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Trace Metals in Waters by GFAAS, in Accordance with U.S. EPA and Health Canada Requirements

Introduction

Several trace elements are recognized as toxic or carcinogenic and are regulated in drinking water by various environmental agencies worldwide. The U.S. Environmental Protection Agency's (EPA) Safe Drinking Water Act includes maximum levels permitted in drinking water for the elements arsenic (As), cadmium (Cd), lead (Pb), selenium (Se) and thallium (Tl). The World Health Organization (WHO) and Health Canada also have limits on these elements in drinking water (Table 1). Water contamination sources can range from naturally occurring deposits exposed from erosion, to agriculture and industrial discharges. There can also be direct contamination from: Pb used in plumbing fixtures, Cd found in galvanized pipes, and electronics manufacturing discharges for Tl.

Precise and accurate measurements at the regulated levels are an important factor for assuring safe drinking water. U.S. EPA Method 200.9[1] is the method cited by EPA, Health Canada, and the WHO for the use of graphite furnace atomic absorption spectroscopy (GFAAS). In evaluating a GFAAS system for determination of these elements, it must provide good sensitivity, low noise, limited drift, and accuracy in matrices with high salt content (hard water) that might be found in drinking waters. In this work, the PinAAcle™ 900T, with a unique optical system, is evaluated for the use of EPA Method 200.9 for As, Cd, Pb, Se, and Tl in drinking waters.

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Table 1. Drinking water limits for regulatory agencies (μg/L).

Organization	As	Cd	Pb	Se	Tl
U.S. EPA	10	5	15	50	2
Health Canada	10	5	10	10	–
WHO	10	3	10	10	–

Experimental

Instrumentation

A PerkinElmer® PinAAcle 900T flame and longitudinal Zeeman atomic absorption spectrometer was used for all measurements. Samples were automatically pipetted into standard transversely heated graphite atomizer (THGA) tubes (Part No. B0504033) using an AS 900 autosampler. PerkinElmer Lumina™ single-element hollow cathode lamps (HCLs) were used as the light source for lead (Part No. N3050157), cadmium (Part No. N3050115), and thallium (Part No. N3050183); while single-element electrodeless discharge lamps (EDLs) were used for arsenic (Part No. N3050605) and selenium (Part No. N3050672).

Figure 1. PinAAcle 900T atomic absorption spectrometer with AS 900 furnace autosampler.

The PinAAcle 900T instrument settings are listed in Table 2 and the furnace program is listed in Table 3. The pyrolysis and atomization temperatures were optimized using a spiked drinking water sample. The Method Development feature of the software (WinLab32™ for AA) automated these experiments. The TubeView™ furnace camera (Figure 2) on the PinAAcle 900T was used to adjust the pipette tip to the most appropriate depth and to watch for potential matrix buildup in the tube. The camera was also used during method development to verify the drying steps, ensuring that no sample boiling or spattering occurred.
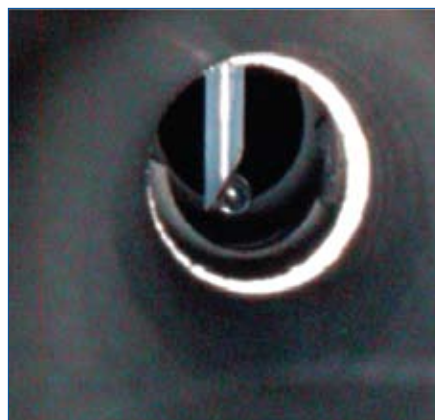

Figure 2. AS 900 autosampler depositing a droplet of water in the THGA tube as seen using the TubeView furnace camera.

Table 2. Instrument settings used for U.S. EPA method 200.9 on the PinAAcle 900T.

Element	Wave-length (nm)	Slit (nm)	Lamp Type	Lamp Current (mA)	Read Delay (s)	Read Time (s)
As	193.7	0.7	EDL	380	1.0	2.5
Cd	228.8	0.7	HCL	4	0.5	2.5
Pb	283.3	0.7	HCL	10	0.5	3.5
Se	196.0	2.0	EDL	280	1.0	3.0
Tl	276.8	0.7	HCL	6	0.5	3.0

Baseline Offset Correction (BOC) was 5 seconds for all analytes.

