

Meeting Worldwide Regulatory Requirements for the Analysis of Trace Metals in Drinking Water Using the Agilent 7500c ICP-MS

Application

Environmental

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Abstract

The Agilent 7500c ICP-MS can be used to meet the regulatory requirements for trace metals in drinking water around the world. Elements previously relegated to other techniques, such as GFAA or ICP-OES due to very high or low concentrations or the presence of interferences, can now be measured in a single analysis.

Introduction

Virtually all developed countries have adopted programs and regulations to monitor and maintain the quality of public water systems. In the US, water quality is regulated by the United States Environmental Protection Agency (USEPA) as mandated by the *Safe Drinking Water Act of 1974*. In the European Union, drinking water is regulated by the *Council Directive 98/83/EC of 3, November, 1998 on the Quality of Water Intended for Human Consumption*. In Japan, quality of drinking water is regulated by the *Japan Water Supply Act*, dating from 1957, and most recently updated in 2001. Most of the rest of the world's developed countries have adopted drinking water quality standards based on World Health Organization (WHO) Standards, *Guidelines for Drinking Water Quality, 1996, 1998*, or on the USEPA standards. While

these guidelines, as they pertain to trace metals, vary somewhat in their lists of regulated metals and concentrations, they are fundamentally similar. They all require accurate, precise measurement of multiple toxic metals in drinking waters at the lowest practical limits of quantification. This application note will demonstrate that the sensitivity, accuracy, and precision requirements for the analysis of trace metals in drinking water worldwide can be met by a single, robust technique using the Agilent 7500c ICP-MS system with Octopole Reaction System (ORS) technology.

US Regulations

In the US, the quality of public drinking water is safeguarded by the provisions of the Safe Drinking Water Act of 1974.

The Safe Drinking Water Act (SDWA) was originally passed by Congress to protect public health by regulating the nation's public drinking water supply. The law, amended in 1986 and 1996, requires many actions to protect drinking water and its sources in rivers, lakes, reservoirs, springs, and ground water wells (SDWA does not regulate private wells, which serve fewer than 25 individuals). SDWA authorizes the USEPA to set primary national health-based standards for drinking water to protect against both naturally-occurring and man-made contaminants that may be found in drinking water. These primary national drinking water standards include maximum contaminant level goals (MCLGs), levels below which there is no known or expected health risk. From these MCLG values, EPA determines maximum contaminant levels (MCLs), which are



enforceable levels that may not be exceeded. The MCLs are set as closely as possible to the MCLGs and are based on best available current technology and economic feasibility. These limits are reviewed and updated periodically as new information becomes available and technology improves.

Japanese Regulations

Drinking water quality in Japan is regulated by the Japan Water Supply Act, which was first promulgated in 1957 with the Quality Standard for Drinking Water set the following year. This standard currently regulates the drinking water quality of more than 97% of the population. The Quality Standard sets maximum allowable concentrations (MAC) for 17 metals. It also requires that quantification limits be set at 1/10 of the MAC to assure accurate measurements at trace levels. Because of this, in 2001 the Drinking Water Test Method was revised and expanded to include the use of ICP-MS for 14 of the 17 metals. The approval of the use of ICP-MS has eliminated the need for costly and time

consuming preconcentration, which was required to meet the required detection limits using ICP-OES.

European Union Regulations

Currently, water quality in the European Union (EU) is regulated by Council Directive 80/778/EEC. This directive applies to all waters intended for human consumption, except natural mineral waters or waters which are medicinal products. As of December 2003, Directive 80/778/EEC will be repealed and replaced by Council Directive 98/83/EC *Directive on the Quality of Water Intended for Human Consumption*, which came into force on December 25, 1998. The standards are based largely on recommendations by the WHO¹. Member states of the European Community, while they must comply fully, are permitted to implement regulation and enforcement locally. As a result, no single regulation exists for the analysis of trace metals in water throughout Europe.

¹World Health Organization Guidelines and International Standards for Drinking-Water Quality, 1998

Table 1. Drinking Water Standards for Trace Metal Content from WHO Recommendations, EU Regulations, Japan Drinking Water Regulations and USEPA.

Analyte	WHO Standard (mg/L)	EC Directive 98/83/EC (mg/L)	Japan Drinking Water Standard (mg/L)	USEPA Primary MCL (mg/L)	Agilent 7500c MDLs*** (mg/L)
Aluminum (Al)		0.2	0.2	0.02-0.2*	0.000054
Antimony (Sb)	0.005**	.005	0.002	0.006	0.000035
Arsenic (As)	0.01**	.01	0.01	0.01	0.000052
Barium (Ba)	0.7			2	0.000027
Beryllium (Be)				0.004	0.000028
Boron (B)	0.5**	1	1.0		
Cadmium (Cd)	0.003	0.005	0.01	0.005	0.000025
Chromium (Cr)	0.05**	0.05		0.1	0.000019
Copper (Cu)	2**	2	1.0	1.3	0.000023
Iron (Fe)		0.2	0.3	0.3*	0.00125
Lead (Pb)	0.01	.01	0.05	0.015	0.000017
Manganese (Mn)	0.5**	.05	0.05	0.05*	0.000020
Mercury (Hg)	0.001	0.001	0.0005	0.002	0.000005
Molybdenum(Mo)	0.07				0.000030
Nickel (Ni)	0.02**	0.02	0.01		0.000024
Selenium (Se)	0.01	0.01	0.01	0.05	0.000047
Silver (Ag)				0.01*	0.000027
Sodium (Na)		200	200		0.0276
Thallium (Tl)				0.002	0.000021
Uranium (U)	0.002**		0.002	0.030	0.000015
Zinc (Zn)				5.0*	0.000101

*Secondary Standard, **Provisional Guideline Value, ***MDLs Calculated as Three Sigma of 10 Replicates of Low Standard, as Described in this Work. MDLs Reported in mg/L to Match Regulatory Requirements.

