. Linear regression of nickel dissolved (Ni DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

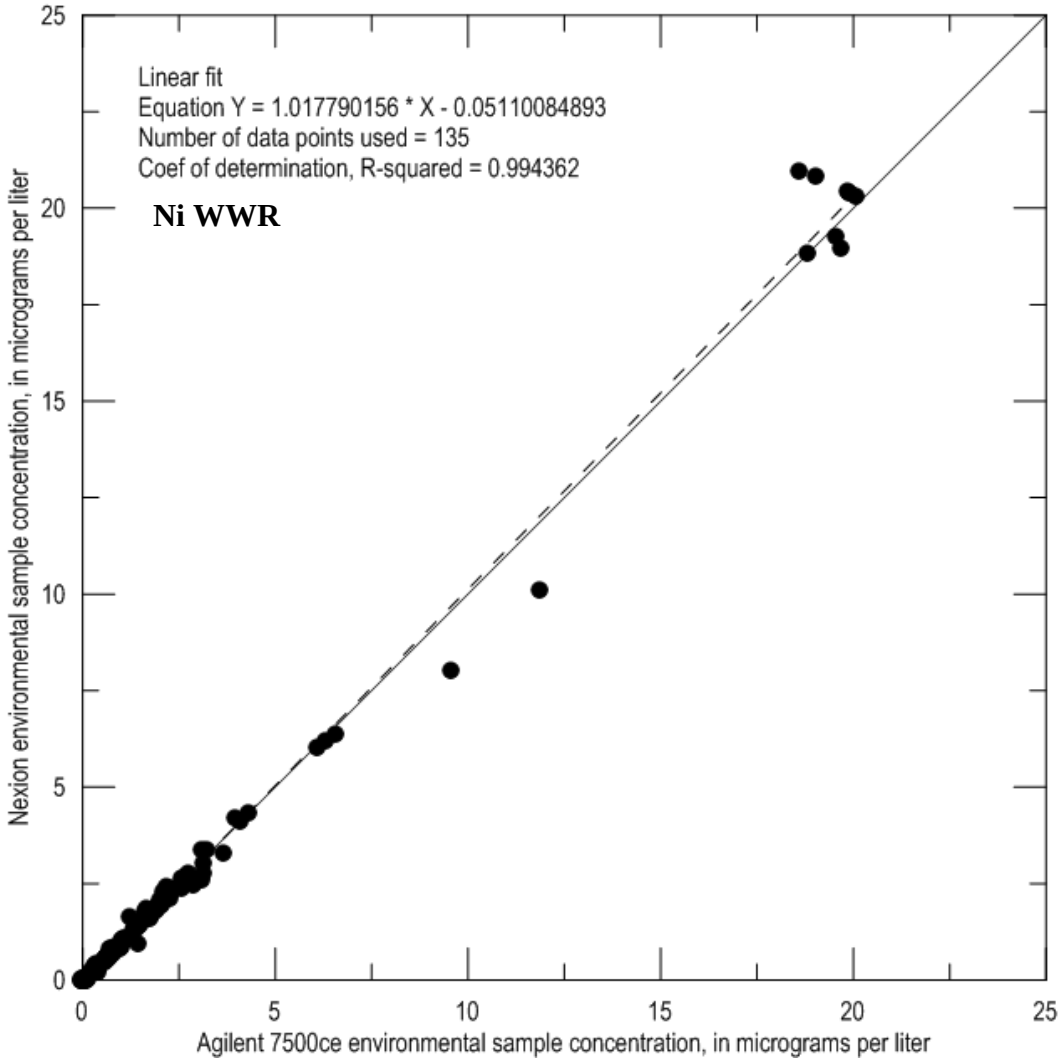


Figure A3.22. Linear regression of nickel whole-water recoverable (Ni WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

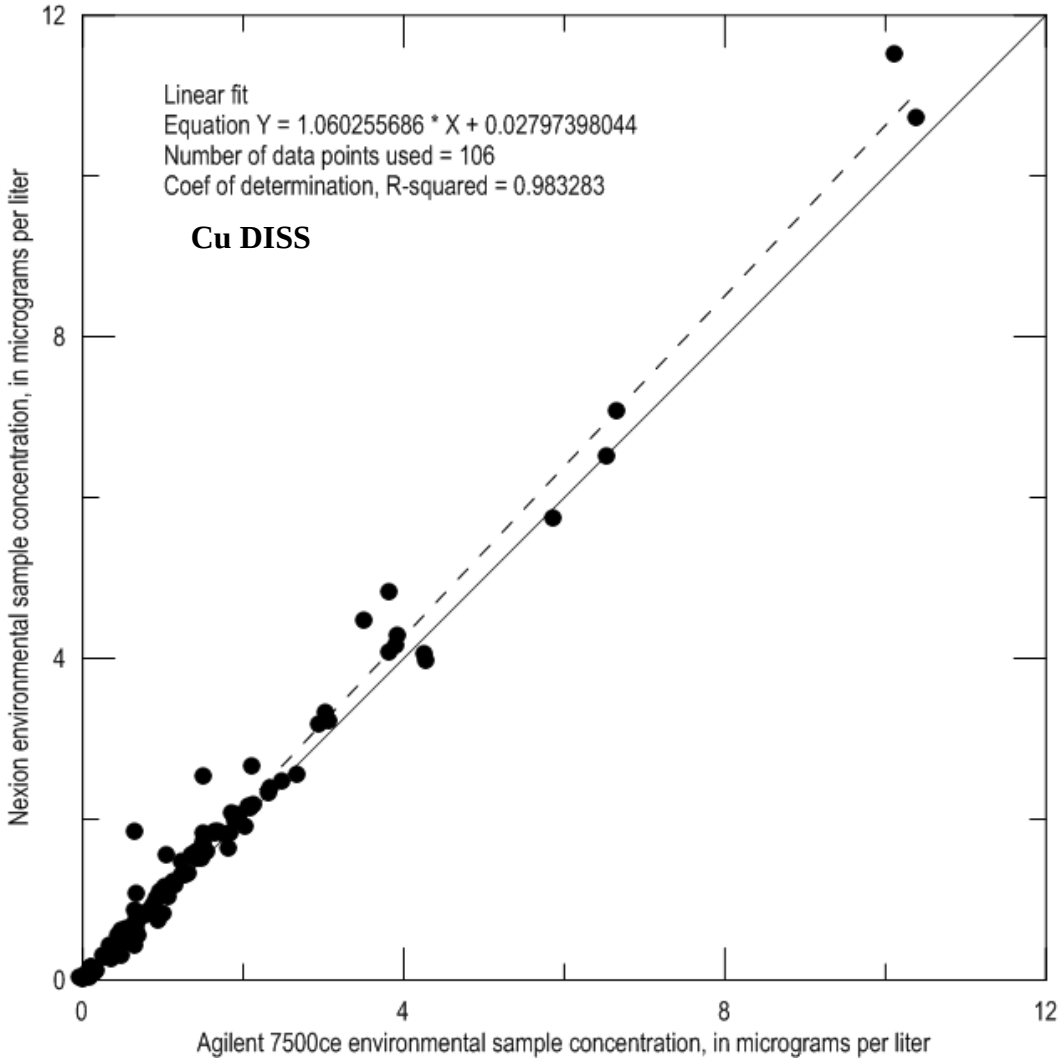


Figure A3.23. Linear regression of copper dissolved (Cu DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

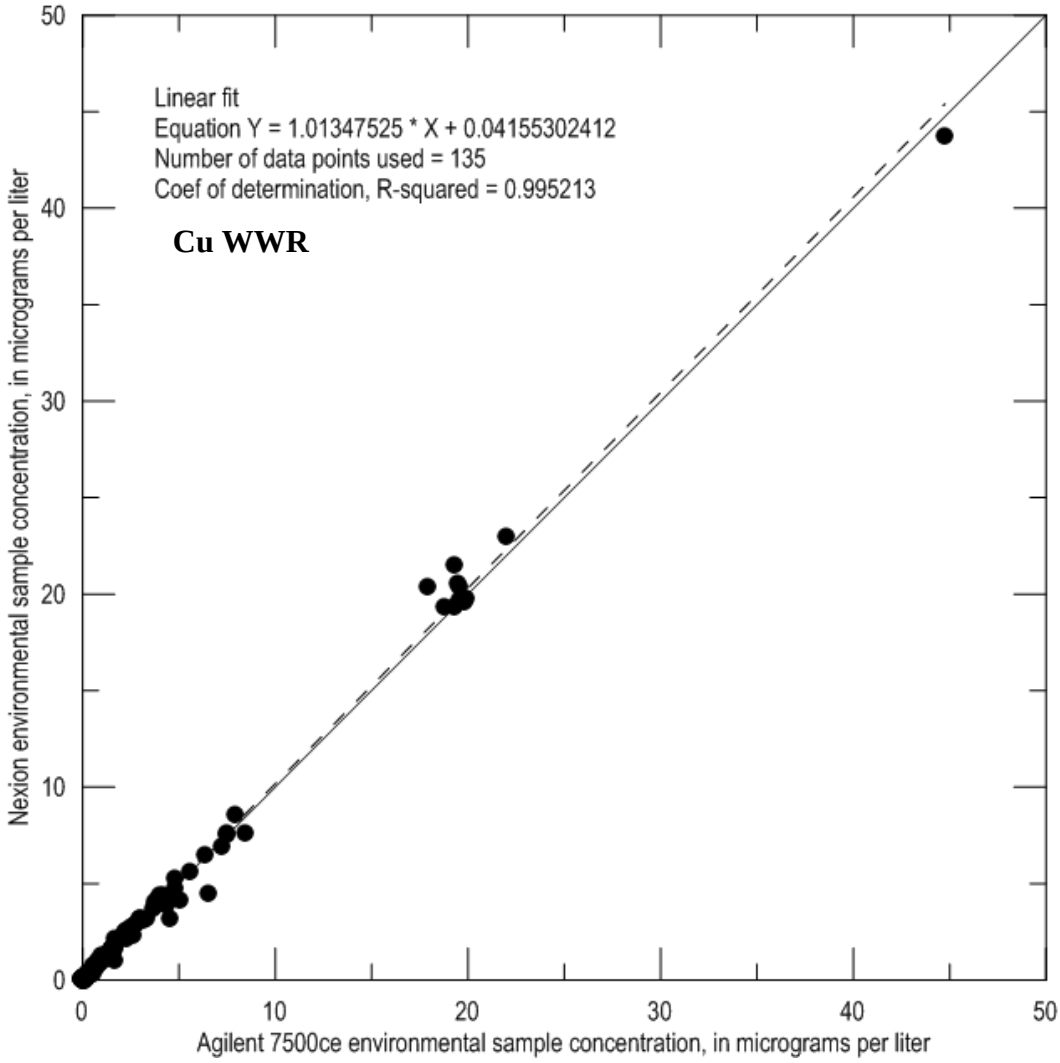


Figure A3.24. Linear regression of copper whole-water recoverable (Cu WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

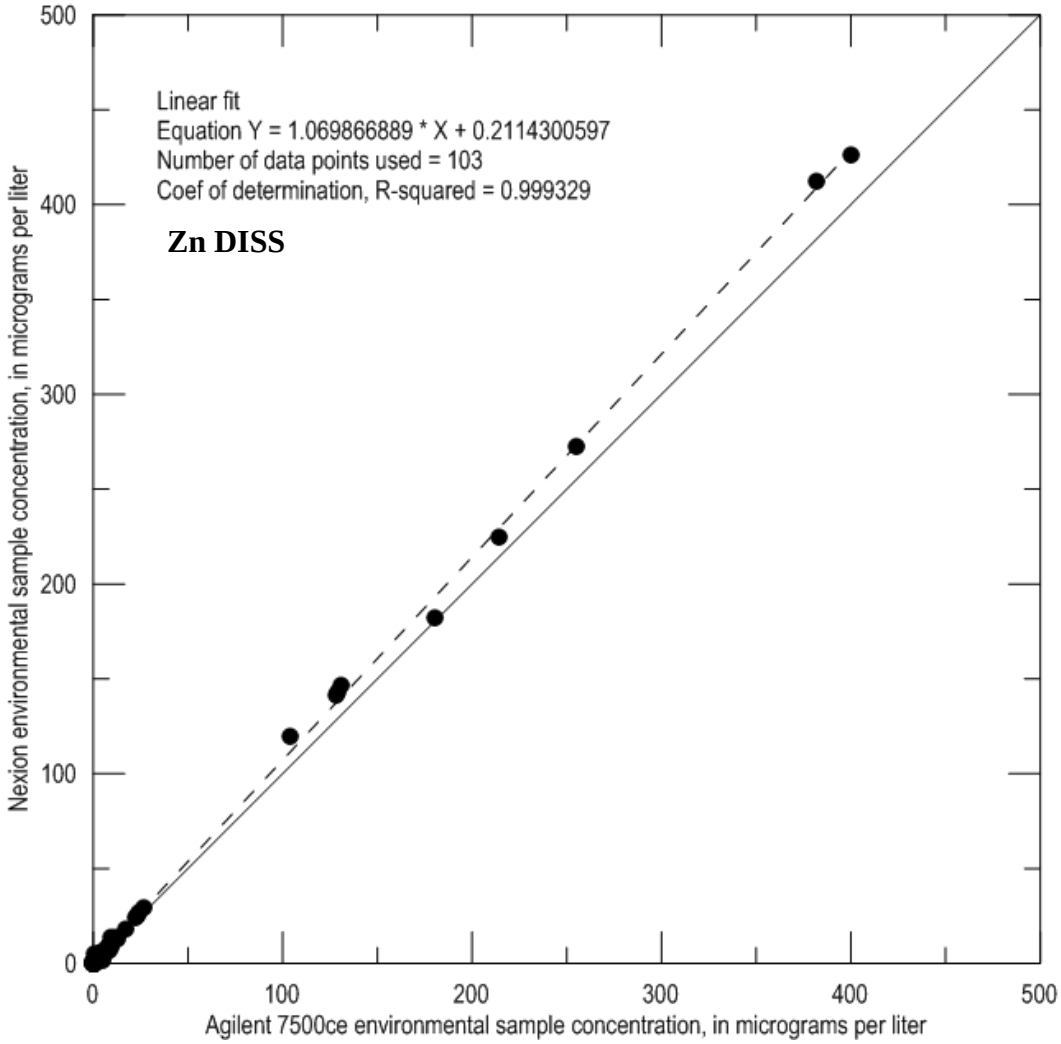


Figure A3.25. Linear regression of zinc dissolved (Zn DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

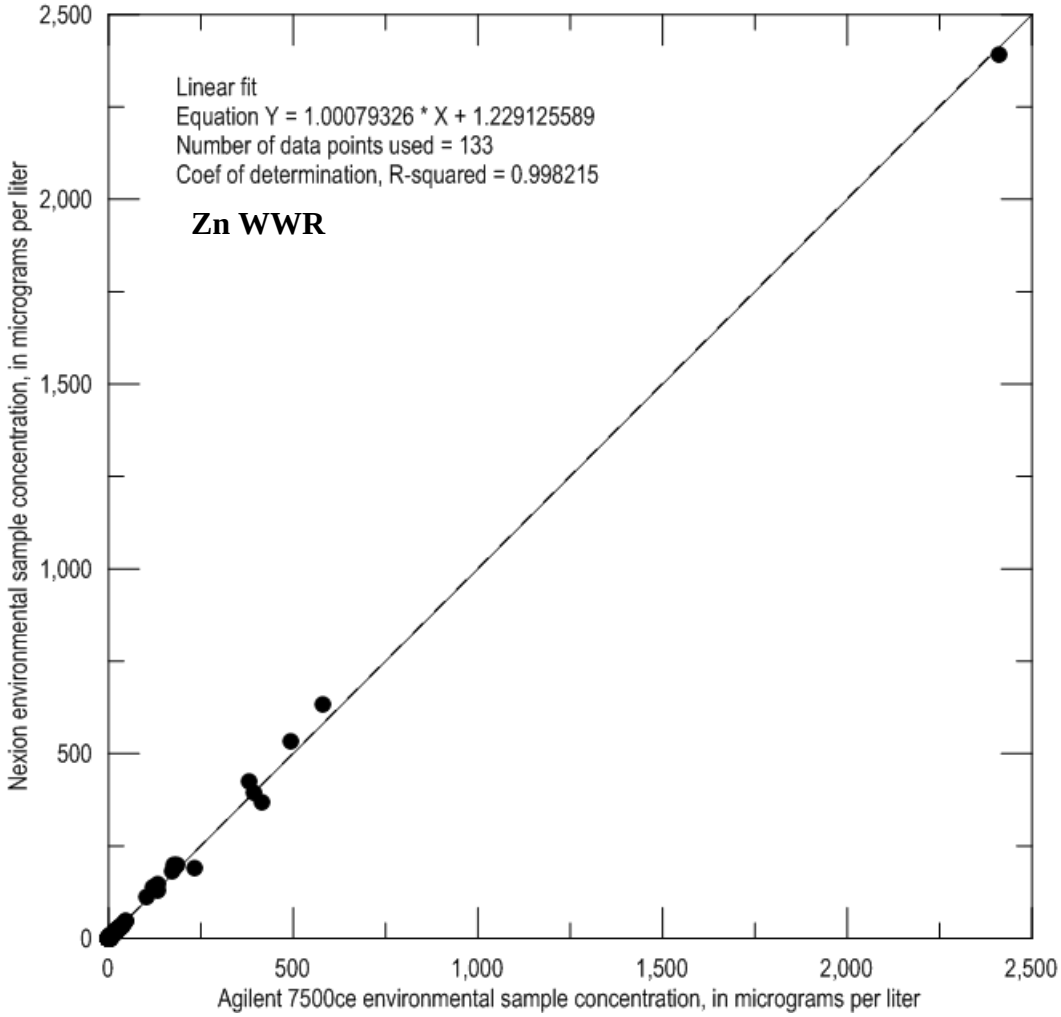


Figure A3.26. Linear regression of zinc whole-water recoverable (Zn WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

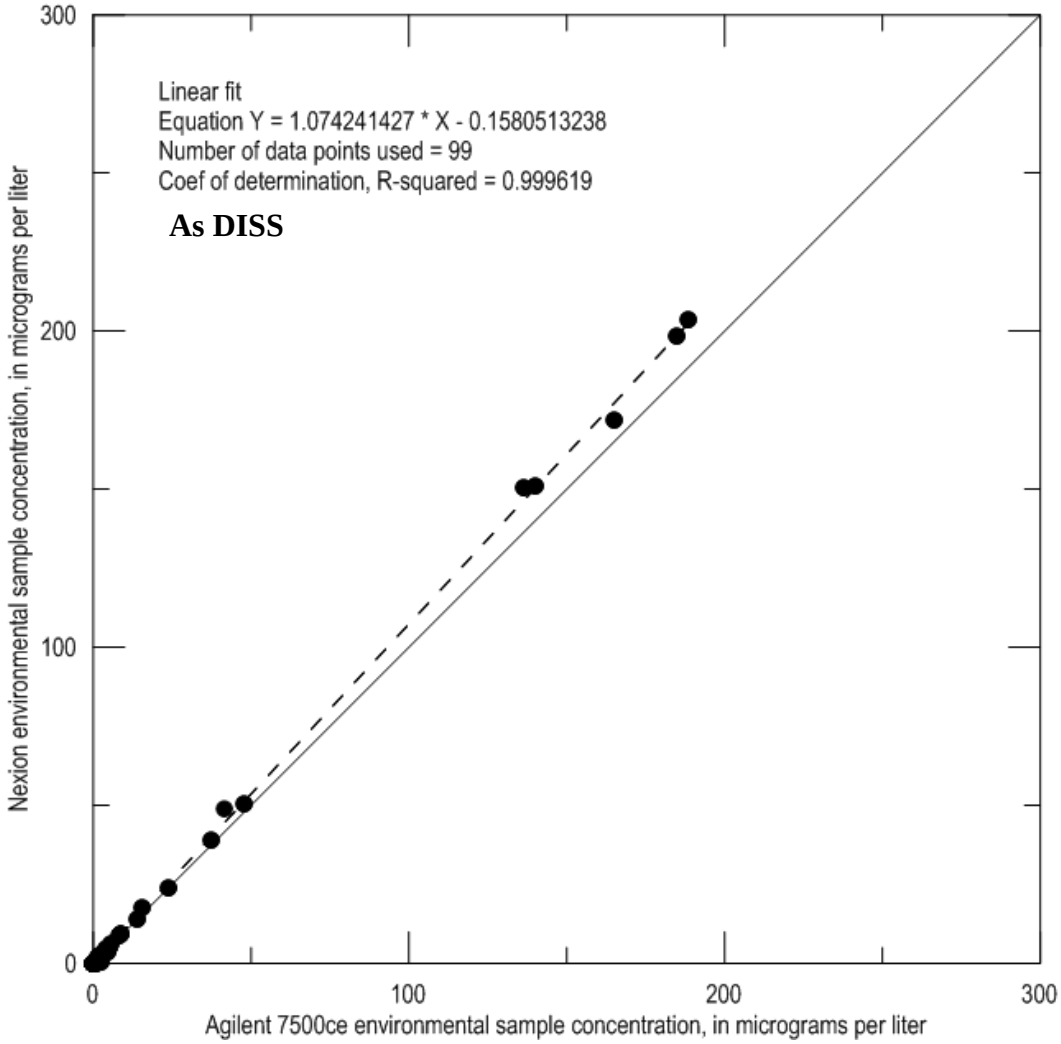


Figure A3.27. Linear regression of arsenic dissolved (As DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