The furnace programs for individual elements are listed in Tables 3-7. Argon was the normal gas type. The special gas type was 95% Ar / 5% H_2 and was used in steps 1-3. Step 4 removed the H_2 gas from the tube before atomization and the read step was Step 5 for all elements. All elements used 0.005 mg Pd (Part No. B0190635) + 0.003 mg $Mg(NO_3)_2$ (Part No. B0190634) as a matrix modifier. All samples and standards used an injection volume of 20 μL sample plus 5 μL of matrix modifier. Each analyte was run in duplicate (2 replicates).

Table 3. Furnace parameters for arsenic (As).

Step	Temp (˚C)	Ramp Time	Hold Time	Internal Flow	Gas Type
1	110	1	30	250	Special
2	130	15	30	250	Special
3	900	10	20	250	Special
4	900	1	15	250	Normal
5*	2300	0	5	0	Normal
6	2450	1	3	250	Normal

*Read step

Table 4. Furnace parameters for cadmium (Cd).

Step	Temp (°C)	Ramp Time	Hold Time	Internal Flow	Gas Type
1	110	1	30	250	Special
2	130	15	30	250	Special
3	700	10	20	250	Special
4	700	1	15	250	Normal
5*	1700	0	5	0	Normal
6	2450	1	3	250	Normal

*Read step

Table 5. Furnace parameters for lead (Pb).

Step	Temp (°C)	Ramp Time	Hold Time	Internal Flow	Gas Type
1	110	1	30	250	Special
2	130	15	30	250	Special
3	850	10	20	250	Special
4	850	1	15	0	Normal
5*	2000	0	5	0	Normal
6	2450	1	3	250	Normal

*Read step

Table 6. Furnace parameters for selenium (Se).

Step	Temp (°C)	Ramp Time	Hold Time	Internal Flow	Gas Type
1	110	1	30	250	Special
2	130	15	30	250	Special
3	800	10	30	250	Special
4	800	1	15	250	Normal
5*	2150	0	4	0	Normal
6	2450	1	3	250	Normal

*Read step

Table 7. Furnace parameters for thallium (Tl).

Step	Temp (°C)	Ramp Time	Hold Time	Internal Flow	Gas Type
1	110	1	30	250	Special
2	130	15	30	250	Special
3	500	10	20	250	Special
4	500	1	15	250	Normal
5*	1600	0	5	0	Normal
6	2450	1	3	250	Normal

*Read step

Results

Calibration Statistics

All elements showed calibration correlation coefficients better than or equal to an r^2 value of 0.999. The method detection limit (MDL) was determined by running seven separate samples of a 0.5 µg/L standard for As, Pb, Se and Tl and a 0.17 µg/L standard for Cd (Table 8). The resulting standard deviation was then multiplied by the Student's t-value ($\rho = 0.01$). The instrument detection limit (IDL) was calculated by analyzing 10 replicates of a blank and multiplying the standard deviation by 3. Linear ranges are the highest standard that was within 5% of its true value.

Table 8. Linear ranges, MDL and IDLs using the PinAAcle 900T and U.S. EPA Method 200.9.

Element	IDL (µg/L)	IDL (pg)	MDL (µg/L)	Linear Range (µg/L)
As	0.30	6.0	0.17	100
Cd	0.056	1.1	0.027	2.50
Pb	0.33	6.6	0.16	100
Se	0.28	5.6	0.30	200
Tl	0.37	7.4	0.18	100

The sensitivity, as indicated by the characteristic mass, was better than the expected value for As, Pb and Tl, while the Se and Cd values were slightly elevated. This could be due to the difference in modifier and lamp type from those detailed in the Atomic Absorption Spectroscopy Analytical Methods "cookbook" guide.

Practical Quantification Limits

In the Arsenic Rule,[2] a standard of 3 µg/L must be recovered within ±30%. This is performed at the practical quantification limit (PQL) for As. Other elements have similar limits[3] and these are listed in Table 9, along with the values determined in this study. A lower standard was used here to demonstrate the ease of this test using the PinAAcle 900T. The low standard was read as five separate samples and the average value with percent relative deviation is given.

Table 9. Results of the PQL study in accordance with U.S. EPA standards.

Element	PQL Level (µg/L)	Acceptance Limit (± in %)	Standard Concentration Used (µg/L)	Average Found (µg/L)	%RSD	%Recovery
As	3	30	1	0.876	4.45	88.0
Cd	2	20	1	1.03	1.33	103
Pb	5	*	5	4.99	3.30	99.8
Se	10	20	1	1.06	13.5	106
Tl	2	30	1	0.810	14.3	81.0

No PQL acceptance limit was found.