Table 1 includes the trace metals that are regulated by various worldwide regulatory and advisory agencies. ICP-MS is the only analytical technique capable of meeting all the required detection limits for all the regulated trace metals. Therefore, while not mandated as the only acceptable technique for most regulations, ICP-MS is becoming the instrument of choice for trace metals analysis in water worldwide.

While the details of QA/QC criteria and reporting requirements vary significantly from jurisdiction to jurisdiction, Table 1 shows that the actual detection limit requirements are very similar. In addition, the fundamental goals of the QA/QC requirements in all jurisdictions are the same. This is to insure that the reported values for all samples meet commonly accepted guidelines for accuracy and precision. Typically, these guidelines are met through the analysis of periodic QC samples inserted into the sample queue. Such QC samples should include: a check on the accuracy of the initial instrument calibration; a control sample of known concentration similar to that of the analytes in a similar matrix; a sample designed to test the ability of the system to eliminate interferences as false positives; a sample designed to detect sample carryover or memory problems; and periodic calibration check samples to check for instrument drift. If samples are to be analyzed outside the calibration range of the analytical method, then a linear range check sample must also be analyzed. It is outside the scope of this application note to detail the specific QA/QC requirements for each regulation where they exist at all. Instead, a general QA/QC protocol will be outlined which will demonstrate the ability of the Agilent 7500c to meet generally accepted guidelines while easily meeting the required reporting limits for drinking water monitoring worldwide. Simple modifications to this procedure can be implemented to insure strict compliance with detailed local requirements.

Advantages to the Use of the ORS for Drinking Water Analysis

Generally, drinking water is not considered a particularly difficult matrix for analysis by ICP-MS. There are, however, a few significant challenges.

These challenges are due to the very low desired reporting limits for several elements (Table 1), as well as the possibly high concentrations for others, such as Ca and Na. This combination of very low and very high analyte concentrations presents a challenge that no other analytical technique can overcome. In order to measure all elements simultaneously, the ICP-MS must be able to accurately measure mercury at 0.05 ppb or less and Na or Ca as high as 1000s of ppm. In addition, the ICP-MS must be able to eliminate common interferences on Fe, As, Se, Cu, V, and other elements which originate in the plasma and interface region. If unmanaged, these interferences make trace level analysis of the above elements difficult or impossible in many water samples.

The ORS serves two purposes. First, it uses collision/reaction cell technology to virtually eliminate polyatomic interferences on most elements. This allows the analyst to select the most abundant isotope of each analyte for analysis and avoid the use of mathematical correction factors. The result is sub-ppb detection limits for virtually all elements of interest. Second, it allows the analyst to use passive collisions in the ORS to reduce the ion current for high concentration, low-mass elements such as Na and Ca. In this way, the dynamic range for these elements is shifted to allow accurate, linear measurement at levels previously impossible by ICP-MS. It is this ability to simultaneously improve the sensitivity for ultra-trace analytes and extend the dynamic range upward for matrix analytes that is unique to the ORS system.

Instrument Conditions

Table 2 shows the instrument conditions used for typical water analysis. Listed are the preferred isotope, the tune mode (normal, hydrogen reaction, or helium collision), integration time, calibration range, and approximate detection limit based on normal commercial laboratory conditions. RF power is typically set high, 1400–1500 W, to maximize decomposition of the matrix. Other tune conditions such as ion optics, quadrupole, and detector parameters are set according to standard instrument tune guidelines. No special tuning is required.

Table 2. Elements of Interest with Appropriate Isotopes, ORS Acquisition Mode, Integration Time, Calibration Range and Measured MDLs for Each Isotope

Analyte	Isotope	ORS mode	Integration time (s)	Calibration range (ppb)	~MDL (ppb)
Aluminum (Al)	27	Normal	0.1	0.5–100	0.054
Antimony (Sb)	121	Normal	0.1	0.5–100	0.035
Arsenic (As)	75	Helium	0.5	0.5–100	0.052
Barium (Ba)	137	Normal	0.1	0.5–100	0.027
Beryllium (Be)	9	Normal	0.1	0.5–100	0.028
Boron (B)	10	Normal	0.1	0.5–100	
Cadmium (Cd)	111	Normal	0.1	0.5–100	0.025
Calcium (Ca)	40	Hydrogen	0.1	50–200,000	2.02
Chromium (Cr)	52	Helium	0.5	0.5–100	0.019
Copper (Cu)	63	Helium	0.5	0.5–100	0.023
Iron (Fe)	56	Hydrogen	0.1	50–200,000	1.25
Lead (Pb)	Sum of isotopes 206, 207, 208	Normal	0.1	0.5–100	0.017
Manganese (Mn)	55	Normal	0.1	0.5–100	0.020
Mercury (Hg)	202	Normal	1.0	0.05–1.0	0.005
Molybdenum (Mo)	95	Normal	0.1	0.5–100	0.030
Nickel (Ni)	60	Helium	0.5	0.5–100	0.024
Potassium (K)	39	Helium	0.5	50–200,000	3.02
Selenium (Se)	78	Hydrogen	0.5	0.5–100	0.047
Silver (Ag)	107	Normal	0.1	0.5–100	0.027
Sodium (Na)	23	Hydrogen	0.1	50–200,000	27.6
Thallium (Tl)	205	Normal	0.1	0.5–100	0.021
Uranium (U)	238	Normal	0.1	0.5–100	0.015
Vanadium (V)	51	Helium	0.5	0.5–100	0.034
Zinc (Zn)	66	Normal	0.1	0.5–100	0.101
Useful Internal Standards					
6Li	6	Normal	0.1	50	
Sc	45	All	0.1	50	
Ge	70,72,74	All	0.1	50	
Y	89	Normal	0.1	50	
In	115	Normal	0.1	50	
Tb	159	Normal	0.1	50	
Pt	195	Normal	0.1	50	
Bi	209	Normal	0.1	50	