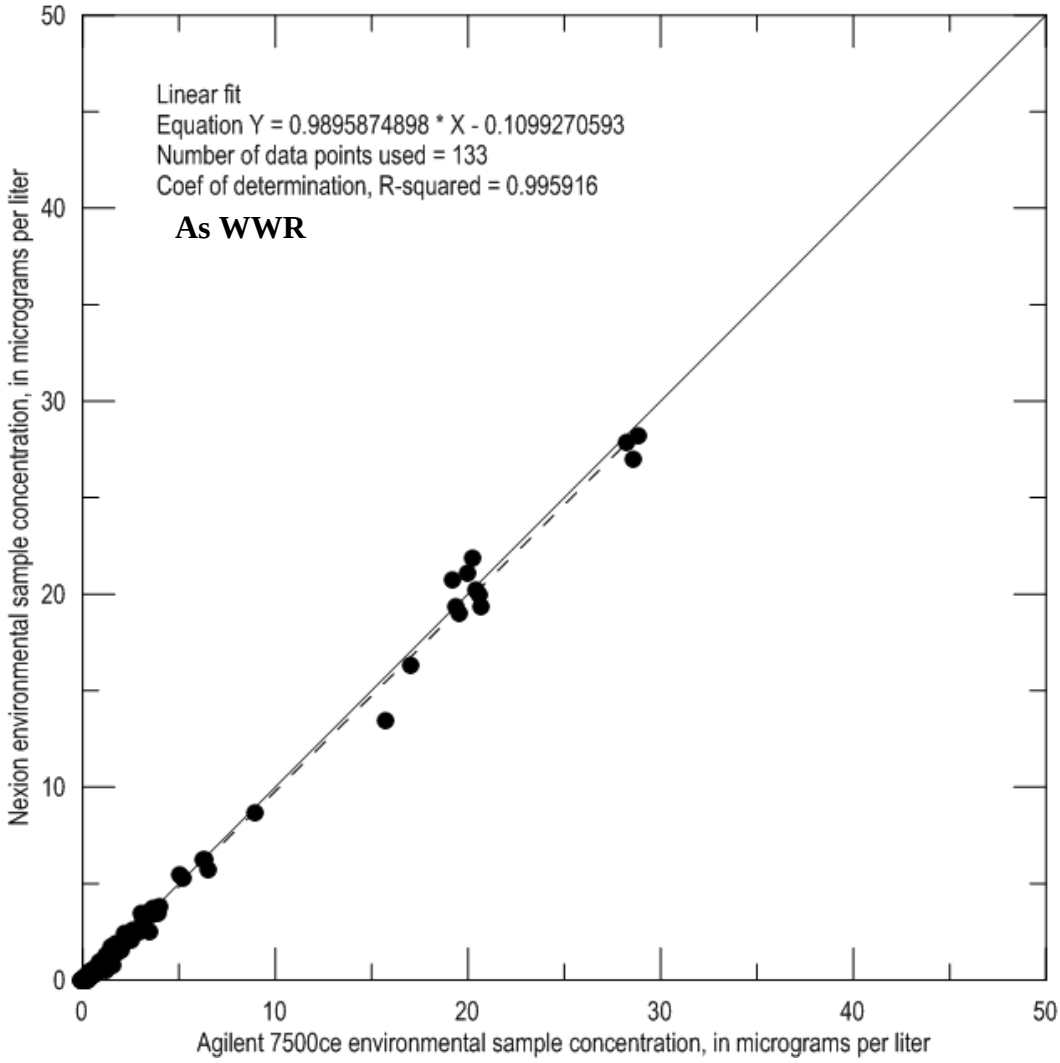


Figure A3.28. Linear regression of arsenic whole-water recoverable (As WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

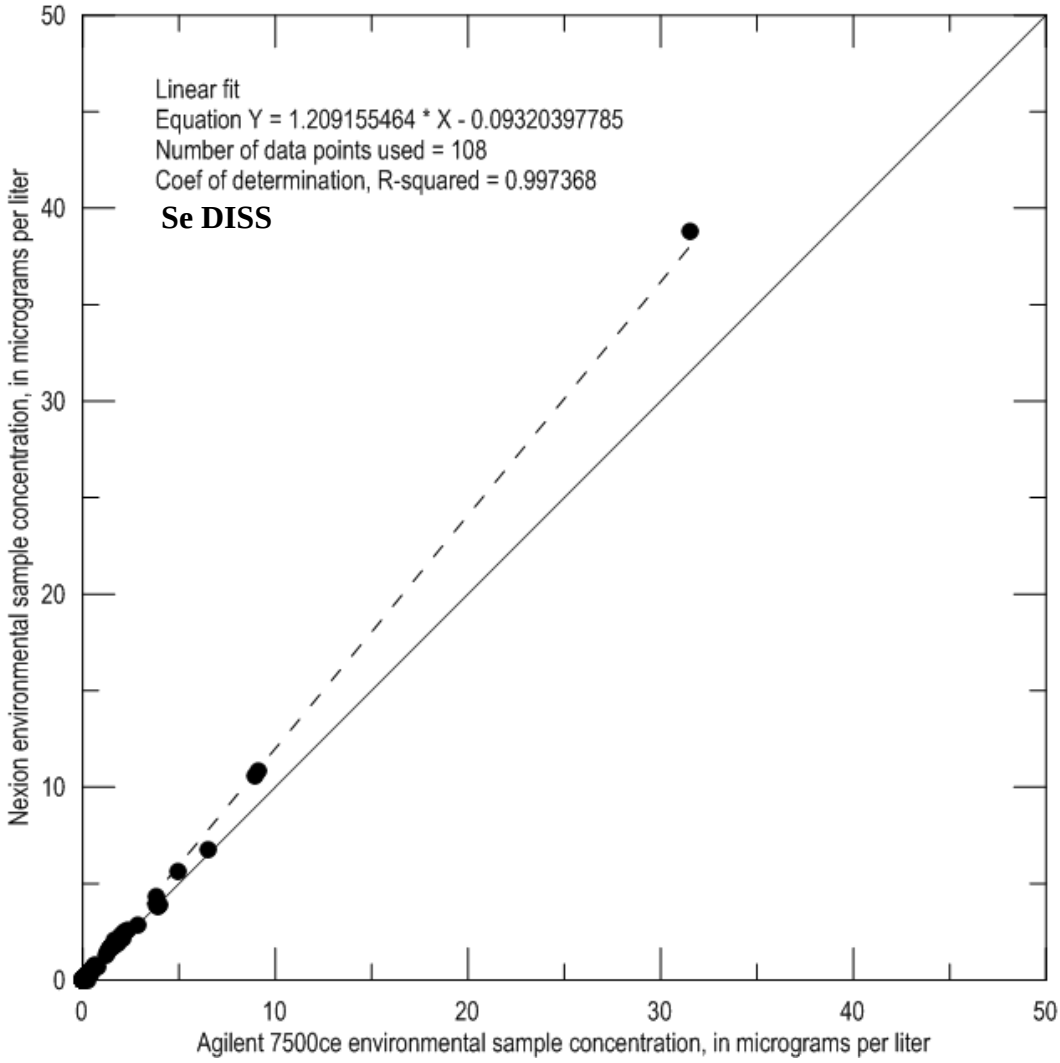


Figure A3.29. Linear regression of selenium dissolved (Se DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

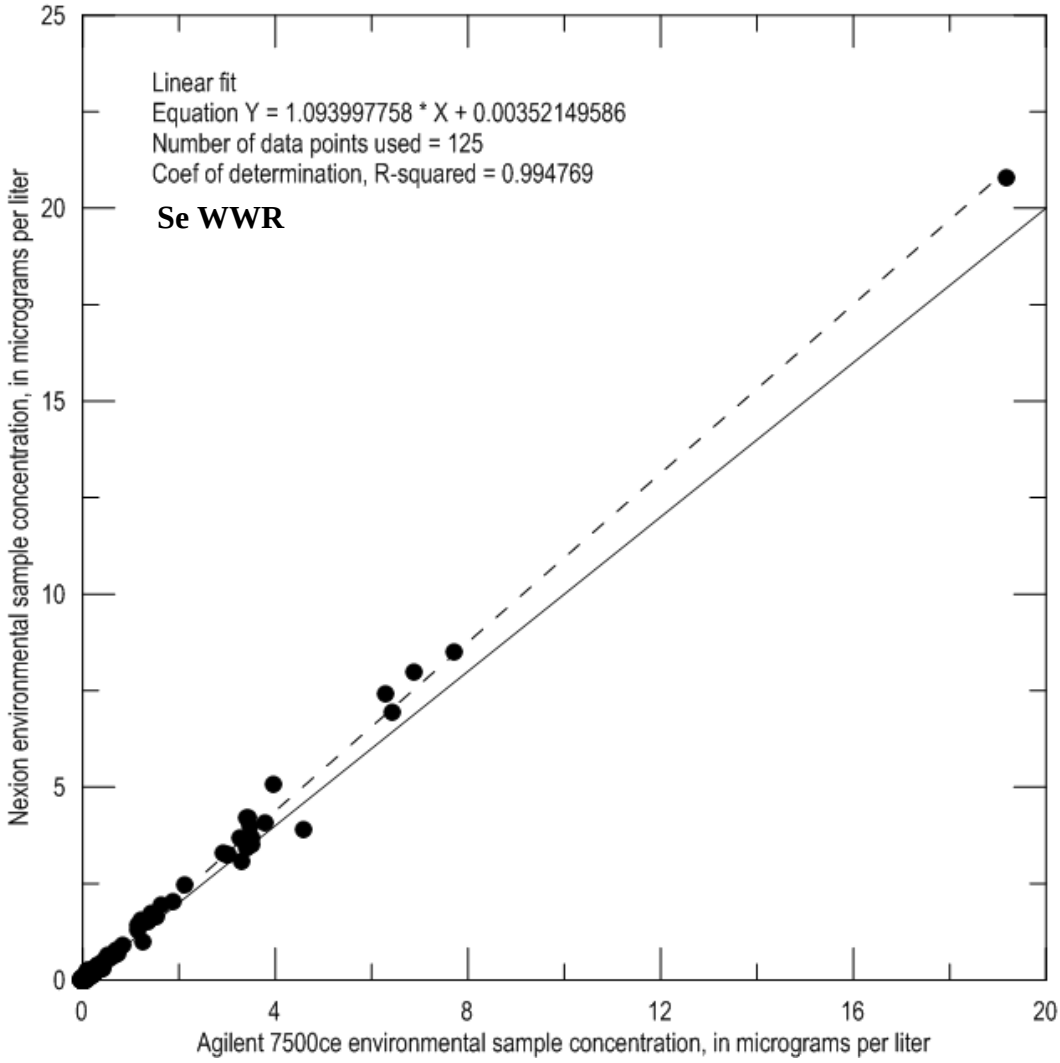


Figure A3.30. Linear regression of selenium whole-water recoverable (Se WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

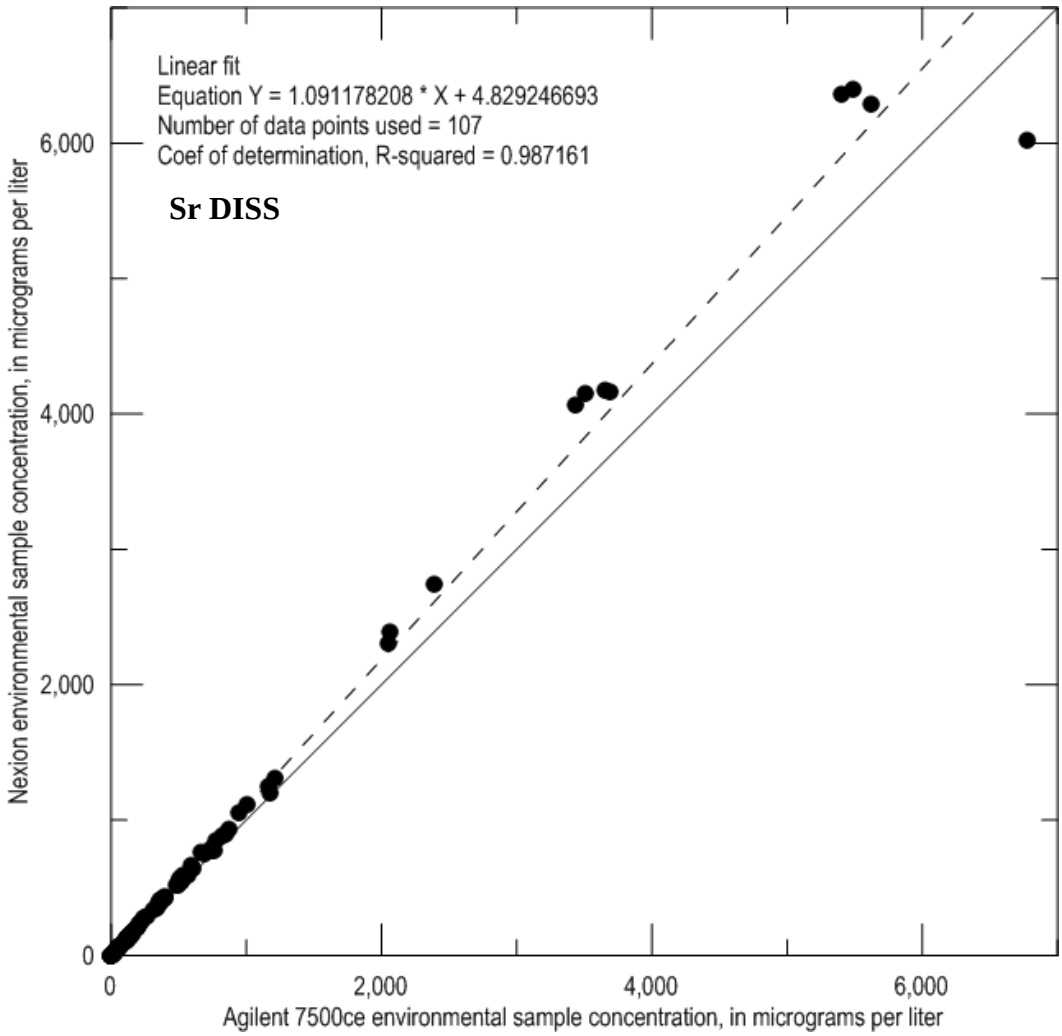


Figure A3.31. Linear regression of strontium dissolved (Sr DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

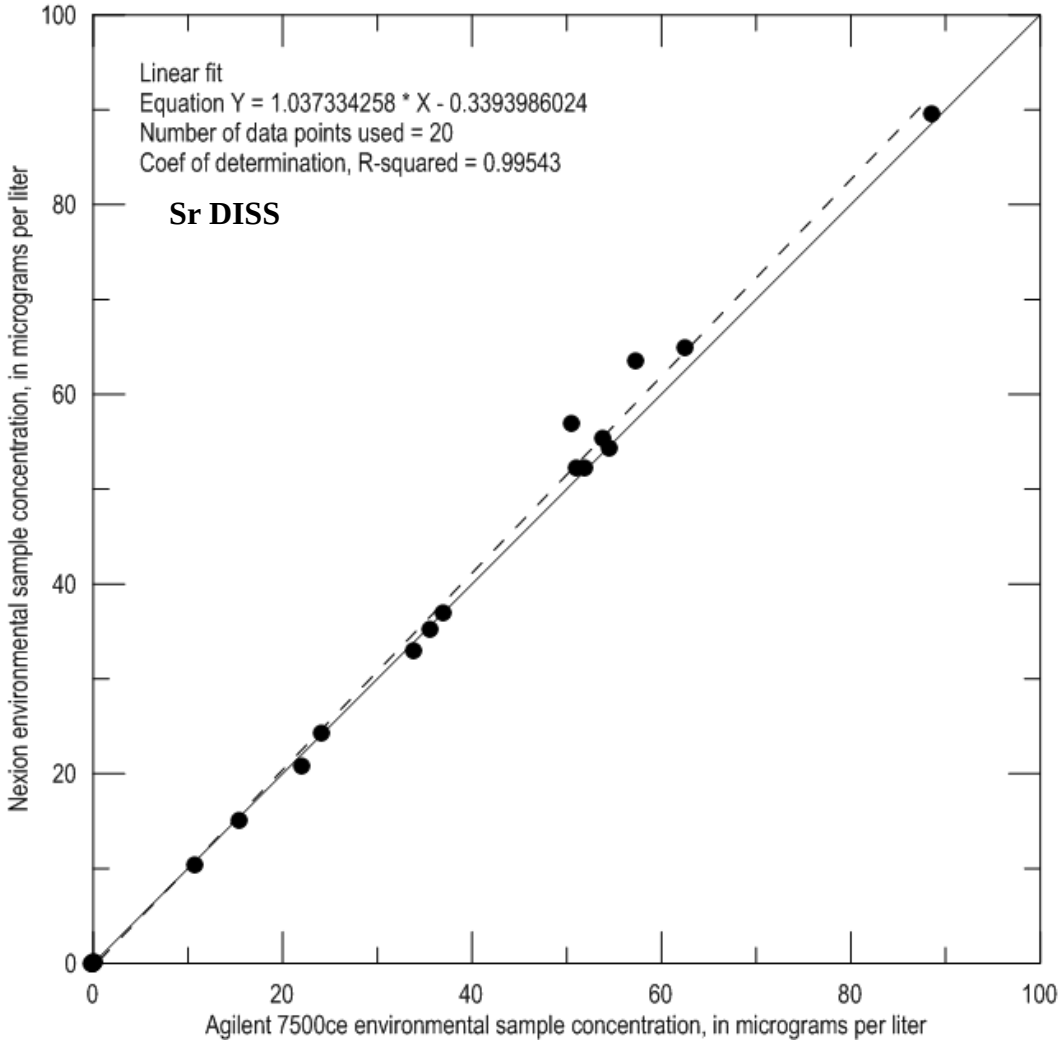


Figure A3.32. Linear regression of a subset of strontium dissolved (Sr DISS) environmental sample data to 100 micrograms per liter analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. There is good agreement between the two methods near the detection limit.