Preparing for Proposed Revision 3.3

In the proposed U.S. EPA Method 200.9 Revision 3.3, there is a requirement to run an Initial Precision and Recovery (IPR) standard. The proposed IPR currently consists of four aliquots of reagent water spiked at 1 to 5 times the lowest standard and run as samples. The percent recovery and standard deviation are calculated for those four samples (Table 10). There are currently no criteria for this test.

Table 10. Data for the proposed initial precision and recovery standard.

	Average Found (µg/L)	Std. Concentration Used (µg/L)	Standard Deviation	%Recovery
As	4.83	5.0	0.15	96.6
Cd	0.293	0.25	0.0096	117
Pb	5.04	5.0	0.10	101
Se	4.94	5.0	0.13	98.7
Tl	5.00	5.0	0.18	99.9

Quality Control

Two quality control (QC) checks were analyzed to determine the accuracy of the method. NIST® 1643e Trace Elements in Water is a fresh water reference material. Data and recoveries are listed in Table 11. The ERA PotableWatR™ Inorganic Metals material was used as the independent QC check during the analytical runs. This ERA reference material is also used in round robin U.S. EPA performance testing. The recoveries and data for this experiment and the U.S. EPA round robin experiment are listed in Table 12. The recovered concentrations are within the proficiency testing (PT) performance acceptance limits (PALs) which closely approximate a 95% confidence interval based on historical data.

Table 11. Recoveries for NIST® 1643e natural waters reference material using PinAAcle 900T.

Element	NIST® 1643e (µg/L)	Limits (±, µg/L)	NIST® Found (µg/L)	Std. Dev. (n=2)	%Recovery
As	60.45	0.70	58.2	0.20	96.2
Cd	6.568	0.073	6.58	0.00080	100
Pb	19.63	0.21	19.5	0.15	99.1
Se	11.97	0.14	10.8	0.12	90.1
Tl	7.445	0.096	6.48	0.010	87.0

Table 12. Recoveries for the determination of metals in ERA PotableWatR™ Inorganic Metals.

	Certified Value (µg/L)	Uncertainty (%)	Round Robin Mean (µg/L)	%Recovery Round Robin	ERA Found (µg/L)	%Recovery Found
As	25.7	2.5	25.2	98.1	26.8	104
Cd	40.5	0.20	40.1	99.0	37.3	92.0
Pb	24.4	1.2	24.6	101	25.5	105
Se	22.6	1.2	22.5	99.6	22.1	97.6
Tl	7.84	1.4	7.75	98.8	7.35	93.8

Matrix Effects

A laboratory fortified blank (LFB) showed good recoveries. One drinking water sample was analyzed with a spike and spike duplicate to check for matrix interferences. The spike recoveries and sample/blank data are shown in Table 13.

Table 13. Sample and LFB recoveries and percent difference of duplicate spikes.

	Spike Level (µg/L)	Lab Blank (µg/L)	LFB (µg/L)	% Recovery LFB	Sample Result (µg/L)	Sample Spike (µg/L)	% Recovery	Sample Spike Dup (µg/L)	% Recovery
As	30	<MDL	29.3	97.5	0.26	32.3	108	31.5	105
Cd	1.5	<MDL	1.42	94.5	0.031	1.49	99.1	1.54	103
Pb	30	<MDL	31.1	104	0.35	28.7	95.8	29.7	98.8
Se	30	<MDL	29.3	97.6	1.5	28.2	89.0	28.2	89.1
Tl	30	0.20	30.5	102	<MDL	30.2	101	33.4	111

Conclusion

The PerkinElmer PinAAcle 900T atomic absorption spectrometer is capable of meeting the accuracy and precision requirements for the U.S. EPA and Health Canada regulations. The method detection limit (MDL) for all elements was determined to be well below the practical quantification limit (PQL) required by the method. This detection limit could be lowered even further by using a larger sample volume or through the use of end-capped THGA tubes (Part No. B3000655). Recoveries for two standard reference materials, spiked samples and lab fortified blanks were all within the method's acceptable limits.

References

1. U.S. EPA Method 200.9, Revision 2.2 and 3.0.

2. Environmental Protection Agency, "National Primary Drinking Water Regulations: Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring, Final Rule," *Federal Register,* vol. 66, no. 14 (January 22, 2001), p. 6981.

3. Environmental Protection Agency, "National Primary Drinking Water Regulations: Inorganic Chemical sampling and analytical requirements," 40 CFR 141.23.

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