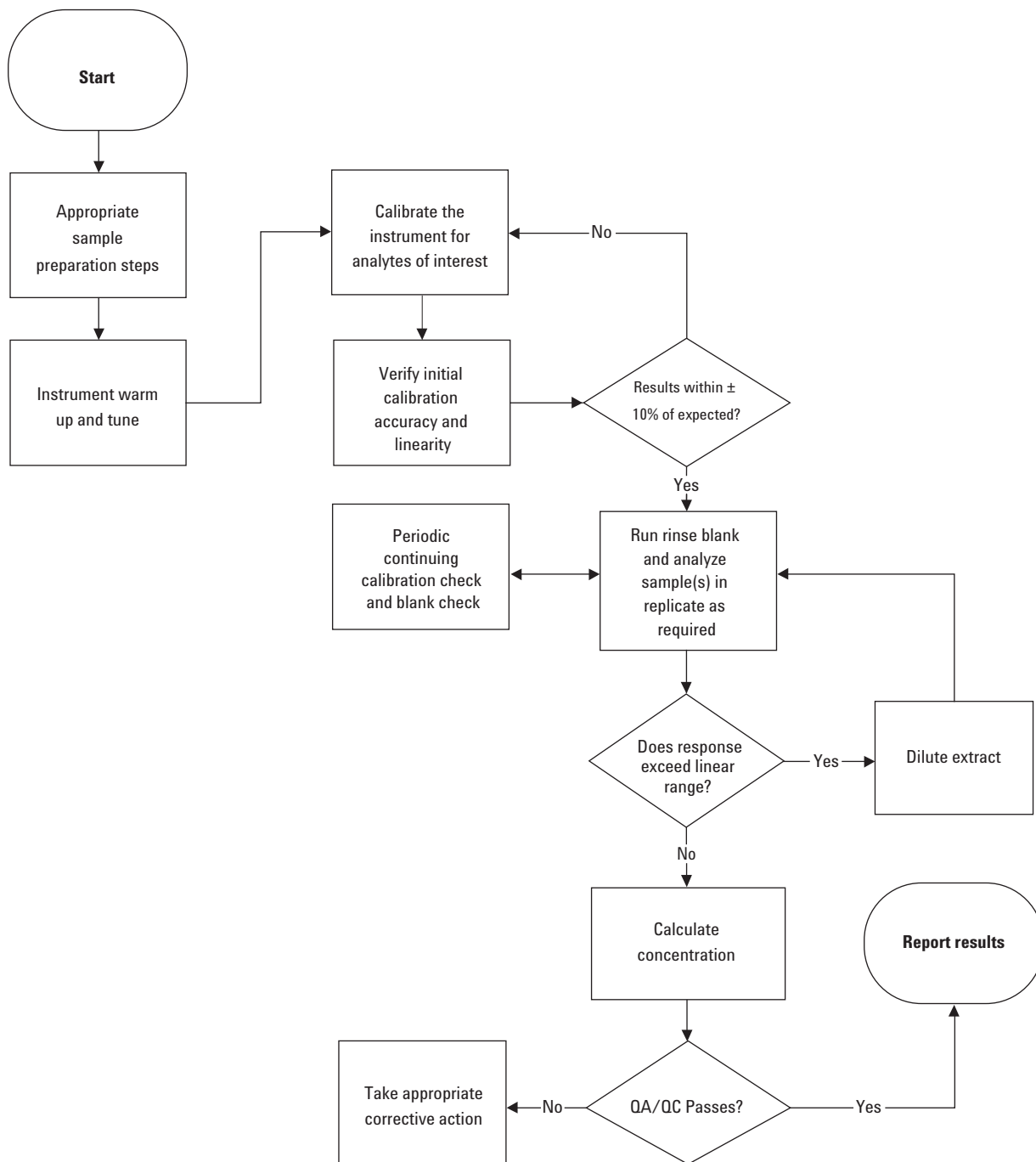


Figure 1. Summary of general water analysis protocol.

Figure 1 depicts the general flow of sample analysis and QA/QC that would be performed to meet the daily requirements of most drinking water regulations. Specific QA/QC details vary from jurisdiction to jurisdiction and are not outlined here. In addition to the daily requirements, less frequent, periodic QA/QC documentation must be performed to ensure ongoing accuracy and precision. Such periodic requirements include: verification of method detection limits, dynamic range,

management of interferences (both isobaric and memory effects), as well as general instrument condition and performance. Specific examples of these requirements are found in USEPA Method 200.8 and the UK Drinking Water Inspectorate publication, “NS-30.”