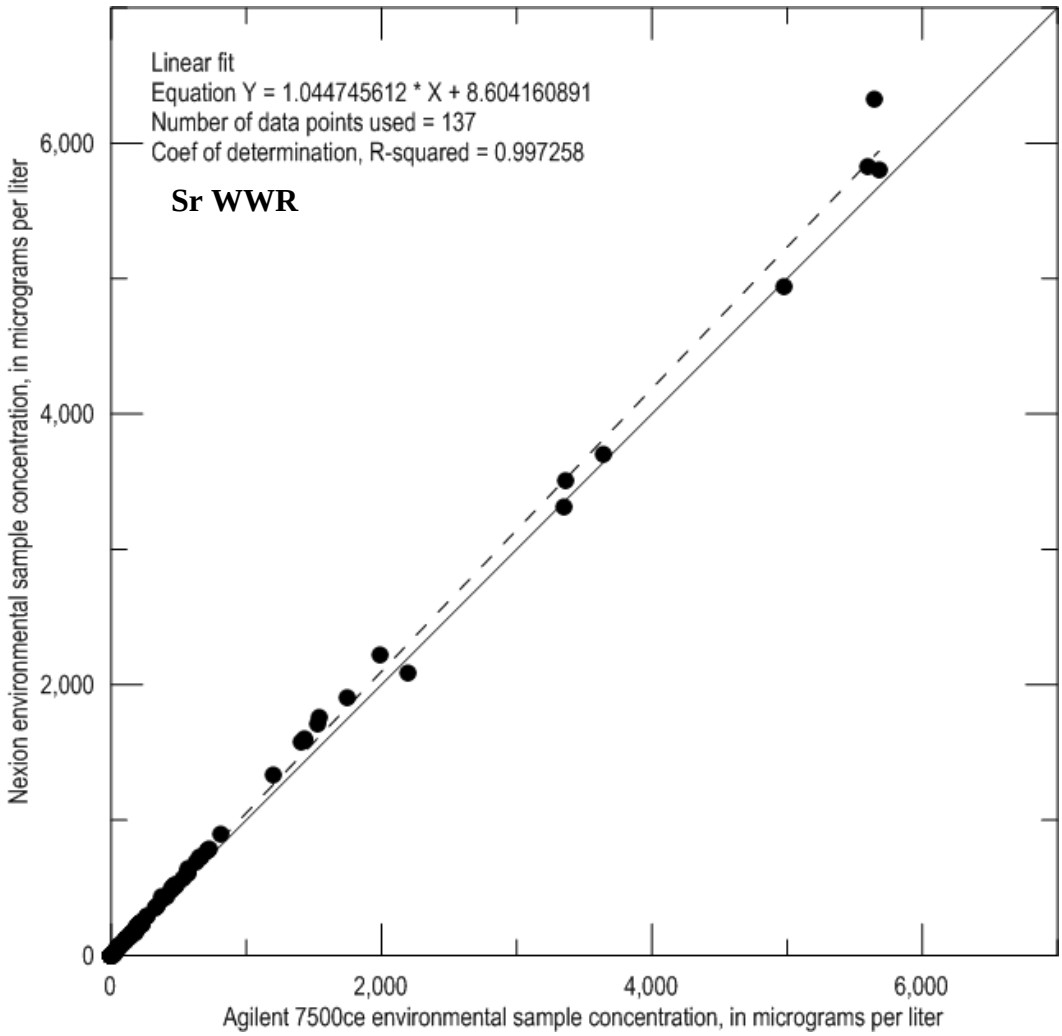


Figure A3.33. Linear regression of strontium whole-water recoverable (Sr WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

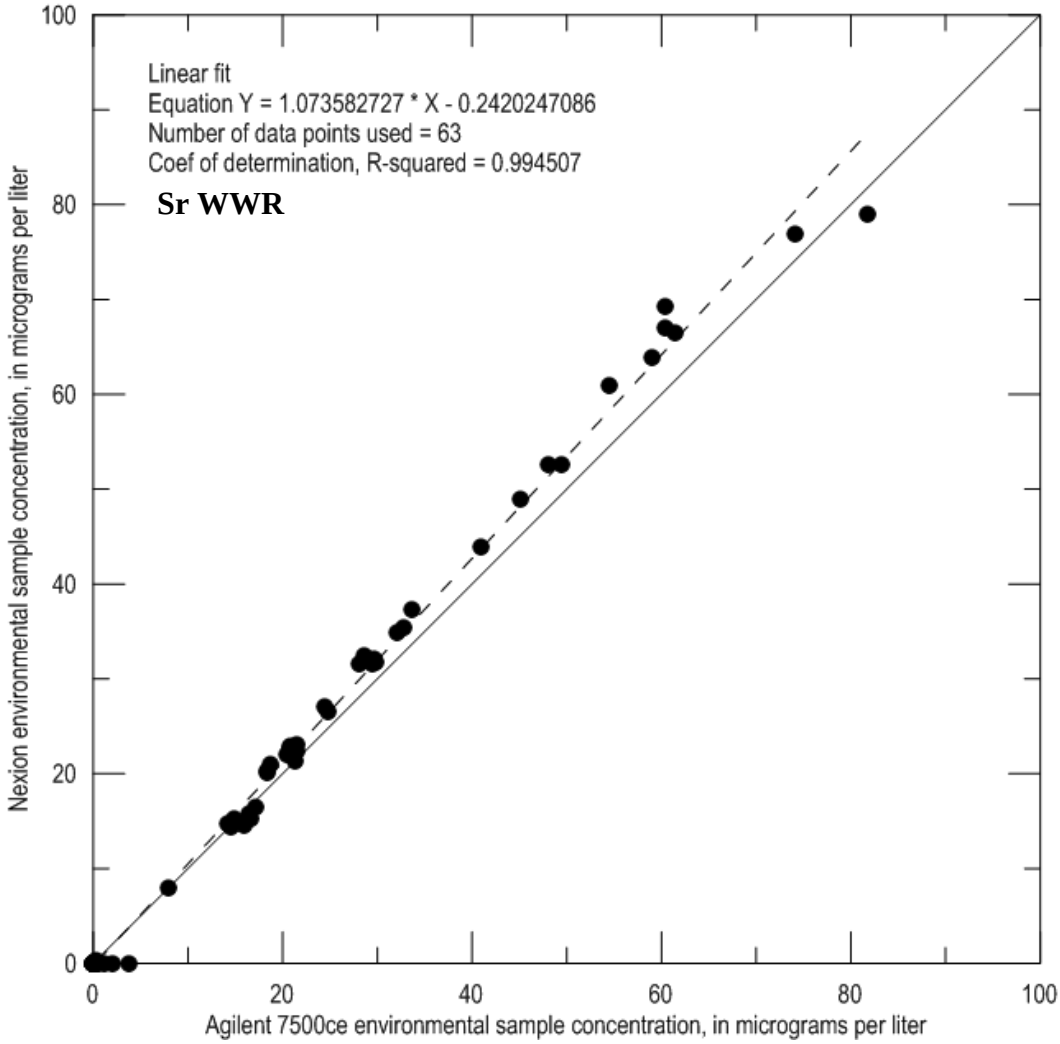


Figure A3.34. Linear regression of a subset of strontium whole-water recoverable (Sr WWR) environmental sample data to 100 micrograms per liter analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. The intercept is small generally indicating good agreement between the two methods near the detection limit, but there is some bias near the detection limit.

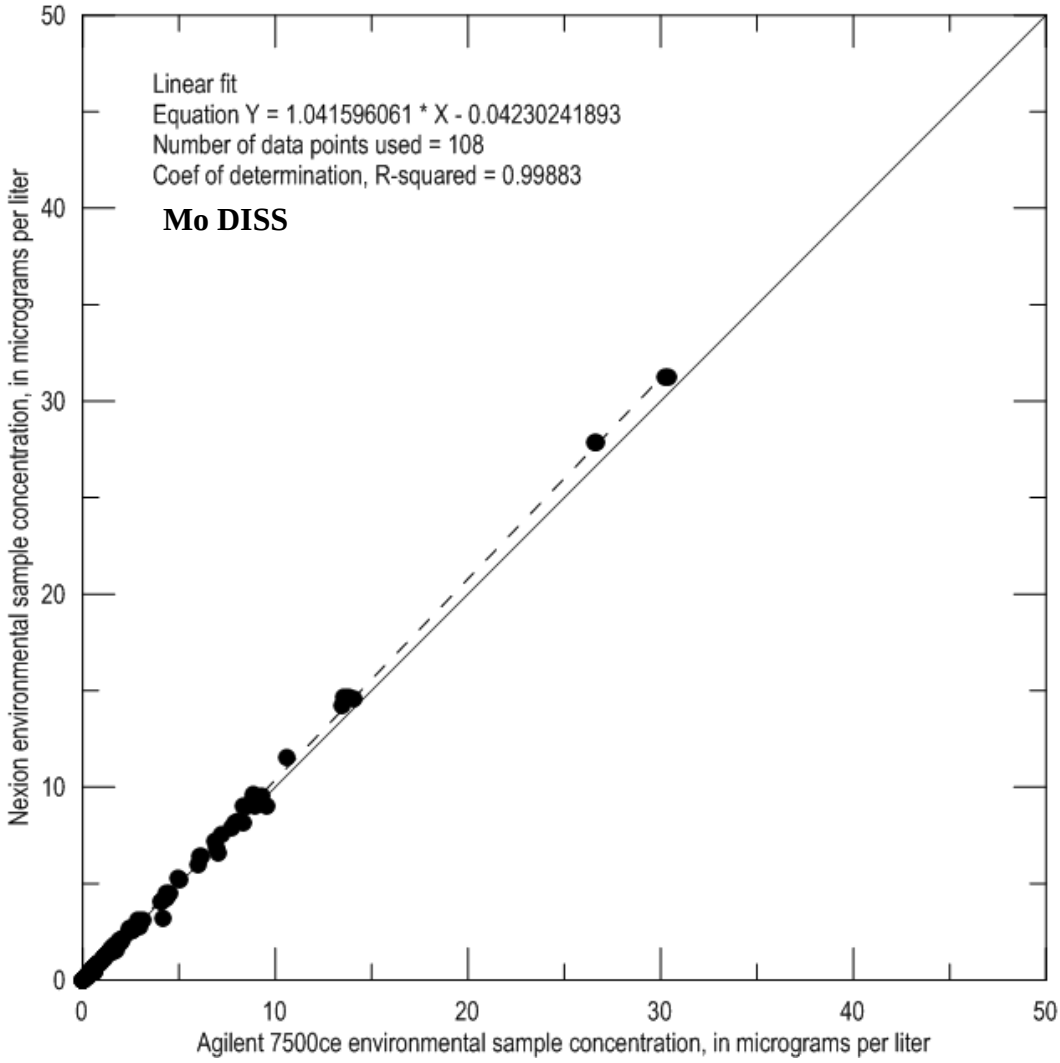


Figure A3.35. Linear regression of molybdenum dissolved (Mo DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

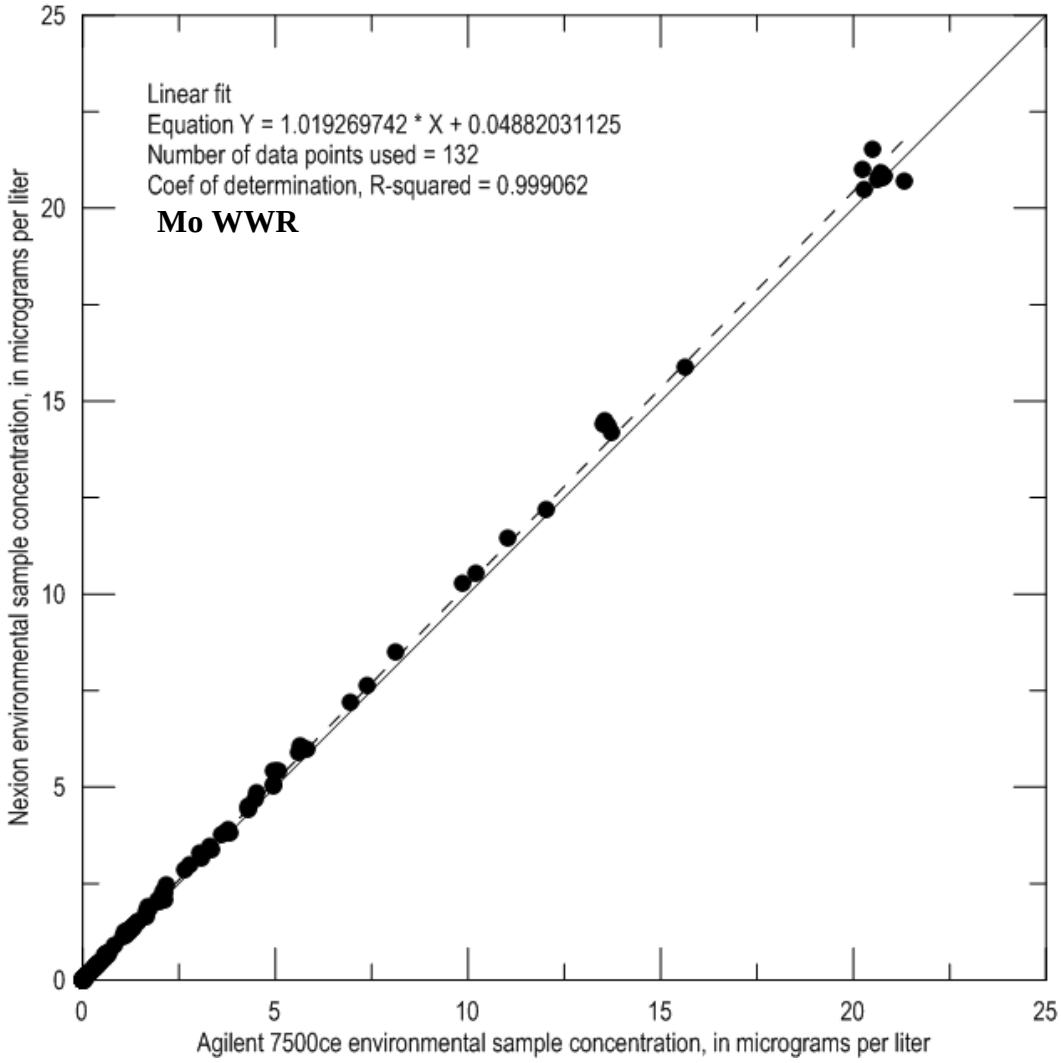


Figure A3.36. Linear regression of molybdenum whole-water recoverable (Mo WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

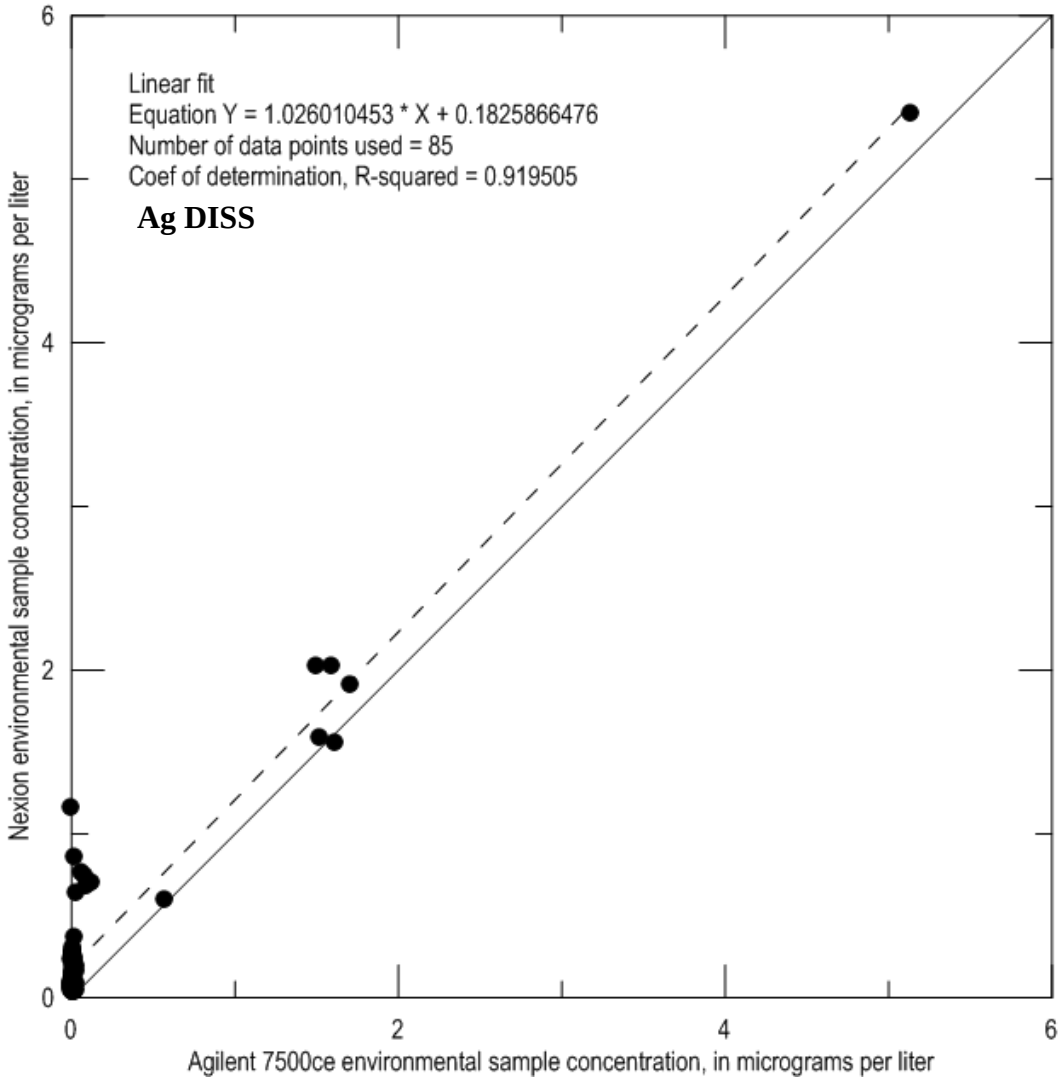


Figure A3.37. Linear regression of silver dissolved (Ag DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

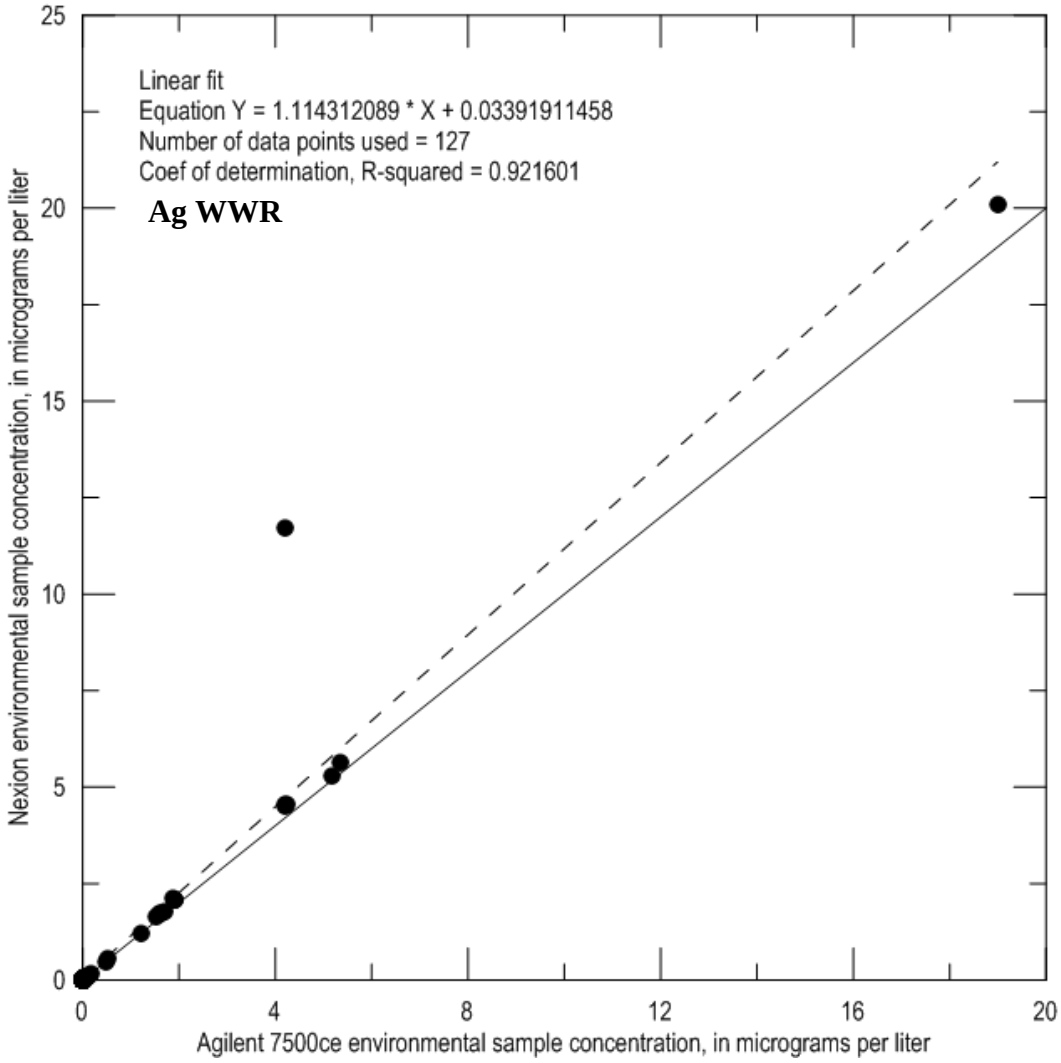


Figure A3.38. Linear regression of silver whole-water recoverable (Ag WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