Interference Correction

Because the ORS is capable of efficiently removing polyatomic interferences and most isobaric

elemental interferences in unknown, complex matrices, the use of mathematical interference correction is all but eliminated. The elements which typically require interference correction in water, Ca, V, Fe, As, Se, Mo, and Cd can all be analyzed without the need for mathematical correction. This simplifies the analysis and improves confidence in the results. In this work, only Li-6, In-115, and Pb are corrected (see Table 3). The Li-6 correction is used to correct the abundance of the Li-6 internal standard in the presence of high concentrations of Li-7 in some samples. The In-115 correction is used to correct an internal standard, In, in the presence of high concentrations of tin. Neither of these cases is common and normally these can be ignored. The Pb correction is used to normalize the lead response in the case of varying lead isotope ratios and is not an interference correction.

Table 3. Typical Mathematical Corrections Used for Water Matrices with the Agilent 7500c ORS System

Mass	Equation
6	$(6)^*1 - (7)^*0.082$
115	$(115)^*1 - (118)^*0.014$
208	$(208)^*1 + (206)^*1 + (207)^*1$

Experiment

The following data and results were all obtained from a single sequence of 44 analyses of standards, blanks, QC samples, unknown groundwater samples, and seawater samples. All calibrations are based on a single set of standards prepared in 1% nitric acid/0.5% hydrochloric acid. No attempt at matrix matching beyond simple acidification was made. The instrument and conditions were like those of a typical commercial environmental laboratory. “Clean room” conditions or ultra-high purity reagents were not employed. The Agilent 7500c ICP-MS with ORS and Integrated Sample Introduction System (ISIS), configured for autodilution, was used.

Quality Control

Quality control in this experiment consisted of four components:

- Verification of tune performance for each ORS mode
- Initial Calibration linearity check
- Verification of accuracy of initial calibration using NIST 1640 standard reference water
- Periodic verification of calibration accuracy through measurement of continuing calibration verification (CCV) samples

Autodilution

The Agilent 7500c was configured with an ISIS for rapid sample uptake and autodilution. ISIS uses flowing stream autodilution rather than discrete sample dilution. This greatly enhances the throughput and minimizes the possibility of contamination compared with other types of autodiluters. In the ISIS autodiluter, the sample stream is mixed with a flowing stream of diluent in an entirely closed system. Dilution factor is controlled by high precision peristaltic pumps that are automatically and periodically monitored for accuracy throughout the run. Autodilution is invoked automatically by the intelligent sequencing software whenever the system encounters a user-definable out-of-range condition, such as an analyte outside the calibration range or an internal standard outside predefined bounds. Autodilution was invoked in a number of the samples in this work. An excellent check on both the linearity of the instrument and the accuracy of the autodilution can be obtained by comparing the results for diluted and undiluted samples. If the results match well, both the instrument linearity and autodilution accuracy are in control. Tables 5 and 7 show excellent examples of this.

Results

QC results are depicted in Tables 4 (CCV results) and 5 (NIST 1640 results). Examples of calibration linearity are depicted in Figures 2, 3, and 4, which are representative. Calibration “R” values of .9998 or greater are considered linear.

Table 4. Recovery of Periodic Calibration Check Standard in a Sequence of Water Samples Including Drinking Waters, Ground Waters, and Seawaters. Calibration Checks were Run After 30 and 43 Real Samples in this Experiment

	CCV		%		
	Actual value	CCV 50/5000/0.5	Recovery	CCV 50/5000/0.5	Recovery
Total DF:		1		1	
File:		031_CCV.D#		044_CCV.D#	
Be/9 [#1]	50	50.62	101.2	50.01	100.0
Na/23 [#2]	5000	4933.00	98.7	4838.00	96.8
Mg/24 [#1]	5000	4700.00	94.0	4802.00	96.0
Al/27 [#1]	50	47.09	94.2	46.84	93.7
K/39 [#3]	5000	5260.00	105.2	5076.00	101.5
Ca/40 [#2]	5000	5053.00	101.1	5063.00	101.3
V/51 [#3]	50	51.52	103.0	50.84	101.7
Cr/52 [#3]	50	51.43	102.9	50.78	101.6
Mn/55 [#1]	50	49.92	99.8	50.89	101.8
Fe/56 [#2]	5000	5067.00	101.3	5068.00	101.4
Co/59 [#1]	50	49.88	99.8	50.16	100.3
Ni/60 [#3]	50	51.99	104.0	51.36	102.7
Cu/63 [#3]	50	52.64	105.3	51.74	103.5
Zn/66 [#1]	50	49.27	98.5	49.44	98.9
As/75 [#3]	50	51.63	103.3	51.58	103.2
Se/78 [#2]	50	50.90	101.8	50.61	101.2
Se/80 [#2]	50	51.45	102.9	51.10	102.2
Mo/95 [#1]	50	49.44	98.9	48.11	96.2
Ag/107 [#1]	50	48.73	97.5	47.02	94.0
Cd/111 [#1]	50	49.34	98.7	48.40	96.8
Sb/121 [#1]	50	47.71	95.4	47.03	94.1
Ba/137 [#1]	50	50.35	100.7	49.19	98.4
Hg/202 [#1]	0.5	0.49	98.3	0.47	94.8
Tl/205 [#1]	50	49.68	99.4	50.46	100.9
Pb/208 [#1]	50	49.41	98.8	49.25	98.5
Th/232 [#1]	50	48.54	97.1	49.09	98.2
U/238 [#1]	50	49.46	98.9	49.84	99.7

Values in brackets after element mass are tune mode, 1= normal, 2 = hydrogen, 3 = helium.

Table 5. Analysis of Certified Reference Water NIST 1640 as a Calibration Check. Sample was Measured Neat and Autodiluted 1/20 (actual measured DF = 21.72), since Na Value Exceeded Upper Calibration Limit. Note that Even in the Undiluted Sample, the Recovery for Na is 101.2%

	Certified value	NIST 1640	% Recovery	NIST 1640	% Recovery
	(ppb)	1	undiluted	21.72	diluted
Total DF:					
Be/9 [#1]	34.94	35.750	102.3	34.860	99.77
Na/23 [#2]	29350	29690.000	101.2	29140.000	99.28
Mg/24 [#1]	5819	5893.000	101.3	6154.000	105.76
Al/27 [#1]	52	49.180	94.6	69.290	133.25
K/39 [#3]	994	947.900	95.4	858.800	86.40
Ca/40 [#2]	7045	7328.000	104.0	7488.000	106.29
V/51 [#3]	12.99	13.030	100.3	12.930	99.54
Cr/52 [#3]	38.6	37.470	97.1	38.540	99.84
Mn/55 [#1]	121.5	119.500	98.4	120.100	98.85
Fe/56 [#2]	34.3	35.840	104.5	31.820	92.77
Co/59 [#1]	20.28	19.400	95.7	20.010	98.67
Ni/60 [#3]	27.4	26.920	98.2	28.000	102.19
Cu/63 [#3]	85.2	86.450	101.5	92.350	108.39
Cu/65 [#3]	85.2	86.350	101.3	91.340	107.21
Zn/66 [#1]	53.2	55.380	104.1	55.560	104.44
As/75 [#3]	26.67	26.910	100.9	28.080	105.29
Se/78 [#2]	21.96	21.990	100.1	20.930	95.31
Mo/95 [#1]	46.75	45.310	96.9	43.280	92.58
Ag/107 [#1]	7.62	7.210	94.6	7.497	98.39
Cd/111 [#1]	22.79	22.560	99.0	22.420	98.38
Sb/121 [#1]	13.79	13.090	94.9	12.590	91.30
Ba/137 [#1]	148	143.900	97.2	142.100	96.01
Hg/202 [#1]		0.017		0.019	
Tl/205 [#1]		0.009		-0.042	
Pb/208 [#1]	27.89	26.690	95.7	26.370	94.55
Th/232 [#1]		0.011		-0.429	
U/238 [#1]		0.725		0.698	

Values in brackets after element mass are tune mode, 1= normal, 2 = hydrogen, 3 = helium.

Table 6. Replicate Analyses of Low Standard After Sequence of 33 High Level Samples, Standards, and Blanks for MDL Calculations. Three Sigma MDL are Calculated in ppb

	MDL rep 01	MDL rep 02	MDL rep 03	MDL rep 04	MDL rep 05	MDL rep 06	MDL rep 07	MDL rep 08	MDL rep 09	MDL rep 10	3 Σ MDL
Be/9 [#1]	0.50	0.50	0.49	0.49	0.50	0.47	0.49	0.49	0.50	0.49	0.028
Na/23 [#2]	53.45	47.78	43.96	39.85	40.52	36.48	34.69	30.58	30.17	22.08	27.617
Mg/24 [#1]	49.82	49.13	49.75	48.94	48.83	48.92	49.32	48.84	48.24	48.41	1.530
Al/27 [#1]	0.30	0.26	0.25	0.25	0.25	0.23	0.24	0.24	0.25	0.26	0.054
K/39 [#3]	56.28	55.34	55.09	53.35	55.02	55.15	53.73	53.25	54.17	53.70	3.023
Ca/40 [#2]	52.33	51.76	51.55	51.81	52.32	51.86	51.28	51.33	53.42	51.15	2.023
V/51 [#3]	0.51	0.53	0.53	0.53	0.54	0.51	0.53	0.50	0.52	0.52	0.034
Cr/52 [#3]	0.52	0.52	0.51	0.51	0.50	0.51	0.52	0.51	0.51	0.51	0.019
Mn/55 [#1]	0.49	0.49	0.49	0.47	0.48	0.48	0.49	0.48	0.48	0.47	0.020
Fe/56 [#2]	53.84	53.69	53.43	53.46	53.97	53.18	53.10	52.91	53.17	52.65	1.251
Co/59 [#1]	0.48	0.48	0.49	0.48	0.48	0.48	0.49	0.49	0.48	0.47	0.016
Ni/60 [#3]	0.50	0.49	0.49	0.48	0.50	0.48	0.48	0.49	0.48	0.49	0.024
Cu/63 [#3]	0.48	0.48	0.46	0.47	0.46	0.48	0.48	0.47	0.46	0.47	0.023
Zn/66 [#1]	0.50	0.45	0.43	0.43	0.43	0.42	0.42	0.46	0.44	0.42	0.074
As/75 [#3]	0.50	0.53	0.53	0.49	0.54	0.54	0.54	0.53	0.52	0.52	0.052
Se/78 [#2]	0.52	0.51	0.53	0.52	0.49	0.52	0.52	0.51	0.48	0.51	0.047
Se/80 [#2]	0.58	0.62	0.56	0.56	0.55	0.57	0.58	0.55	0.54	0.57	0.066
Mo /95 [#1]	0.47	0.46	0.46	0.46	0.45	0.46	0.48	0.44	0.47	0.45	0.030
Ag/107 [#1]	0.45	0.47	0.46	0.44	0.46	0.46	0.46	0.45	0.44	0.45	0.027
Cd/111 [#1]	0.45	0.43	0.44	0.44	0.44	0.44	0.44	0.44	0.45	0.43	0.025
Sb/121 [#1]	0.46	0.45	0.44	0.45	0.43	0.44	0.46	0.45	0.43	0.45	0.035
Ba/137 [#1]	0.49	0.47	0.47	0.49	0.48	0.47	0.47	0.47	0.46	0.48	0.027
Hg/202 [#1]	0.04	0.04	0.04	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.005
Tl/205 [#1]	0.40	0.42	0.42	0.43	0.42	0.42	0.42	0.42	0.41	0.41	0.021
Pb/208 [#1]	0.46	0.46	0.46	0.45	0.46	0.45	0.45	0.45	0.45	0.45	0.017
Th/232 [#1]	0.29	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.050
U/238 [#1]	0.43	0.44	0.44	0.43	0.43	0.43	0.44	0.44	0.43	0.43	0.015