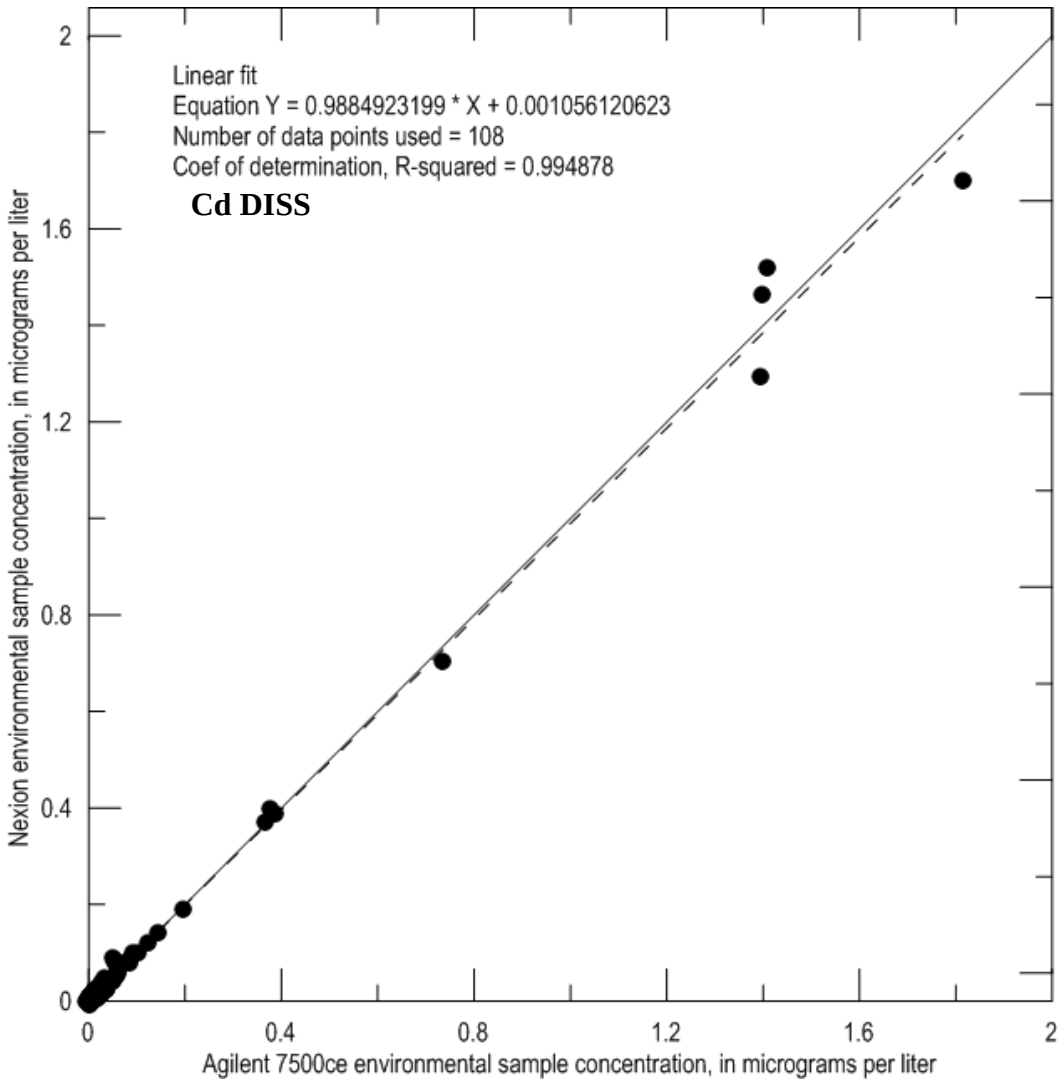


Figure A3.39. Linear regression of cadmium dissolved (Cd DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

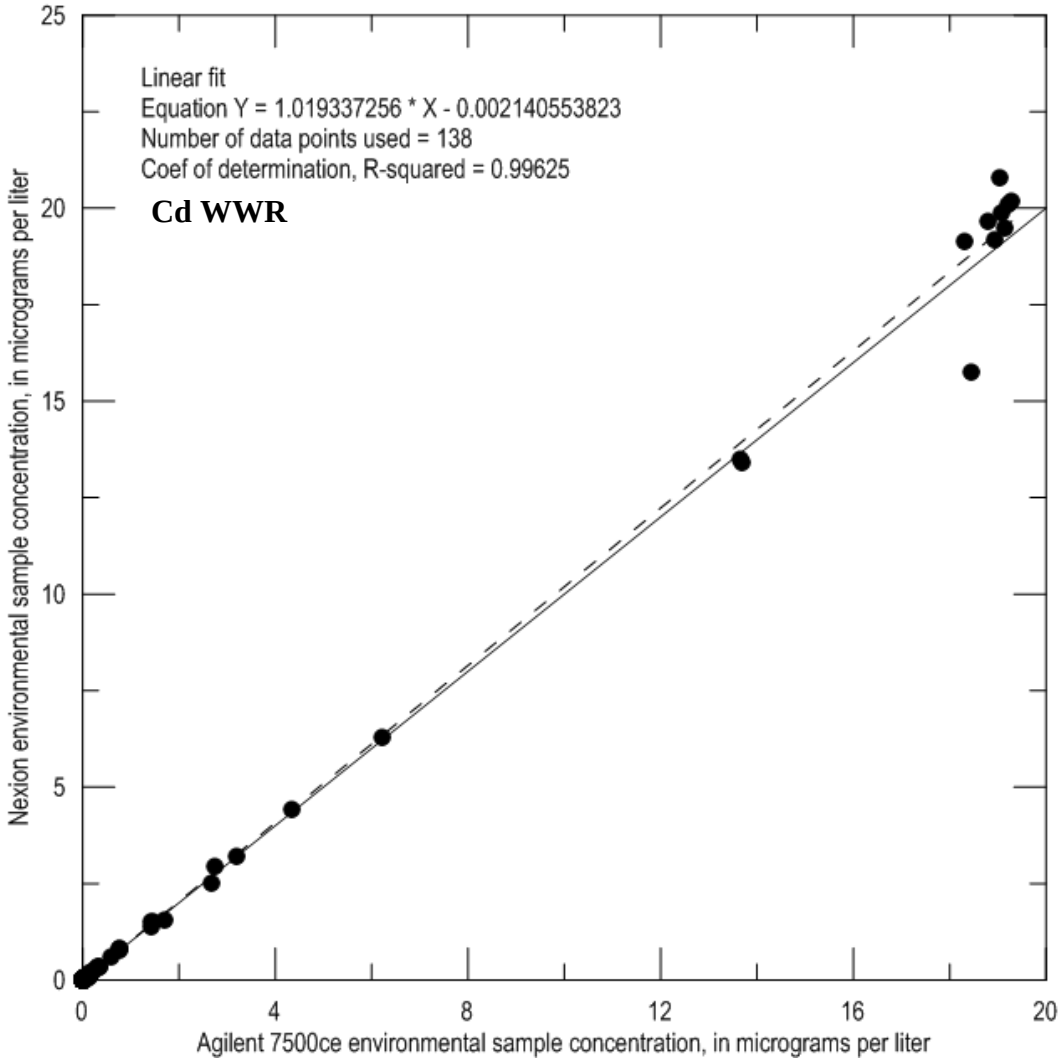


Figure A3.40. Linear regression of cadmium whole-water recoverable (Cd WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

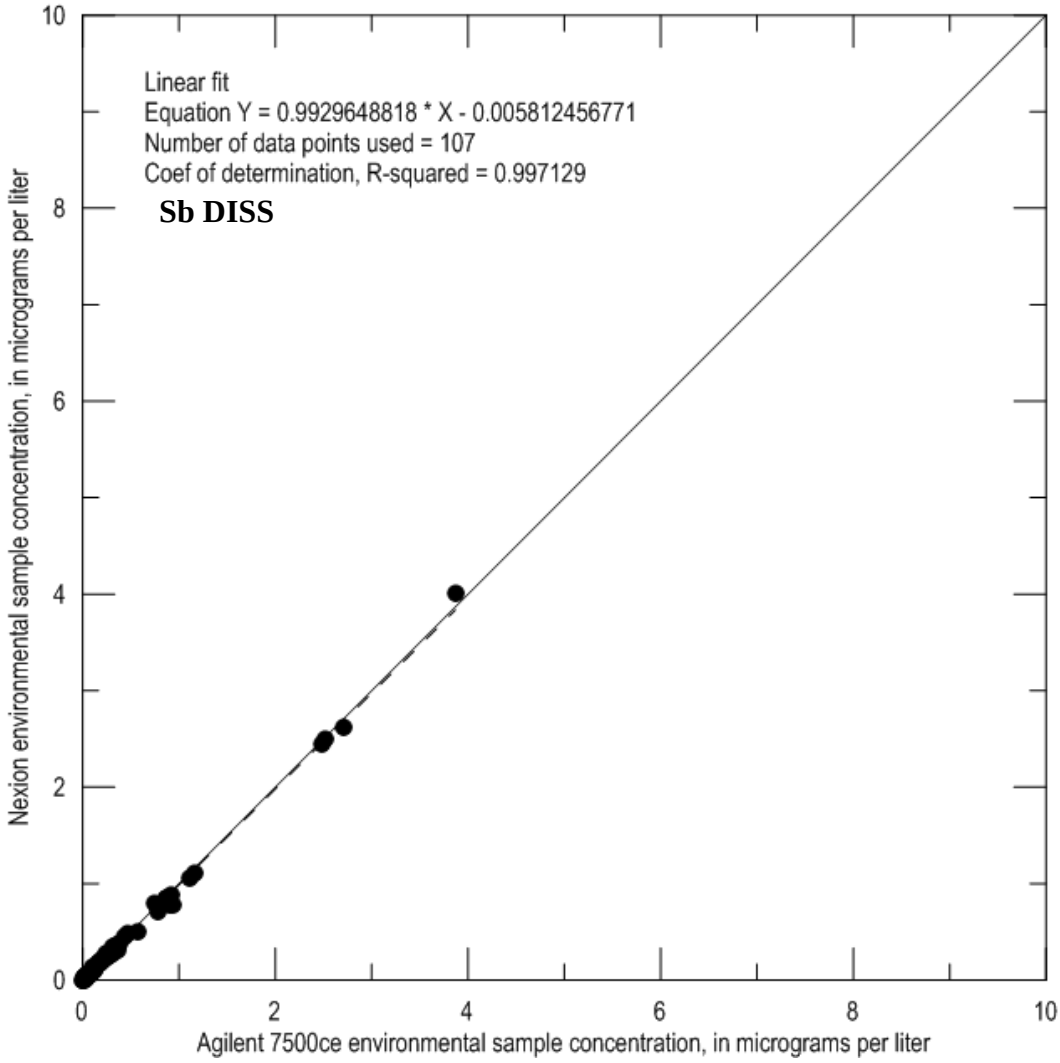


Figure A3.41. Linear regression of antimony dissolved (Sb DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

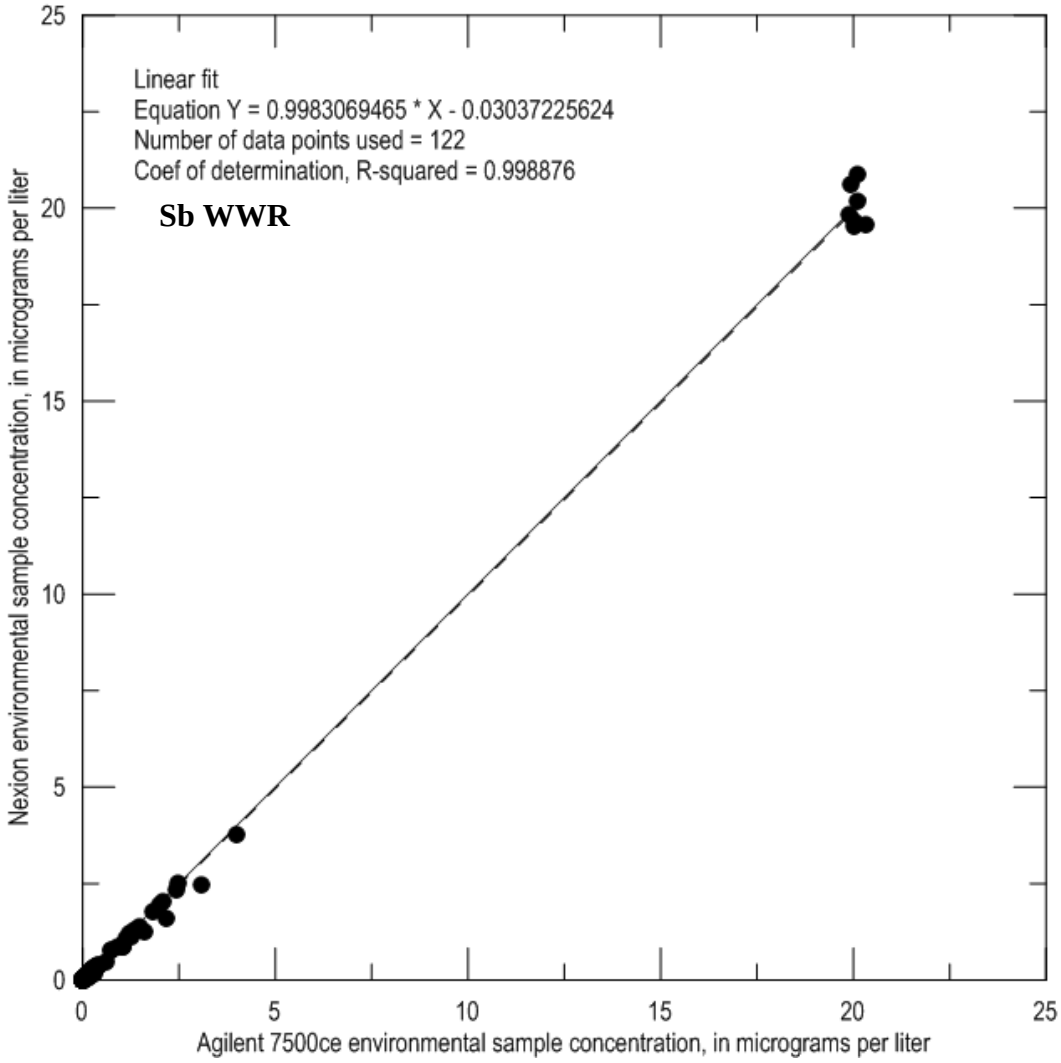


Figure A3.42. Linear regression of antimony whole-water recoverable (Sb WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

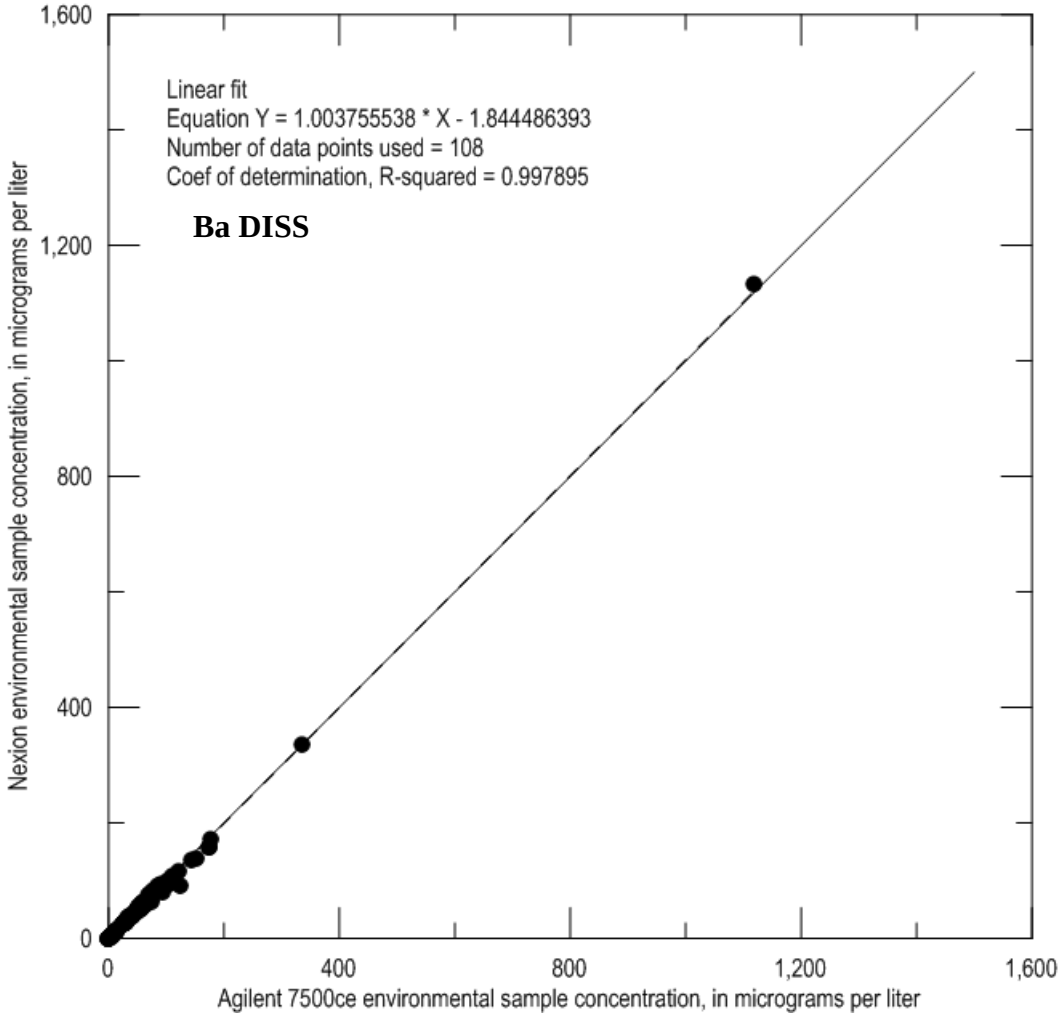


Figure A3.43. Linear regression of barium dissolved (Ba DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

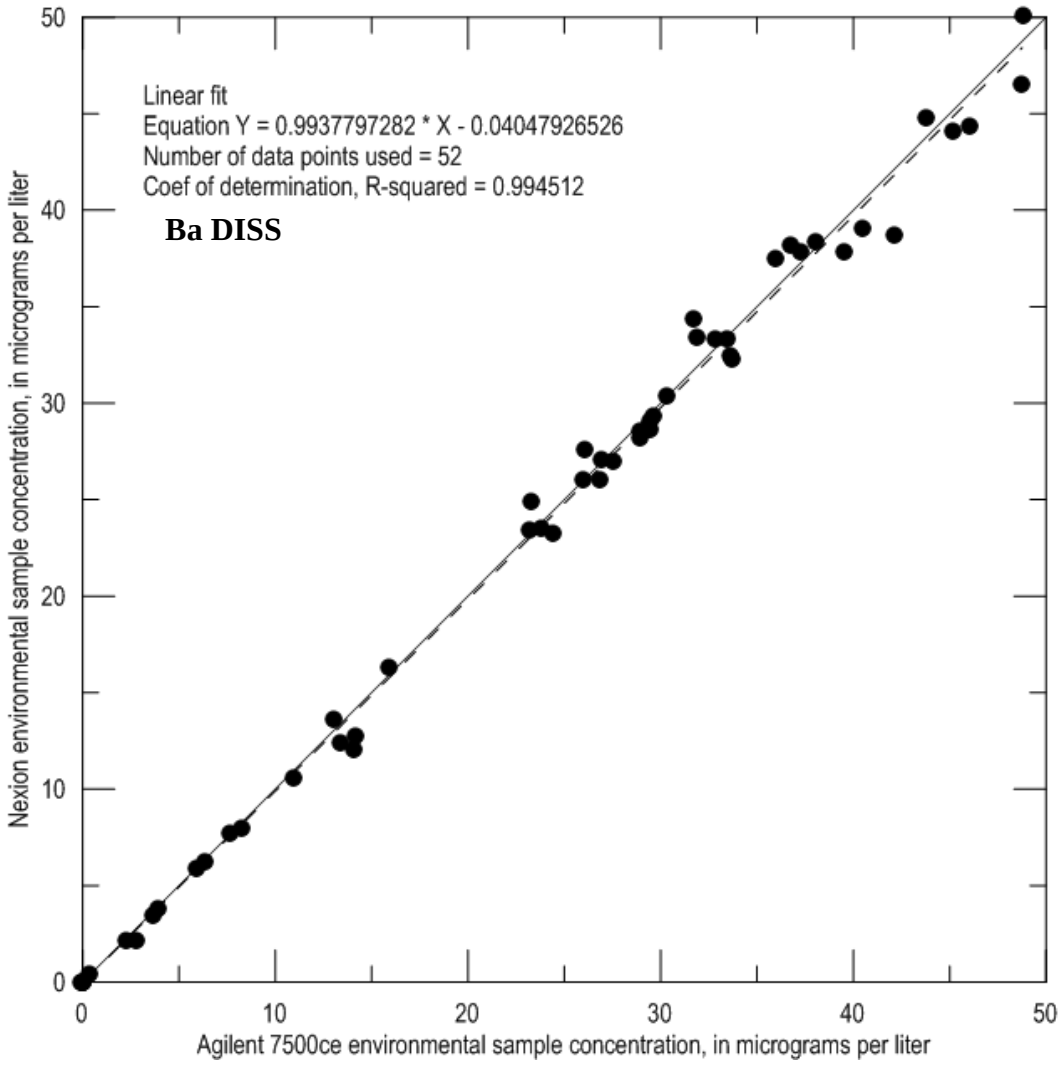


Figure A3.44. Linear regression of a subset of barium dissolved (Ba DISS) environmental sample data to 50 micrograms per liter analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. There is good agreement between the two methods near the detection limit.