Values in brackets after element mass are tune mode, 1= normal, 2 = hydrogen, 3 = helium.

Detection Limits

The method detection limits reported in Table 6 were generated at the end of a sequence of 33 real world samples, standards, and blanks. Column one lists the isotope and ORS acquisition mode, #1 = Normal Mode, #2 = Hydrogen Mode, #3 = Helium Mode. Actual method detection limits will vary depending on instrument and laboratory conditions. These detection limits should be achievable with normal levels of laboratory cleanliness, using trace metal grade acids and ASTM type 1 water. The instrument used for this work was equipped with the ISIS, which typically improves DLs somewhat by increasing sample introduction precision and minimizing carryover.

Dynamic Range

One of the advantages of using the ORS is its ability to reduce interferences on certain trace level analytes and simultaneously attenuate the signal on high concentration or matrix elements. In this work, calibrations were generated from a low of 50 ppt for Hg to a high of 200 ppm for the mineral elements, Na, K, Ca, Mg, and Fe. Sample calibration curves follow. Additionally, while Na was calibrated only as high as 200 ppm, which is the highest regulated concentration in any of the elements in the worldwide drinking water regulations (see Table 1), it yields linear response at much higher concentrations.

Table 7. A Series on Analyses on Three High Dissolved Solids Ground Water Samples. Each Sample was Analyzed Undiluted and Automatically Autodiluted. Elements which were Undetected were Removed for Simplicity.

	Water 1	Water 1	Water 2	Water 2	Water 3	Water 3
Total DF:	1	21.72	1	21.72	1	21.72
File:	014SMPL.D	015SMPL.D	016SMPL.D	017SMPL.D	018SMPL.D	019SMPL.D
Na/23 [#2]	489100.000	492500.000	330500.000	324100.000	563700.000	554000.000
Na/23 [#3]	480300.000	505800.000	337200.000	342800.000	563000.000	571800.000
Mg 24 [#1]	559.000	599.900	511.700	534.800	3099.000	3407.000
K/39 [#3]	1564.000	1365.000	794.000	721.400	2513.000	2333.000
Ca/40 [#2]	8708.000	8760.000	2337.000	2255.000	13350.000	13400.000
Mo/95 [#1]	0.776	0.773	1.482	1.535	49.070	49.180
Ba/137 [#1]	17.070	16.990	29.250	28.800	5.263	5.154
U/238 [#1]	0.043	0.037	0.036	0.034	0.115	0.103

Values in brackets after element mass are tune mode, 1= normal, 2 = hydrogen, 3 = helium.

Table 7 shows the results of the analysis of three brackish ground water samples. Each sample was analyzed directly and then autodiluted. Both sets of results show both the dynamic range of the Agilent 7500c and the accuracy of the autodilution. The autodilution factor of 21.72 is the result of the system automatically calibrating the dilution

factor at the beginning of the sequence and periodically, as needed. Note that for the uranium result, where the undiluted concentration is only 30–40 ppt, the autodiluted result agrees very well. This translates to accurate measurement of uranium in the diluted samples of $\sim 35/21.7 = 1.6$ ppt.

Table 8. Results of Analysis of a 1/10 "Synthetic Seawater" Blank (High Purity 0.3% NaCl) Plus a Spike at 5 ppb for Trace Elements and 500 ppb for Matrix Elements.