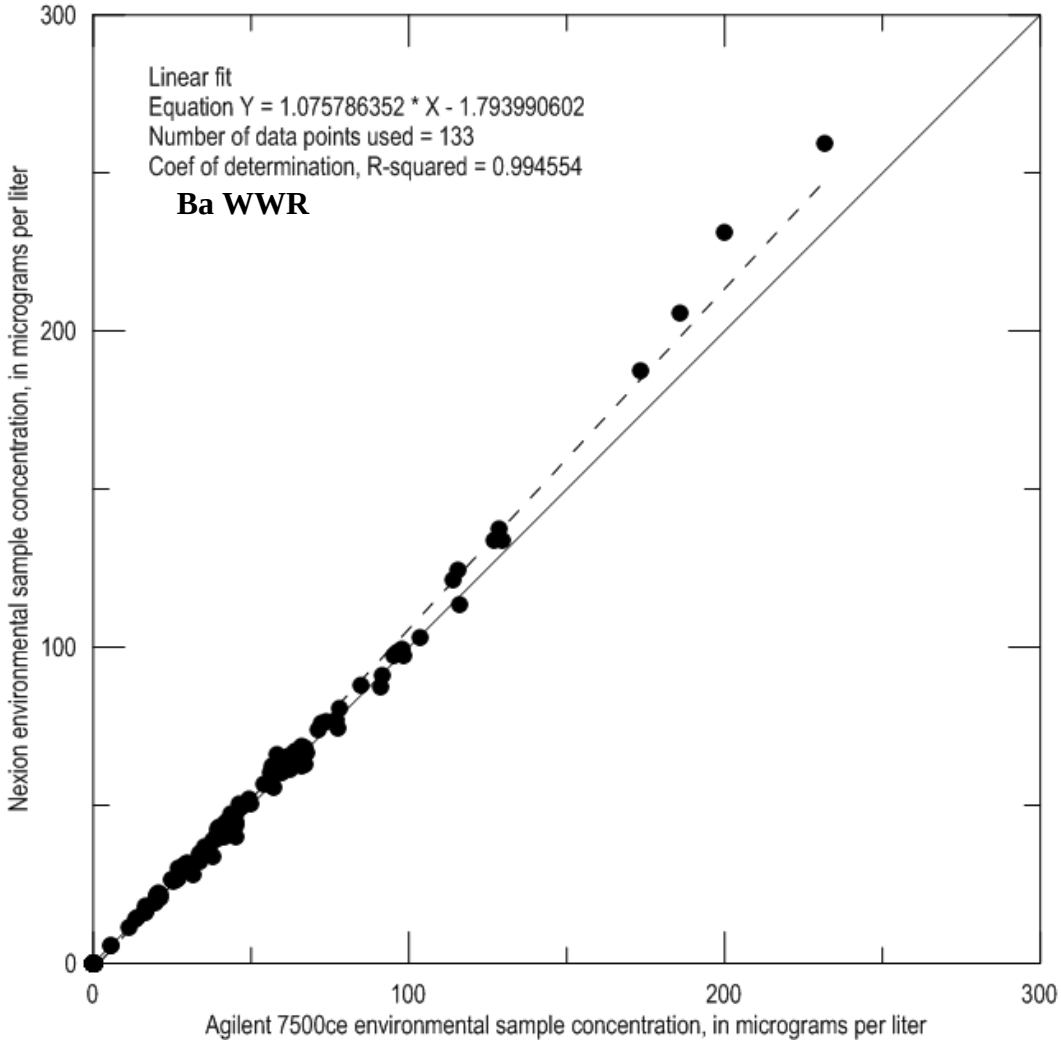


Figure A3.45. Linear regression of barium whole-water (Ba WWR) recoverable environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

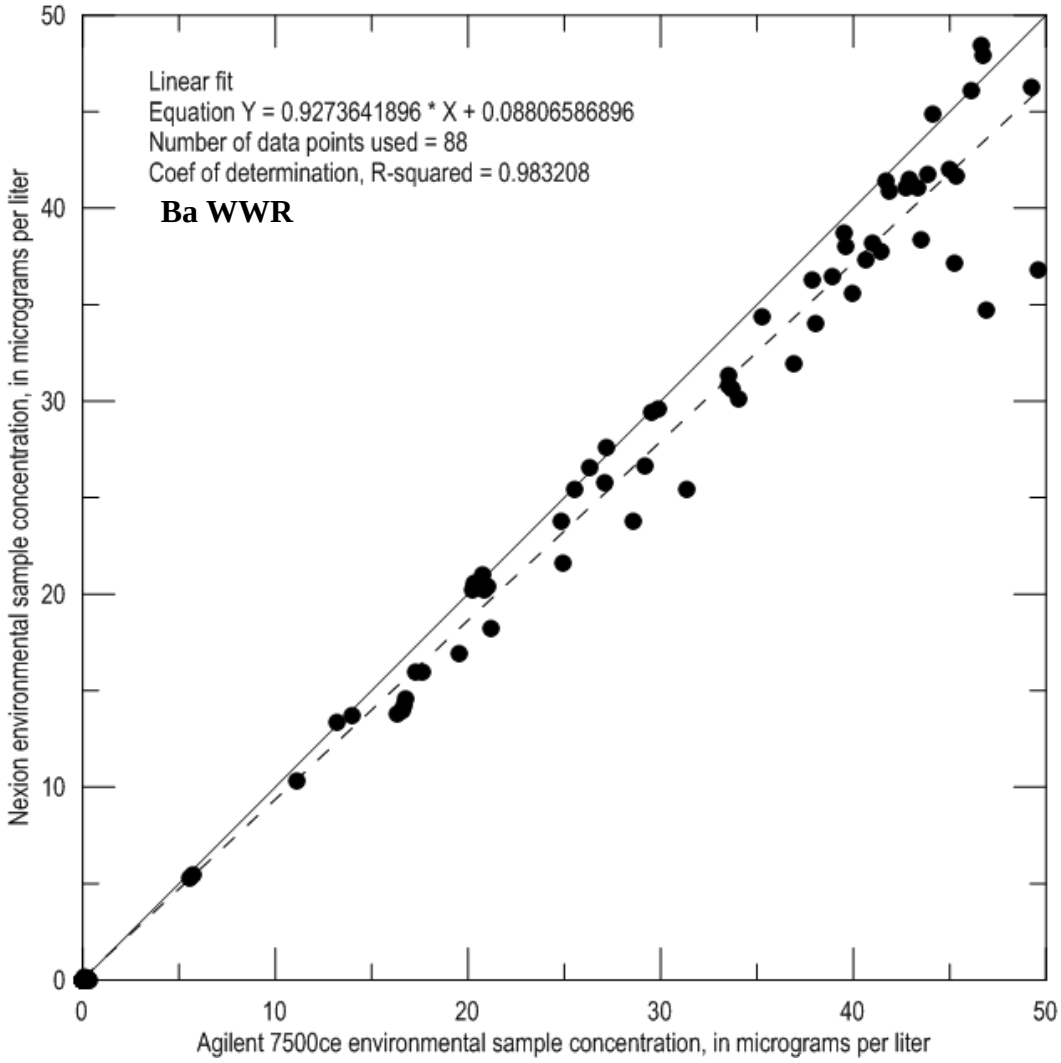


Figure A3.46. Linear regression of a subset of barium whole-water recoverable (Ba WWR) environmental sample data to 50 micrograms per liter analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. There is good agreement between the two methods near the detection limit.

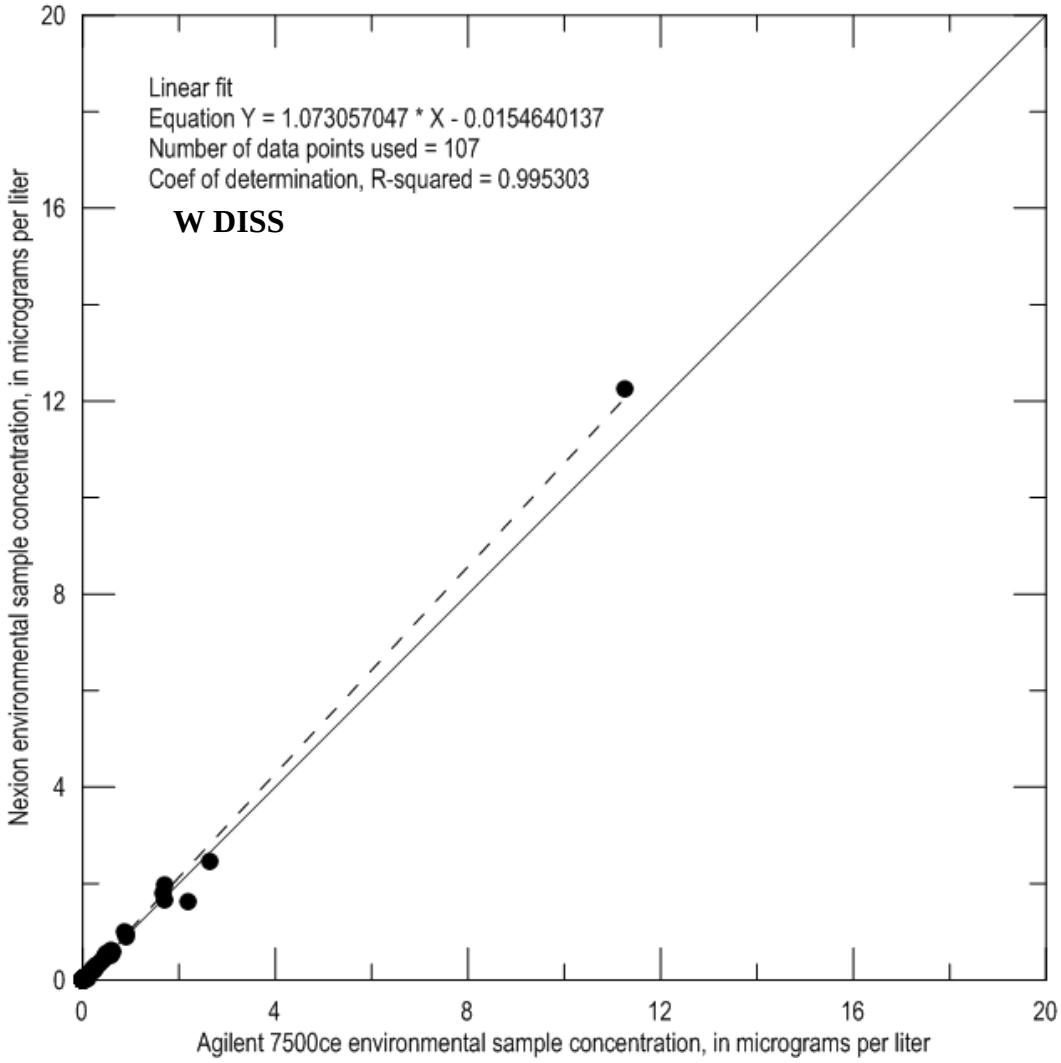


Figure A3.47. Linear regression of tungsten dissolved (W DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

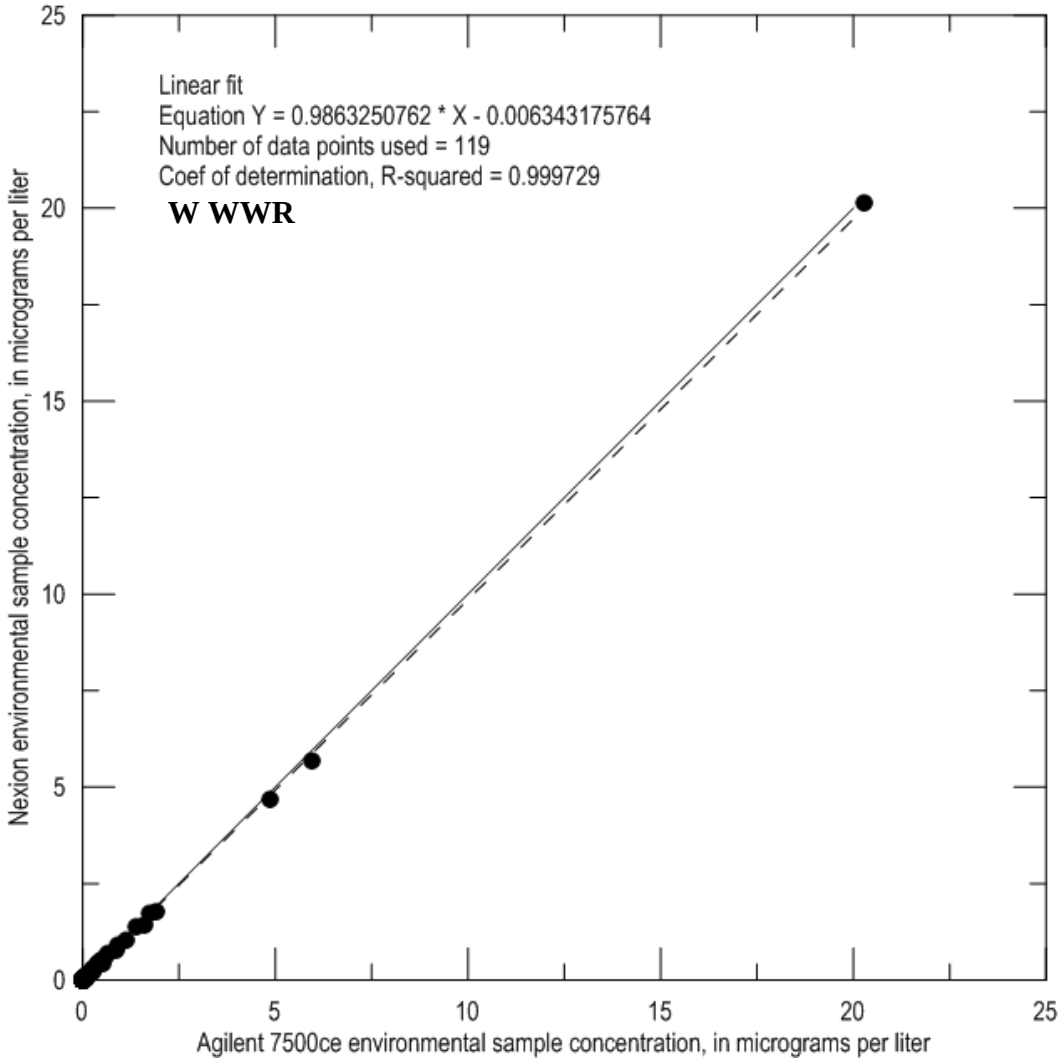


Figure A3.48. Linear regression of tungsten whole-water recoverable (W WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

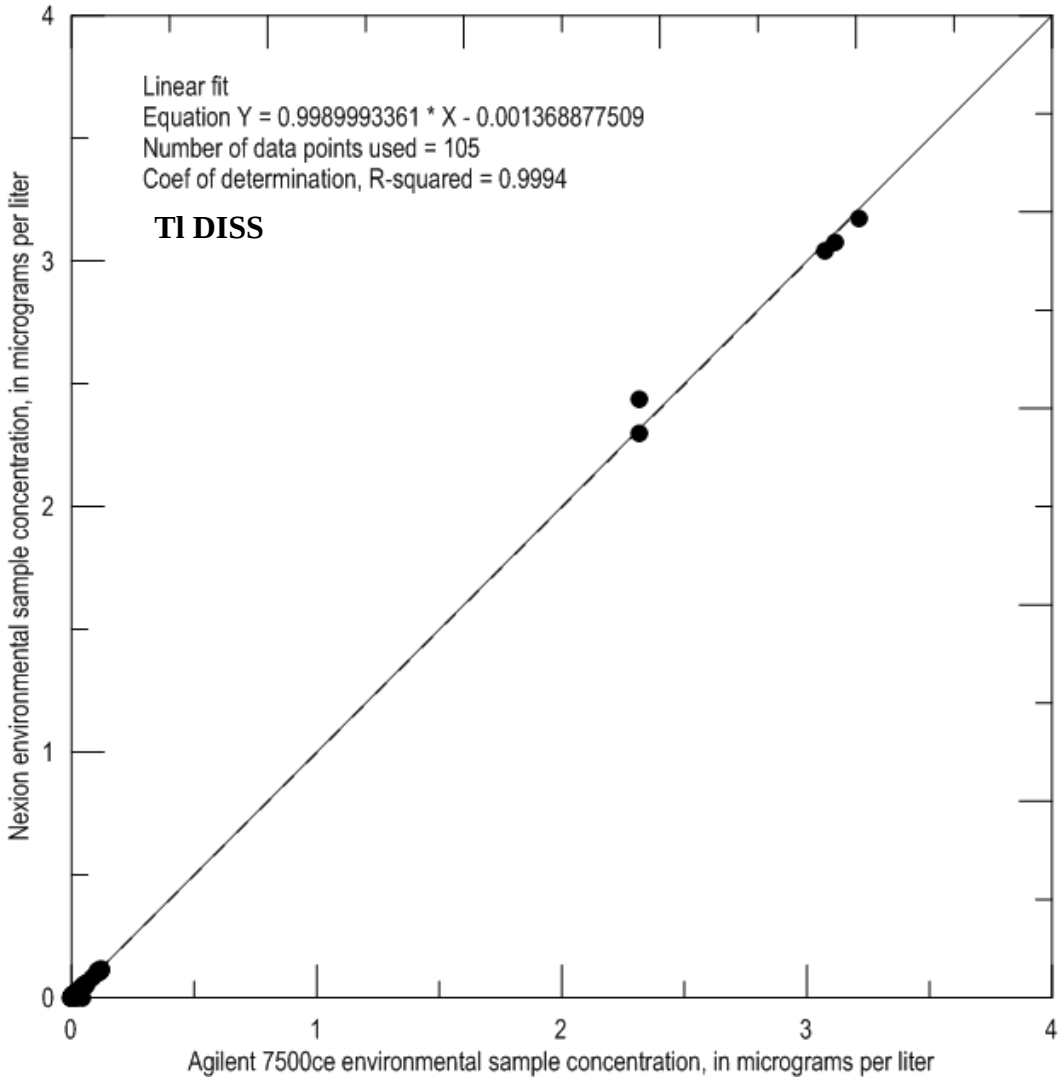


Figure A3.49. Linear regression of thallium dissolved (Tl DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

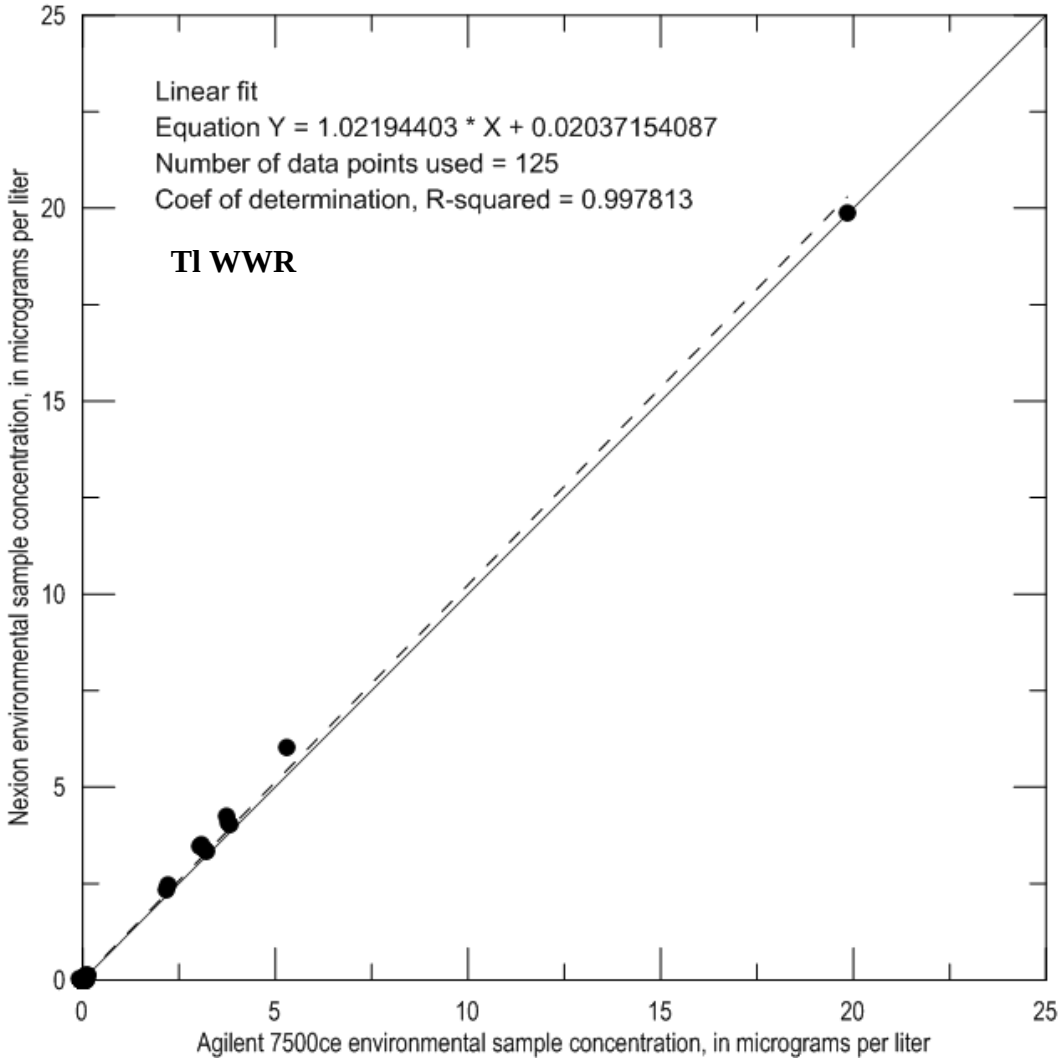


Figure A3.50. Linear regression of thallium whole-water recoverable (Tl WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

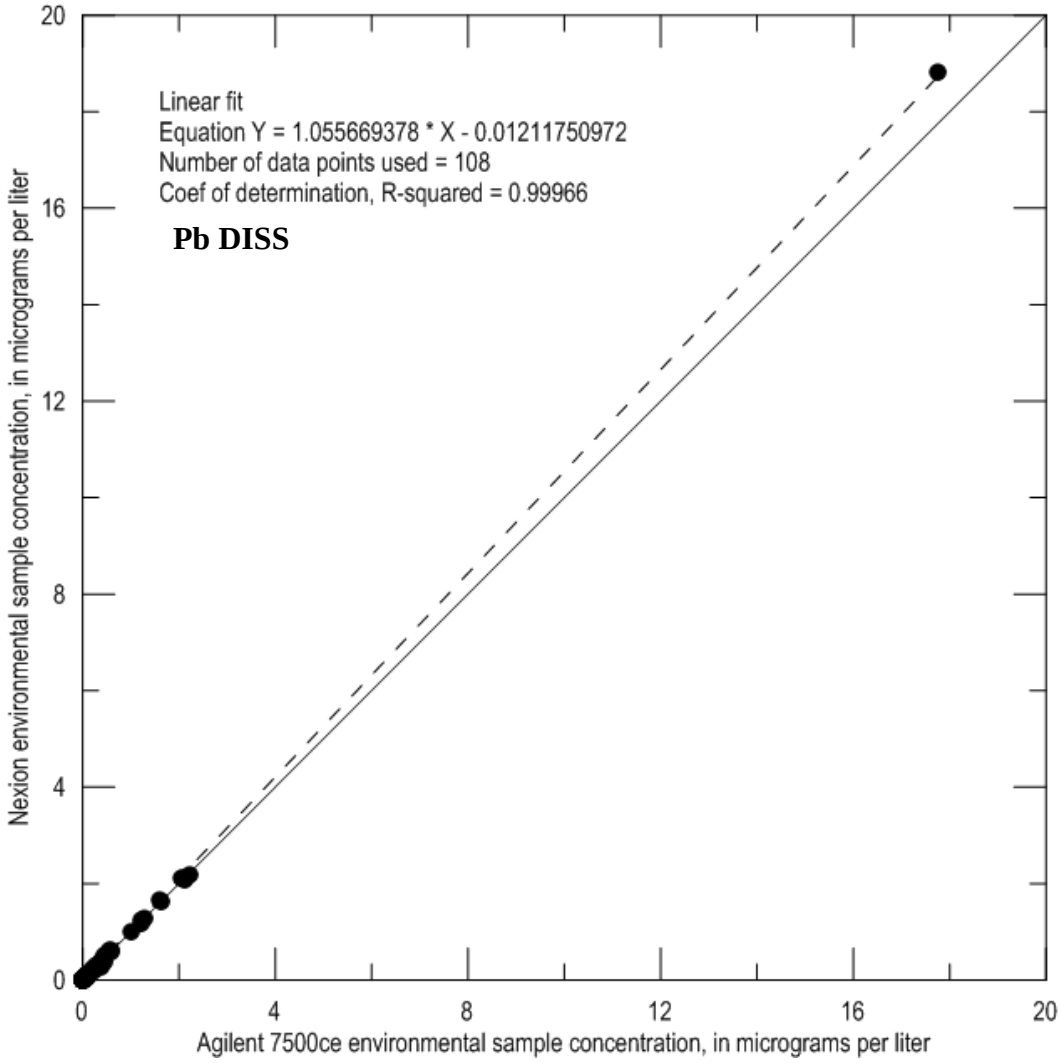


Figure A3.51. Linear regression of lead dissolved (Pb DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

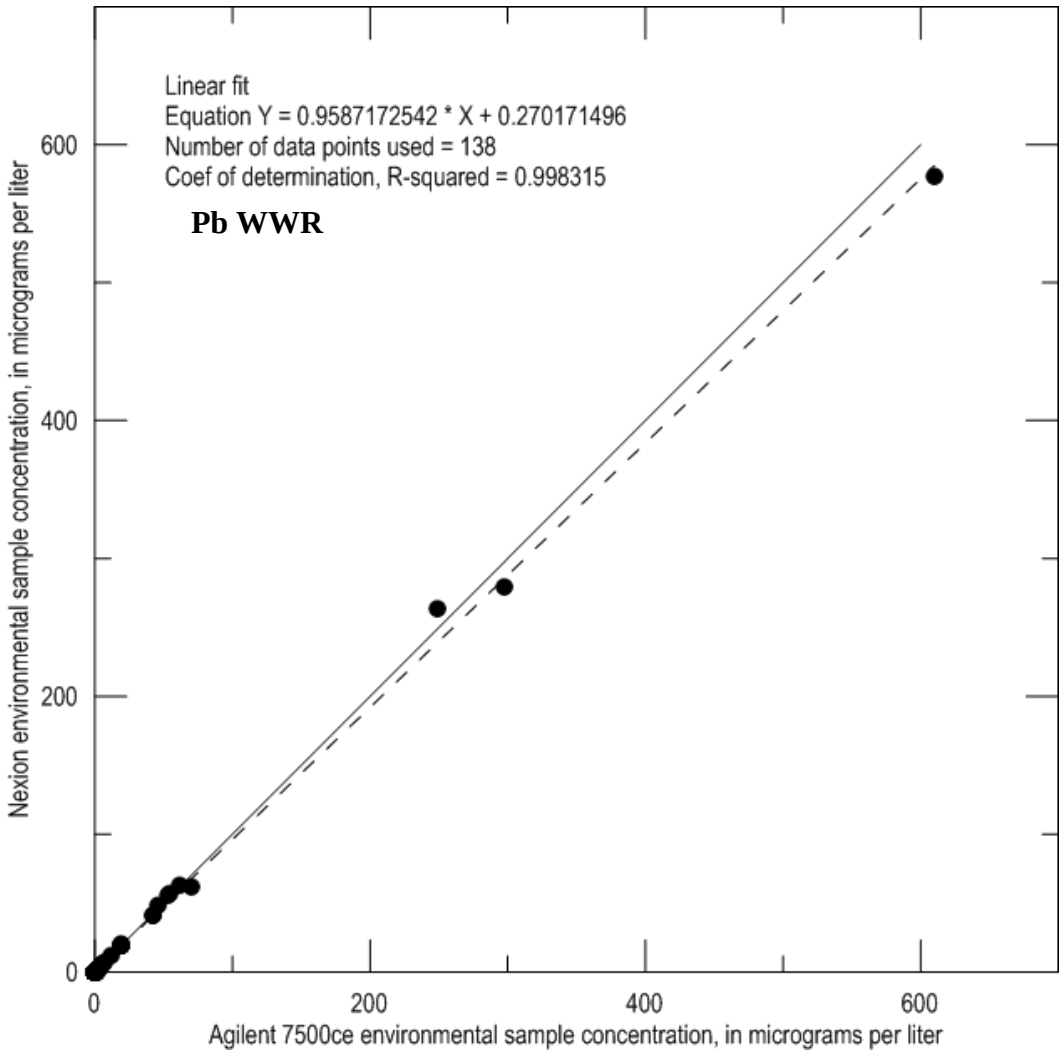


Figure A3.52. Linear regression of lead whole-water recoverable (Pb WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

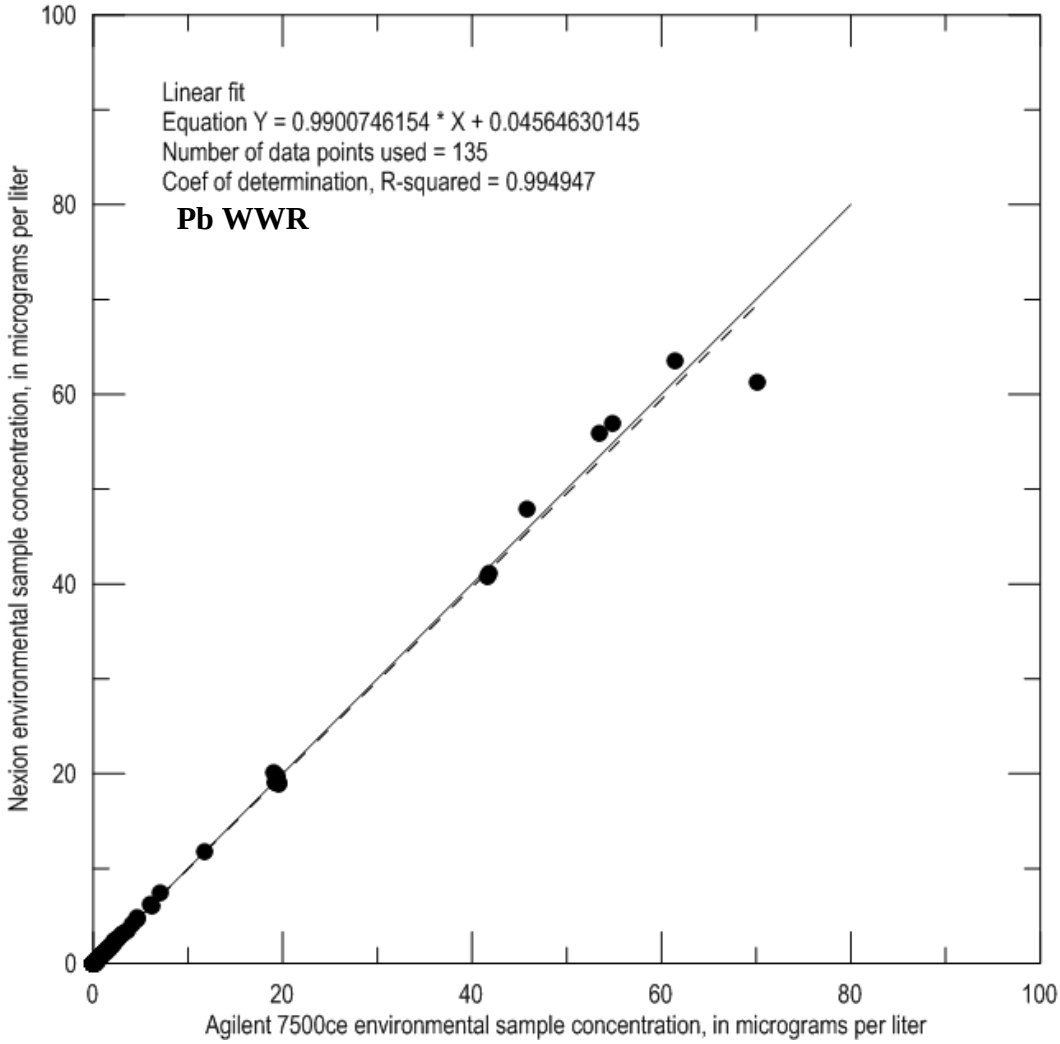


Figure A3.53. Linear regression of a subset of lead whole-water recoverable (Pb WWR) environmental sample data to 100 micrograms per liter analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. There is good agreement between the two methods near the detection limit.

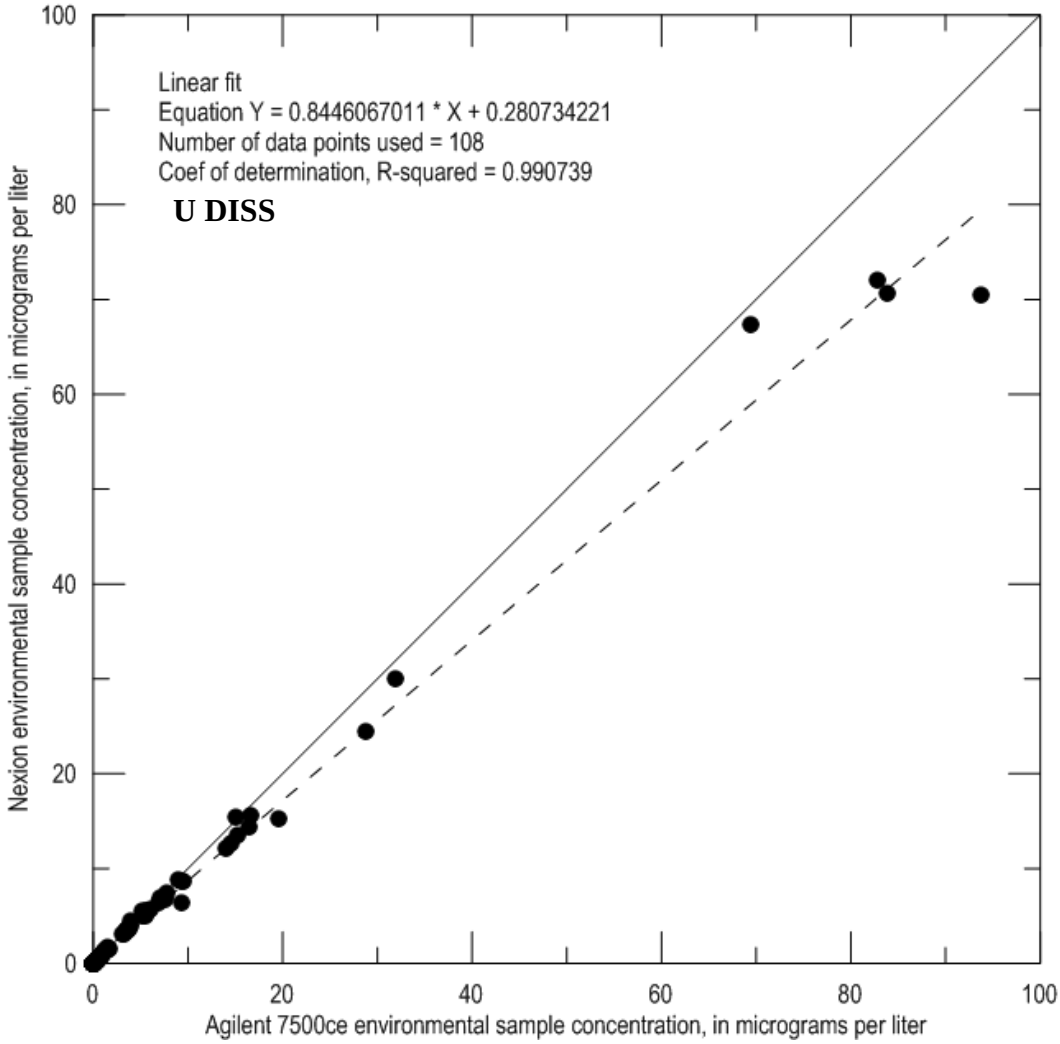


Figure A3.54. Linear regression of uranium dissolved (U DISS) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

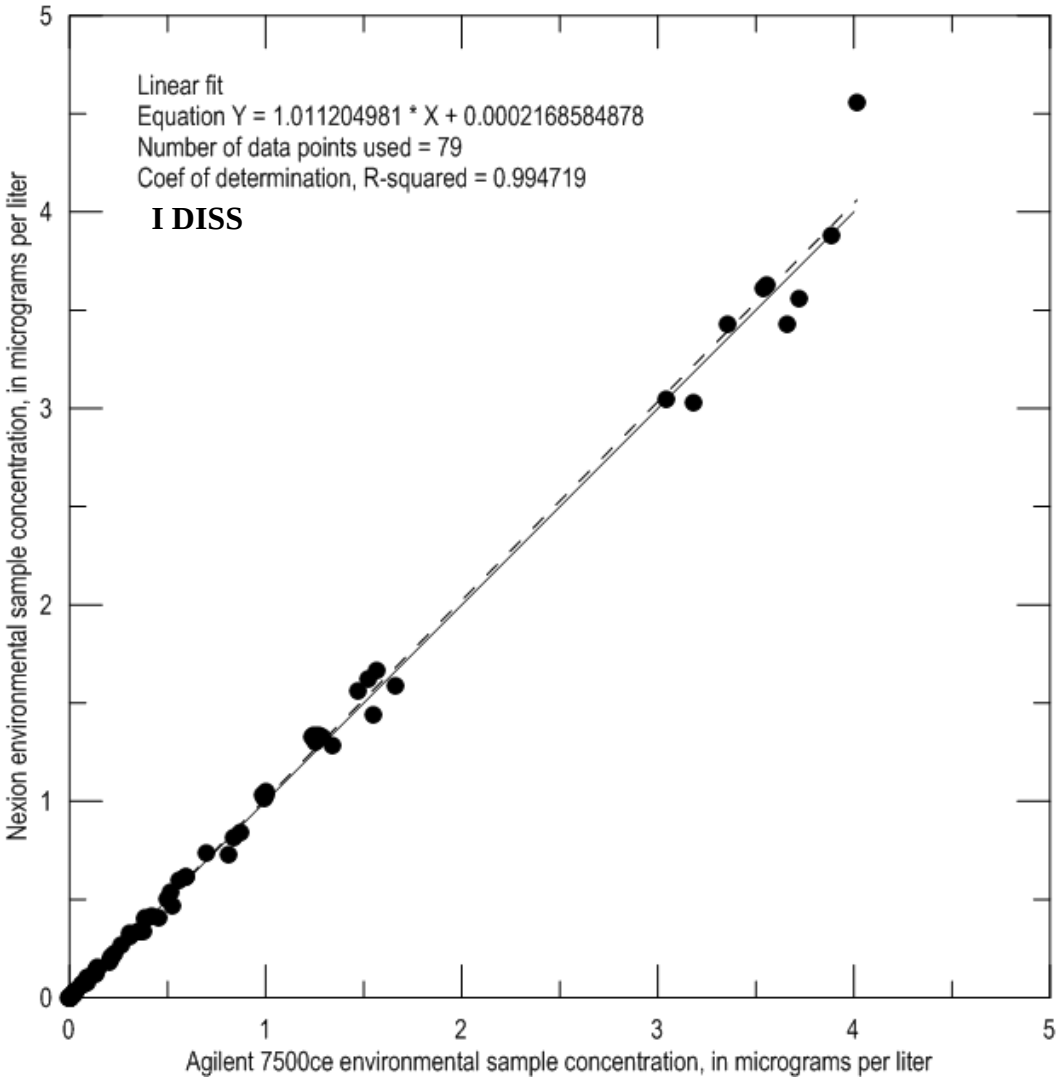


Figure A3.55. Linear regression of a subset of uranium dissolved (U DISS) environmental sample data to 5 micrograms per liter analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS. There is good agreement between the two methods near the detection limit.