File:	1/10 Synth Sea H₂O 020SMPL.D#	Spike 1/10 Synth Sea H₂O + 5 ppb 021SMPL.D#	% Recovery 5/500 ppb spike
Be/9 [#1]	0.000	4.591	91.8
Na/23 [#1]	over range	over range	N/A
Na/23 [#2]	1233000.000	1215000.000	N/A
Na/23 [#3]	1193000.000	1193000.000	N/A
Mg/24 [#1]	2.382	477.000	94.9
I/27 [#1]	-0.409	4.250	93.2
K/39 [#1]	13.730	491.500	95.6
K/39 [#2]	8.195	548.600	108.1
K/39 [#3]	16.510	597.400	116.2
Ca/40 [#2]	6.740	532.600	105.2
V/51 [#3]	0.031	5.426	107.9
Cr/52 [#3]	0.045	5.287	104.8
Mn/55 [#1]	-0.003	4.497	90.0
Fe/56 [#2]	-0.258	508.600	101.8
Co/59 [#1]	0.122	4.569	89.0
Ni/60 [#1]	0.024	4.318	85.9
Ni/60 [#3]	-0.040	4.801	96.8
Cu/63 [#3]	-0.117	4.691	96.2
Cu/65 [#3]	-0.117	4.564	93.6
Zn/66 [#1]	0.025	4.520	89.9
Zn/67 [#1]	0.007	4.714	94.1
As/75 [#3]	0.011	5.027	100.3
Se/78 [#2]	0.006	4.366	87.2
Se/80 [#2]	0.143	4.620	89.5
Mo/95 [#1]	0.043	5.040	99.9
Ag/107 [#1]	-0.010	4.254	85.3
Cd/111 [#1]	0.033	4.545	90.2
Sb/121 [#1]	0.034	4.598	91.3
Ba/137 [#1]	0.010	4.789	95.6
Hg/202 [#1]	0.017	0.020	N/A
Tl/205 [#1]	-0.003	4.883	97.7
Pb/208 [#1]	0.175	5.066	97.8
U/238 [#1]	0.000	4.968	99.4

Values in brackets after element mass are tune mode, 1 = normal, 2 = hydrogen, 3 = helium.

Table 8 shows the results of the analysis of a 0.3% 3000 ppm NaCl or 1180.5 ppm Na, both unspiked and spiked with trace elements and other matrix elements. Recoveries are reported in column 4. Note that in this case, for demonstration purposes, Na was acquired in all three ORS modes (normal, hydrogen, and helium). As expected, in the normal mode, the sodium signal was over range and the detector was protected from excessive signal. However, sodium was measurable in both hydrogen

and helium modes at 1233 and 1193 ppm respectively, yielding recoveries of 104% and 101% respectively without further dilution or any other manipulation of instrument conditions. Under identical conditions, in the same run at the same time, Arsenic in the spike was also measured using He collision mode at 5.03 ppb to give 100.3% recovery.

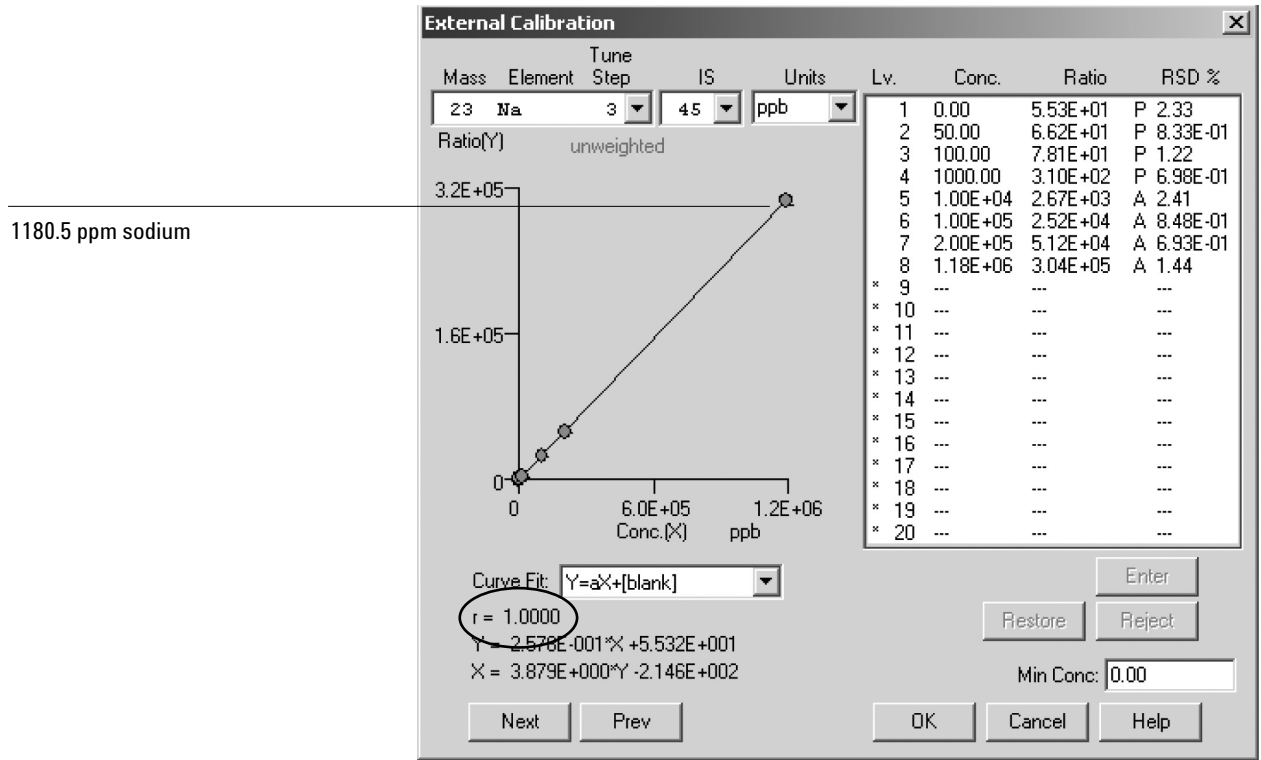


Figure 2. Calibration curve for Na in Helium collision mode showing linearity from 50 ppb to 1180 ppm (0.3% NaCl).