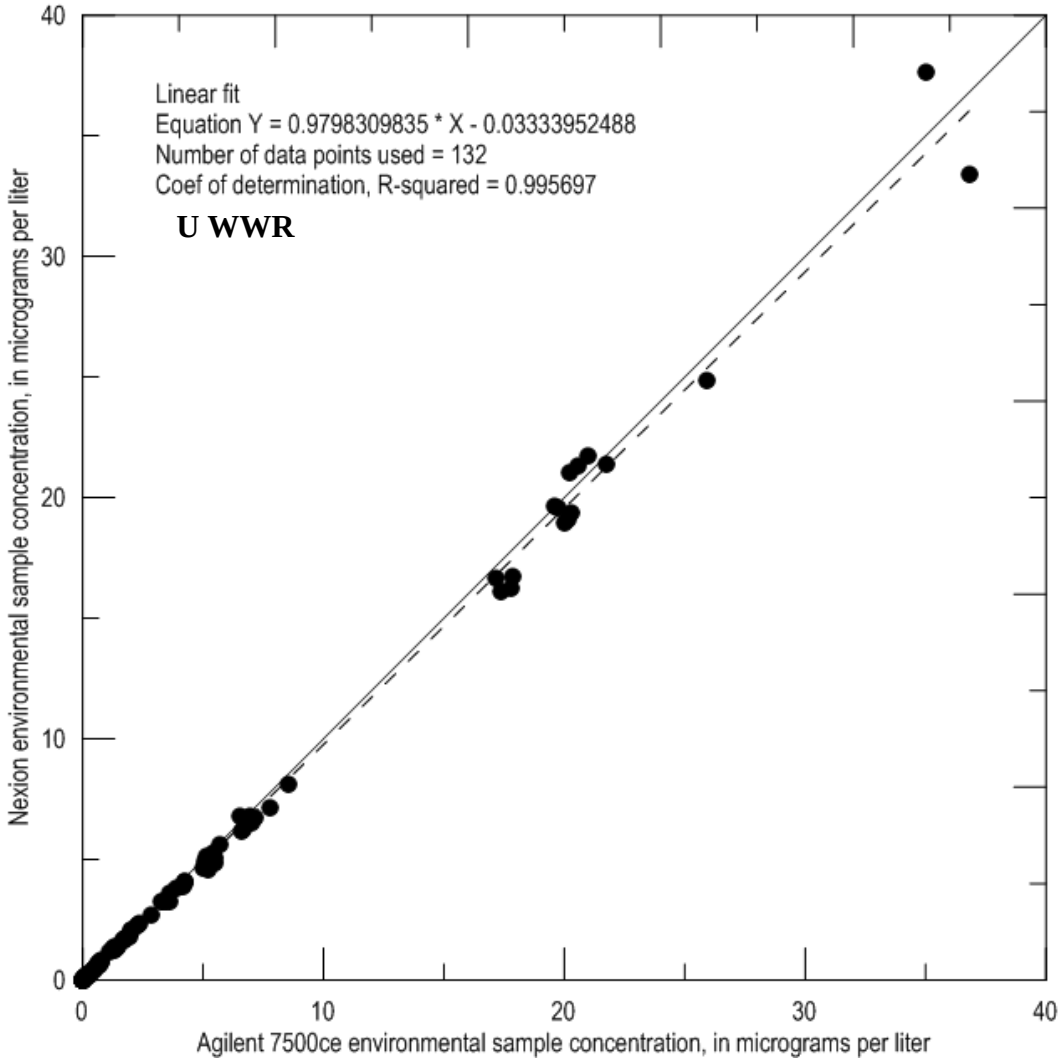
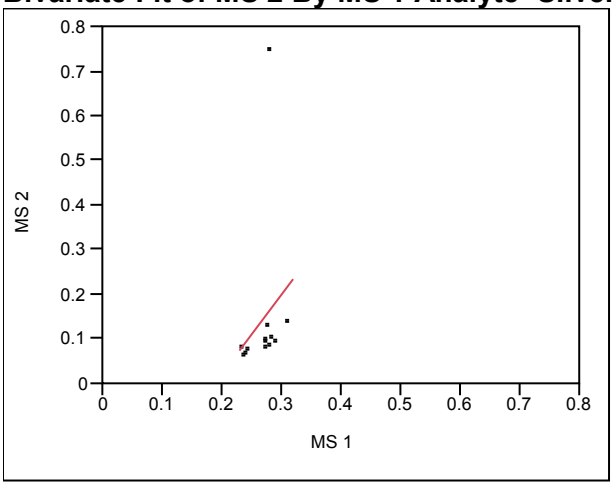


Figure A3.56. Linear regression of uranium whole-water recoverable (U WWR) environmental sample data analyzed on the Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) and on the Nexion 350D ICP-MS.

Attachment 4. Linear regression plots of each analyte comparing data, in micrograms per liter (µg/L), obtained on two Nexion inductively coupled plasma mass spectrometers, MS1 compared to MS2

Bivariate Fit of MS 2 By MS 1 Analyte=Silver (µg/L)



Linear Fit

Linear Fit

MS 2 = -0.335834 + 1.7787627*MS 1

Summary of Fit

RSquare	0.048832
RSquare Adj	-0.03764
Root Mean Square Error	0.186956
Mean of Response	0.142196
Observations (or Sum Wgts)	13

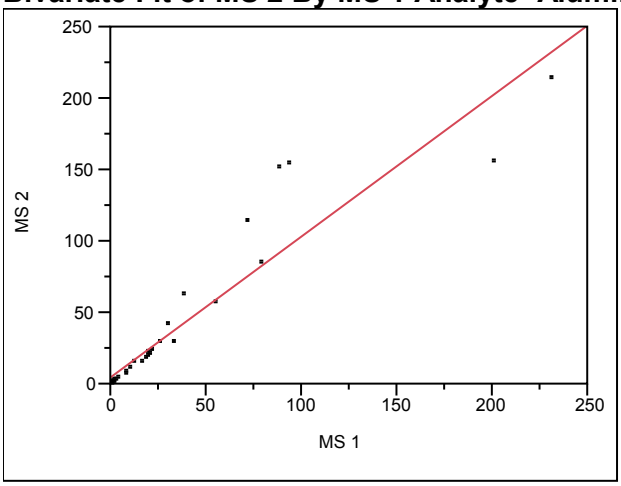
Analysis of Variance

Source	DF	Sum of squares	Mean square	F ratio
Model	1	0.01973851	0.019739	0.5647
Error	11	0.38447683	0.034952	**Prob > F**
C. Total	12	0.40421534		0.4681

Parameter Estimates

Term	Estimate	Standard error	t ratio	Prob>|t|
Intercept	-0.335834	0.638226	-0.53	0.6092
MS 1	1.7787627	2.367007	0.75	0.4681

Bivariate Fit of MS 2 By MS 1 Analyte=Aluminum (µg/L)



Linear Fit

Linear Fit

MS 2 = 4.260478 + 0.9853024*MS 1

Summary of Fit

RSquare	0.888214
RSquare Adj	0.885109
Root Mean Square Error	18.25681
Mean of Response	33.7234
Observations (or Sum Wgts)	38

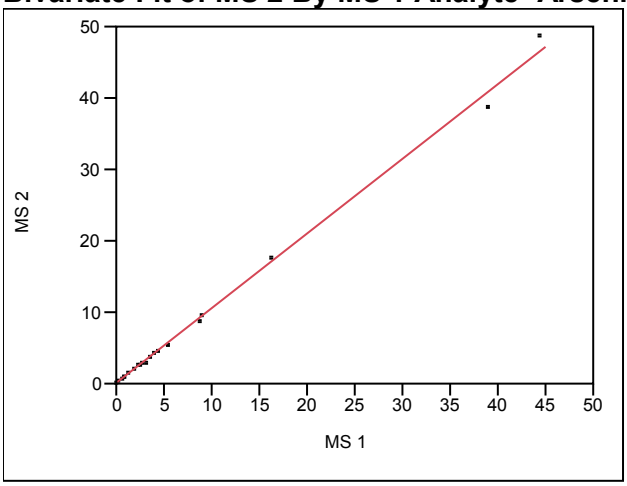
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	95341.65	95341.7	286.0442
Error	36	11999.19	333.3	**Prob > F**
C. Total	37	107340.85		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	4.260478	3.435995	1.24	0.2230
MS 1	0.9853024	0.058258	16.91	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Arsenic (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.1079854 + 1.045567*MS 1

Summary of Fit

RSquare	0.989722
RSquare Adj	0.989429
Root Mean Square Error	1.042396
Mean of Response	4.614405
Observations (or Sum Wgts)	37

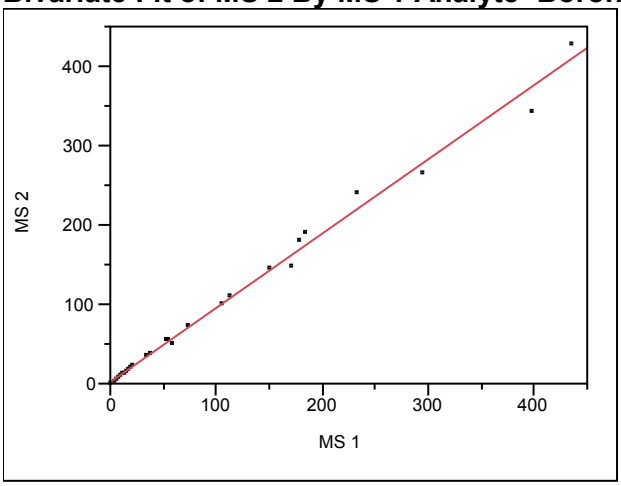
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	3662.3336	3662.33	3370.487
Error	35	38.0306	1.09	**Prob > F**
C. Total	36	3700.3642		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.1079854	0.188129	0.57	0.5696
MS 1	1.045567	0.01801	58.06	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Boron (µg/L)



Linear Fit

Linear Fit

MS 2 = 1.8680826 + 0.9363091*MS 1

Summary of Fit

RSquare	0.993296
RSquare Adj	0.993093
Root Mean Square Error	8.778328
Mean of Response	75.82075
Observations (or Sum Wgts)	35

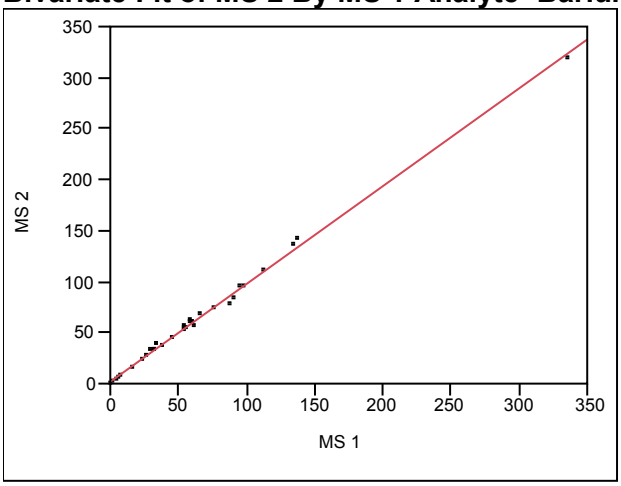
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	376801.36	376801	4889.775
Error	33	2542.95	77	**Prob > F**
C. Total	34	379344.31		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	1.8680826	1.822126	1.03	0.3127
MS 1	0.9363091	0.01339	69.93	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Barium (µg/L)



Linear Fit

Linear Fit

MS 2 = 1.8251045 + 0.9586181*MS 1

Summary of Fit

RSquare	0.997639
RSquare Adj	0.997576
Root Mean Square Error	2.803392
Mean of Response	53.28649
Observations (or Sum Wgts)	39

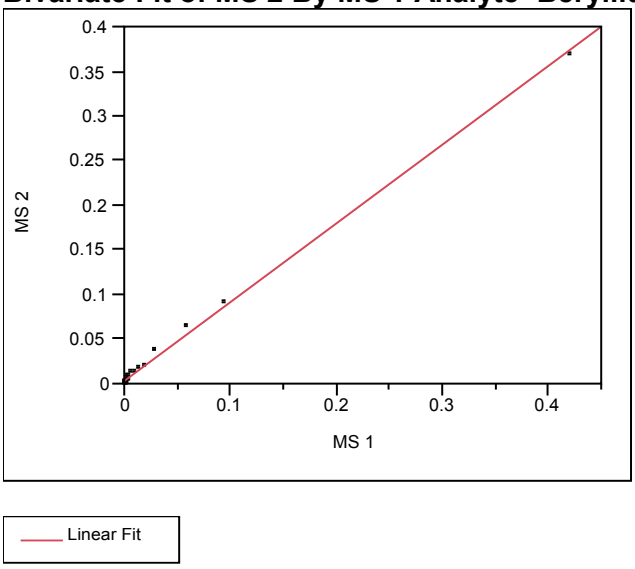
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	122893.19	122893	15637.24
Error	37	290.78	7.859008	**Prob > F**
C. Total	38	123183.97		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	1.8251045	0.608991	3.00	0.0048*
MS 1	0.9586181	0.007666	125.05	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Beryllium (µg/L)



Linear Fit

MS 2 = 0.002921 + 0.8821614*MS 1

Summary of Fit

RSquare	0.99624
RSquare Adj	0.996114
Root Mean Square Error	0.004157
Mean of Response	0.021098
Observations (or Sum Wgts)	32

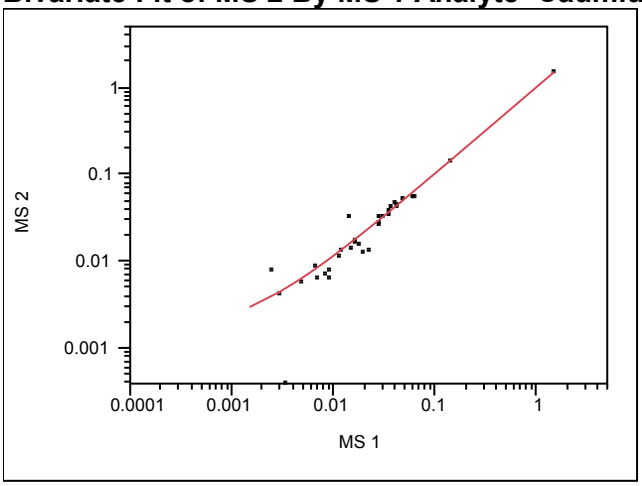
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	0.13731865	0.137319	7948.128
Error	30	0.00051831	0.000017	**Prob > F**
C. Total	31	0.13783695		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.002921	0.000763	3.83	0.0006*
MS 1	0.8821614	0.009895	89.15	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Cadmium (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.0014377 + 0.9976211*MS 1

Summary of Fit

RSquare	0.999408
RSquare Adj	0.999392
Root Mean Square Error	0.005578
Mean of Response	0.057382
Observations (or Sum Wgts)	41

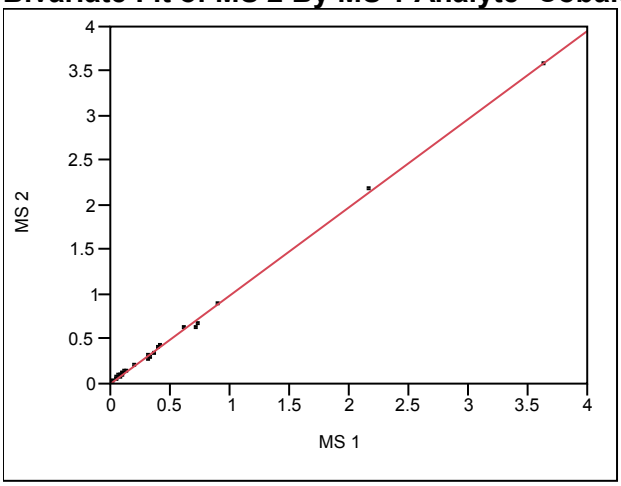
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	2.0472441	2.04724	65790.95
Error	39	0.0012136	3.112e-5	**Prob > F**
C. Total	40	2.0484577		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.0014377	0.000898	1.60	0.1175
MS 1	0.9976211	0.003889	256.50	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Cobalt (µg/L)



Linear Fit

Linear Fit

MS 2 = -0.004003 + 0.9884126*MS 1

Summary of Fit

RSquare	0.998991
RSquare Adj	0.99896
Root Mean Square Error	0.022572
Mean of Response	0.354662
Observations (or Sum Wgts)	34

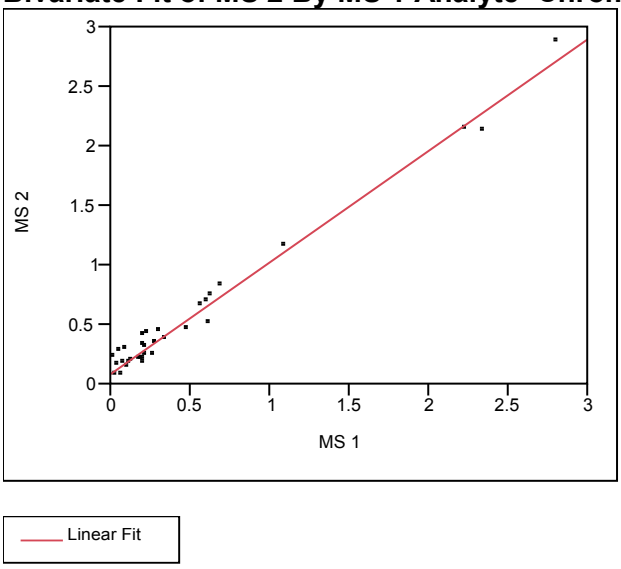
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	16.144302	16.1443	31688.17
Error	32	0.016303	0.000509	**Prob > F**
C. Total	33	16.160605		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	-0.004003	0.004364	-0.92	0.3659
MS 1	0.9884126	0.005553	178.01	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Chromium (µg/L)



Linear Fit

MS 2 = 0.0781314 + 0.9374537*MS 1

Summary of Fit

RSquare	0.853299
RSquare Adj	0.848985
Root Mean Square Error	0.26724
Mean of Response	0.479836
Observations (or Sum Wgts)	36

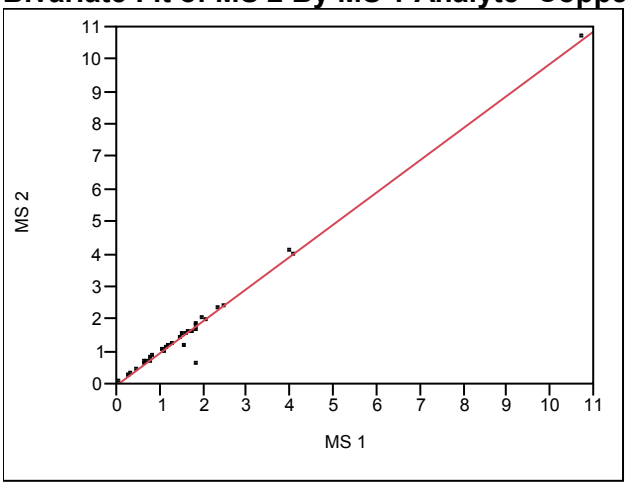
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	14.123794	14.1238	197.7644
Error	34	2.428188	0.0714	**Prob > F**
C. Total	35	16.551982		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.0781314	0.052913	1.48	0.1490
MS 1	0.9374537	0.066662	14.06	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Copper (µg/L)