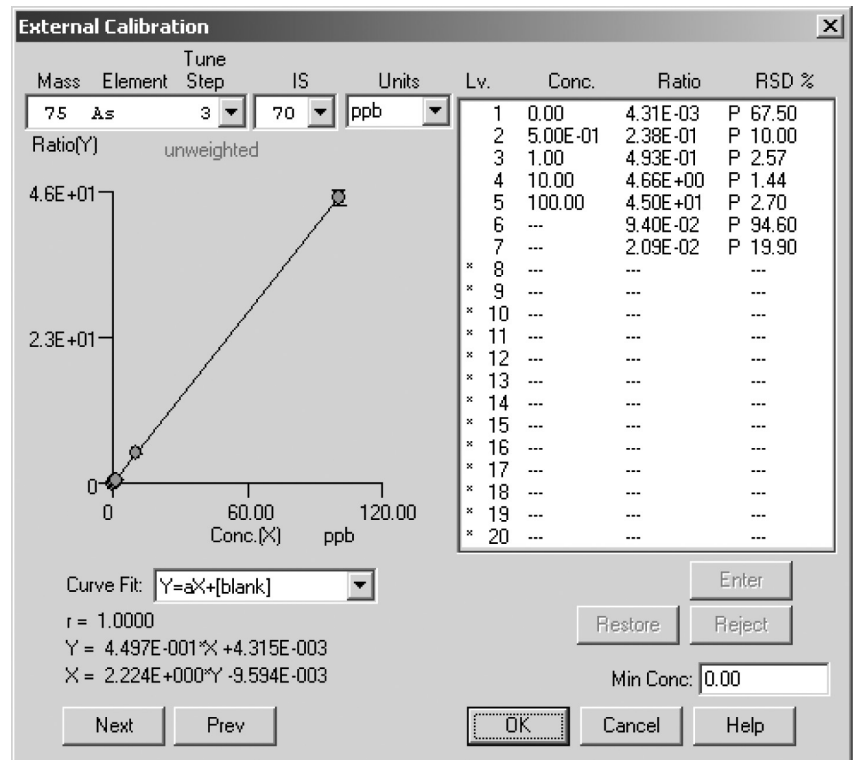


Figure 3. Arsenic calibration acquired in helium collision mode (same as Na in Figure 2) from 0.5 to 100 ppb.

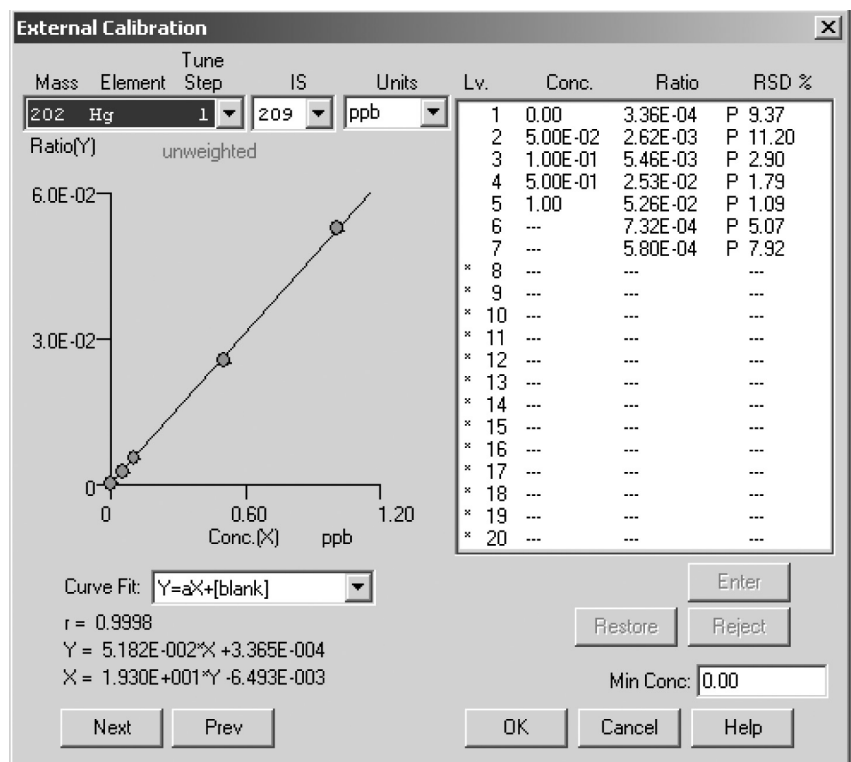


Figure 4. Mercury calibration acquired in normal (no gas) mode from 0.05–1 ppb.

The calibration curves in Figures 2–4 were all acquired from the same mixes of standard elements in dilute nitric/hydrochloric acid. That means that the low standard contained 50 ppt of mercury, 500 ppt of the other trace elements and 50 ppb of the mineral elements (Na, K, Ca, Mg, and Fe), and so on through the levels. In the sodium curve, the actual calibration was performed up to 200 ppm (level 7 in Figure 2); the 1180.5 ppm level was the 1/10 “synthetic seawater” NaCl solution.

Conclusions

While the specific details for drinking water monitoring vary from country to country around the world, the overall requirements, both from a reporting limit and quality control standpoint, are

very similar. Currently, of the many available techniques for monitoring trace metals in water, only ICP-MS has the sensitivity and elemental coverage to meet all worldwide requirements. In addition, the use of collision/reaction cell technology in the form of the Agilent 7500c ORS allows the user both to easily meet the strictest ultra-trace reporting limits and to measure mineral or matrix elements at 1000s of ppm simultaneously, without fear of false positives from polyatomic interferences or out-of-range elements.

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