Linear Fit

Linear Fit

MS 2 = -0.06186 + 0.9909046*MS 1

Summary of Fit

RSquare	0.985521
RSquare Adj	0.985107
Root Mean Square Error	0.220388
Mean of Response	1.486374
Observations (or Sum Wgts)	37

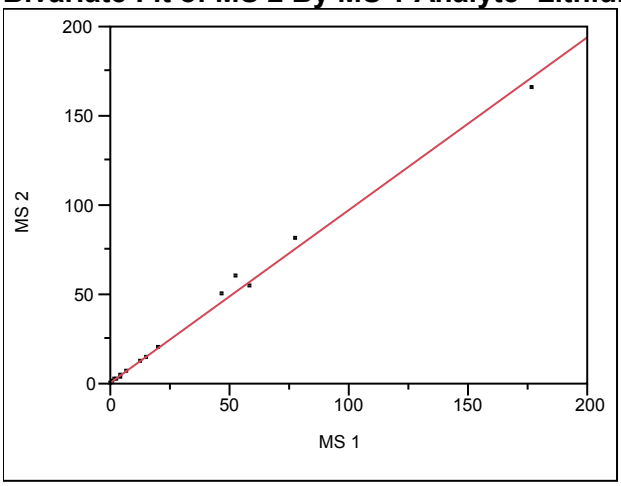
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	115.70612	115.706	2382.215
Error	35	1.69998	0.049	**Prob > F**
C. Total	36	117.40609		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	-0.06186	0.048155	-1.28	0.2074
MS 1	0.9909046	0.020302	48.81	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Lithium (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.4703234 + 0.967459*MS 1

Summary of Fit

RSquare	0.995113
RSquare Adj	0.994956
Root Mean Square Error	2.384141
Mean of Response	15.79165
Observations (or Sum Wgts)	33

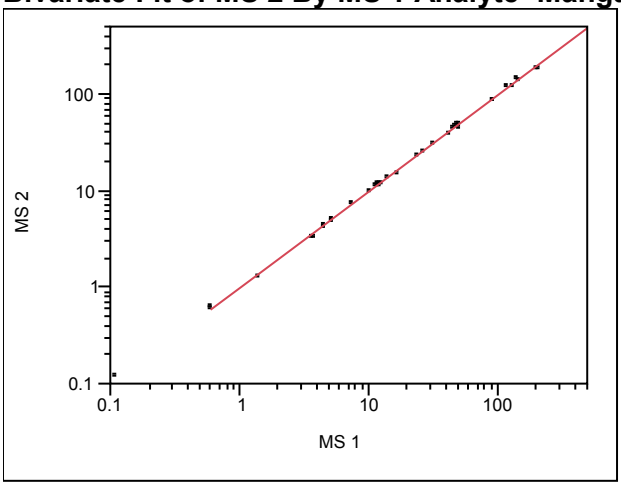
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	35882.546	35882.5	6312.763
Error	31	176.208	5.7	**Prob > F**
C. Total	32	36058.754		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.4703234	0.457637	1.03	0.3120
MS 1	0.967459	0.012177	79.45	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Manganese (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.0056852 + 0.9616926*MS 1

Summary of Fit

RSquare	0.998314
RSquare Adj	0.998271
Root Mean Square Error	3.659542
Mean of Response	50.64416
Observations (or Sum Wgts)	41

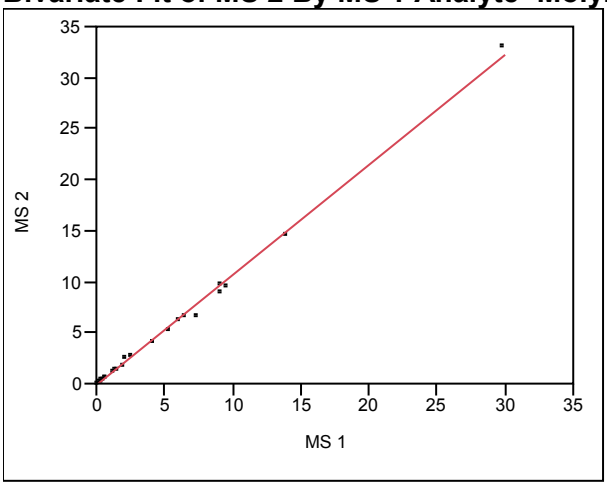
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	309269.34	309269	23093.16
Error	39	522.30	13	**Prob > F**
C. Total	40	309791.63		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.0056852	0.661574	0.01	0.9932
MS 1	0.9616926	0.006328	151.96	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Molybdenum (µg/L)



Linear Fit

Linear Fit

MS 2 = -0.151303 + 1.079299*MS 1

Summary of Fit

RSquare	0.996888
RSquare Adj	0.996808
Root Mean Square Error	0.33331
Mean of Response	3.633232
Observations (or Sum Wgts)	41

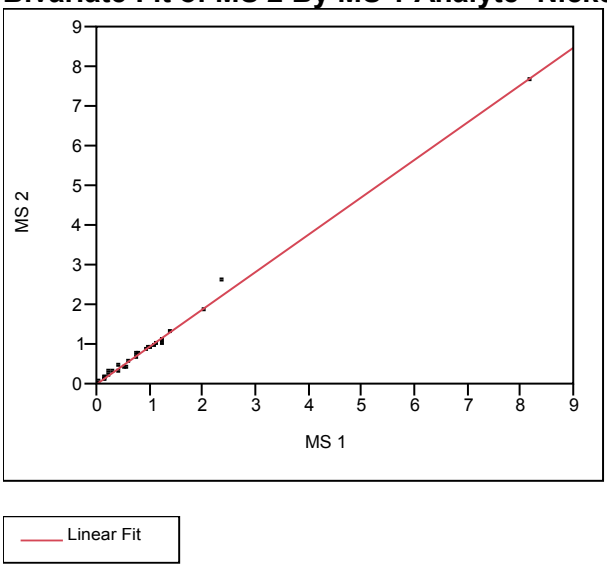
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	1387.9547	1387.95	12493.37
Error	39	4.3327	0.11	**Prob > F**
C. Total	40	1392.2874		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	-0.151303	0.062097	-2.44	0.0195*
MS 1	1.079299	0.009656	111.77	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Nickel (µg/L)



Linear Fit

MS 2 = -0.017783 + 0.9423385*MS 1

Summary of Fit

RSquare	0.995356
RSquare Adj	0.995227
Root Mean Square Error	0.087799
Mean of Response	0.770309
Observations (or Sum Wgts)	38

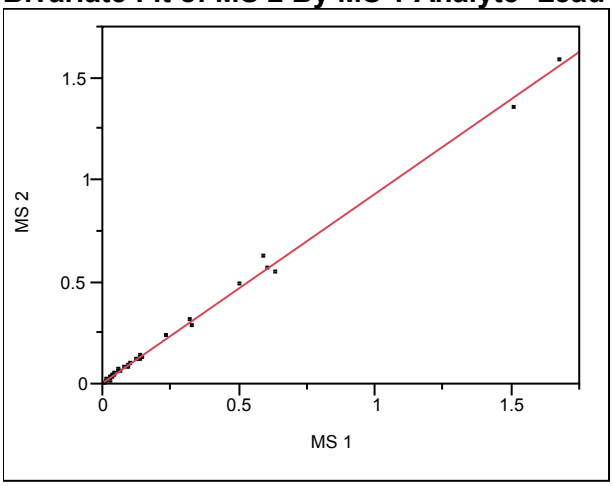
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	59.480664	59.4807	7716.120
Error	36	0.277510	0.0077	**Prob > F**
C. Total	37	59.758175		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	-0.017783	0.016833	-1.06	0.2978
MS 1	0.9423385	0.010728	87.84	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Lead (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.0013828 + 0.9280705*MS 1

Summary of Fit

RSquare	0.997001
RSquare Adj	0.996924
Root Mean Square Error	0.018687
Mean of Response	0.185335
Observations (or Sum Wgts)	41

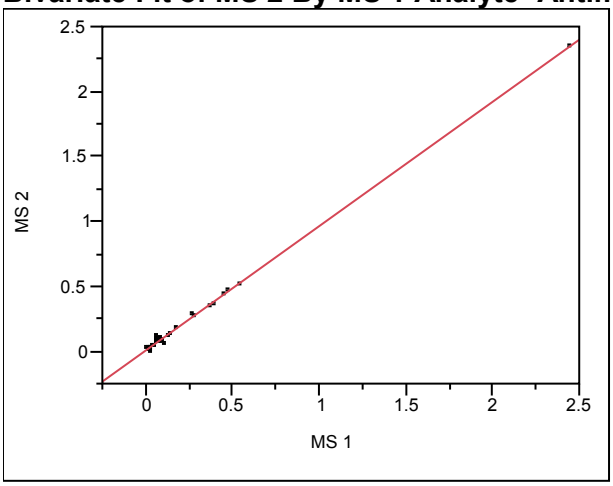
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	4.5272495	4.52725	12964.63
Error	39	0.0136188	0.00035	**Prob > F**
C. Total	40	4.5408683		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.0013828	0.003336	0.41	0.6807
MS 1	0.9280705	0.008151	113.86	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Antimony (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.0048777 + 0.9575373*MS 1

Summary of Fit

RSquare	0.997995
RSquare Adj	0.997943
Root Mean Square Error	0.017185
Mean of Response	0.167854
Observations (or Sum Wgts)	40

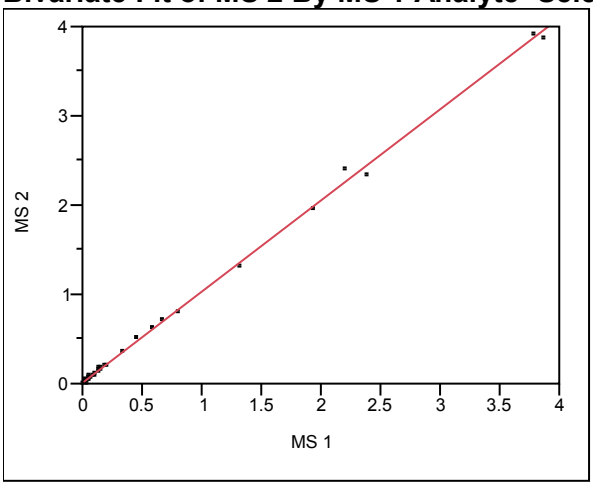
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	5.5868517	5.58685	18917.42
Error	38	0.0112225	0.00030	**Prob > F**
C. Total	39	5.5980742		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.0048777	0.002964	1.65	0.1081
MS 1	0.9575373	0.006962	137.54	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Selenium (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.0079676 + 1.0214461*MS 1

Summary of Fit

RSquare	0.998923
RSquare Adj	0.998894
Root Mean Square Error	0.037509
Mean of Response	0.622418
Observations (or Sum Wgts)	40

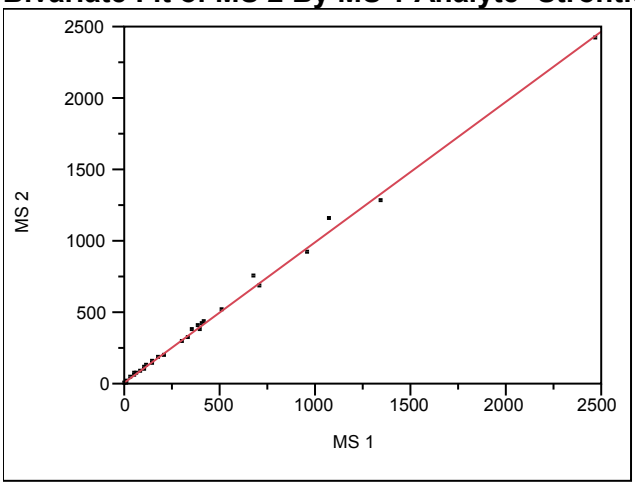
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	49.564553	49.5646	35229.90
Error	38	0.053462	0.0014	**Prob > F**
C. Total	39	49.618015		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.0079676	0.006774	1.18	0.2468
MS 1	1.0214461	0.005442	187.70	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Strontium (µg/L)



Linear Fit

Linear Fit

MS 2 = 5.7793544 + 0.9835585*MS 1

Summary of Fit

RSquare	0.99714
RSquare Adj	0.997065
Root Mean Square Error	24.76685
Mean of Response	320.3388
Observations (or Sum Wgts)	40

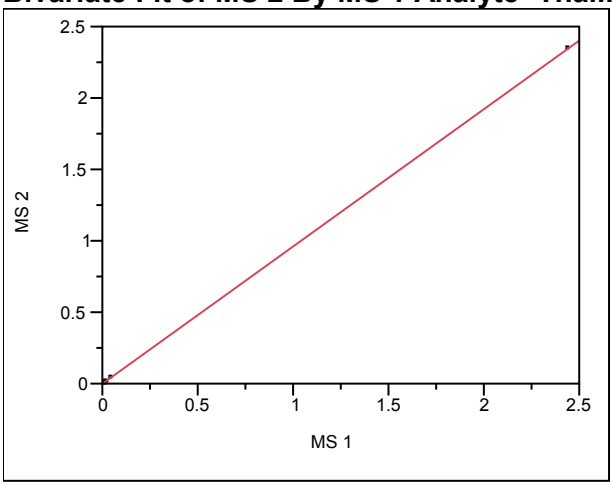
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	8126956.4	8126956	13249.10
Error	38	23309.1	613	**Prob > F**
C. Total	39	8150265.5		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	5.7793544	4.775267	1.21	0.2337
MS 1	0.9835585	0.008545	115.10	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Thallium (µg/L)



Linear Fit

Linear Fit

MS 2 = -0.000951 + 0.9611422*MS 1

Summary of Fit

RSquare	0.999982
RSquare Adj	0.999981
Root Mean Square Error	0.001632
Mean of Response	0.067231
Observations (or Sum Wgts)	38

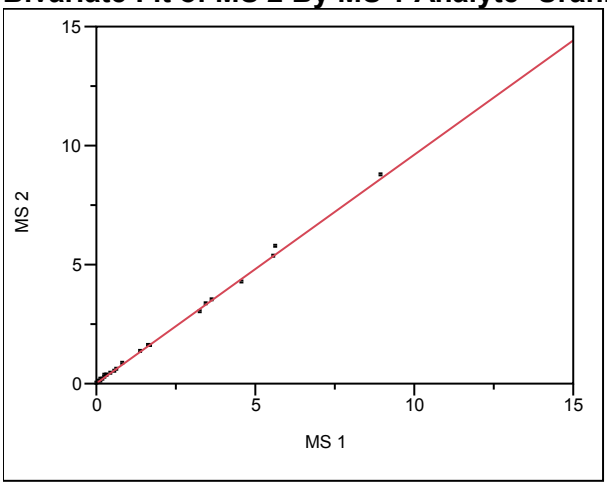
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	5.3150812	5.31508	1995316
Error	36	0.0000959	2.664e-6	**Prob > F**
C. Total	37	5.3151771		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	-0.000951	0.000269	-3.54	0.0011*
MS 1	0.9611422	0.00068	1412.6	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Uranium (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.0102651 + 0.9605452*MS 1

Summary of Fit

RSquare	0.999352
RSquare Adj	0.999335
Root Mean Square Error	0.074285
Mean of Response	1.494875
Observations (or Sum Wgts)	40

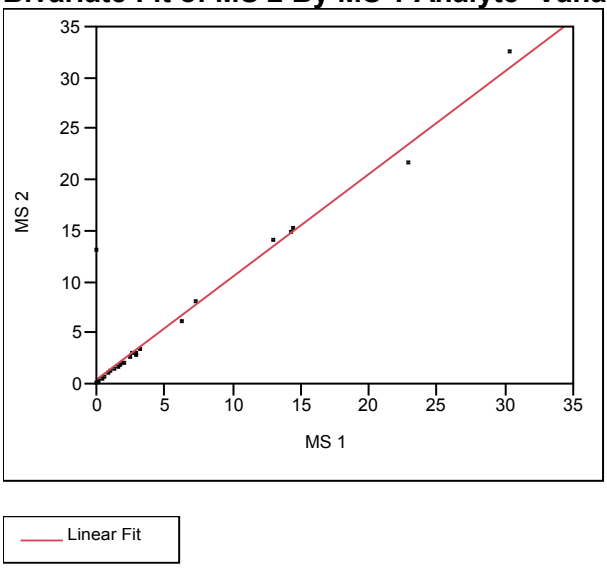
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	323.48033	323.480	58620.70
Error	38	0.20969	0.005518	**Prob > F**
C. Total	39	323.69003		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.0102651	0.01325	0.77	0.4433
MS 1	0.9605452	0.003967	242.12	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Vanadium (µg/L)



Linear Fit

MS 2 = 0.3882238 + 1.0077458*MS 1

Summary of Fit

RSquare	0.910179
RSquare Adj	0.907876
Root Mean Square Error	2.086236
Mean of Response	3.887763
Observations (or Sum Wgts)	41

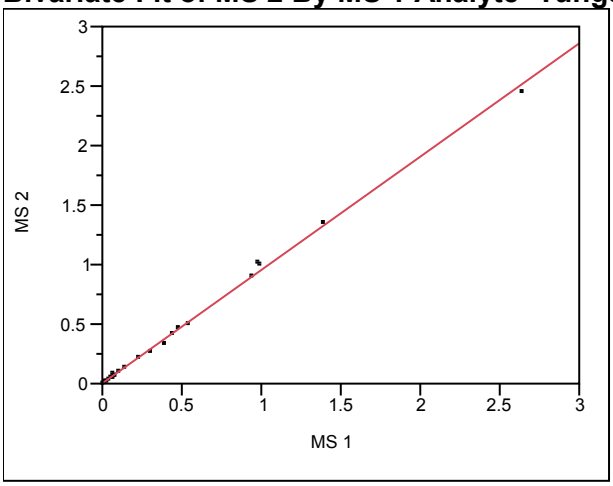
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	1720.0467	1720.05	395.1969
Error	39	169.7428	4.35	**Prob > F**
C. Total	40	1889.7894		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.3882238	0.37033	1.05	0.3009
MS 1	1.0077458	0.050693	19.88	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Tungsten (µg/L)



Linear Fit

Linear Fit

MS 2 = 0.0026077 + 0.9521367*MS 1

Summary of Fit

RSquare	0.998079
RSquare Adj	0.998028
Root Mean Square Error	0.021643
Mean of Response	0.243083
Observations (or Sum Wgts)	40

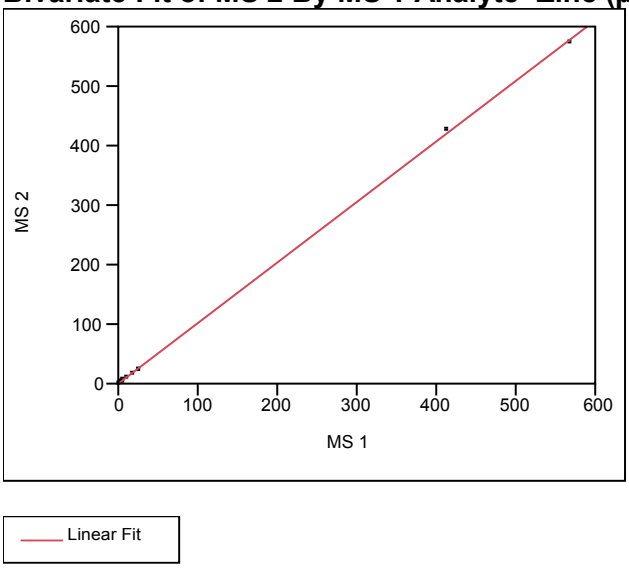
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	9.2457501	9.24575	19738.77
Error	38	0.0177994	0.00047	**Prob > F**
C. Total	39	9.2635495		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	0.0026077	0.003826	0.68	0.4997
MS 1	0.9521367	0.006777	140.49	<.0001*

Bivariate Fit of MS 2 By MS 1 Analyte=Zinc (µg/L)



Linear Fit

MS 2 = -0.04093 + 1.017365*MS 1

Summary of Fit

RSquare	0.999871
RSquare Adj	0.999867
Root Mean Square Error	1.469639
Mean of Response	37.83497
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	469579.17	469579	217414.0
Error	28	60.48	2.159839	**Prob > F**
C. Total	29	469639.64		<.0001*

Parameter Estimates

Term	Estimate	Standard Error	t Ratio	Prob>|t|
Intercept	-0.04093	0.280344	-0.15	0.8850
MS 1	1.017365	0.002182	466.28	<.0001*