

# Determination of Arsenic in Drinking Water by EPA Method 200.9 Using THGA Graphite Furnace Atomic Absorption

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## Introduction

The U.S. Environmental Protection Agency (EPA) has lowered the maximum contaminate level (MCL) for arsenic (As) in drinking water from the current level of 50 µg/L to 10 µg/L.<sup>1</sup> As of January 2006, water supply systems will be required to meet this level in accordance with 40 CFR Parts 9, 141 and 142. The analytical methodologies capable of meeting this new lower As level are limited to ICP-MS (200.8), graphite furnace atomic absorption (200.9) and two ASTM methods using either furnace or hydride generation. The procedure detailed in the CFR document sets a practical quantifiable level (PQL) of 3 µg/L for graphite-furnace determination with an acceptance limit of ±30%.

In the western and southwestern regions of the United States, As occurs naturally in soils and rock formations. The As in water levels in these areas can be quite high even by the current standard of 50 µg/L. The new lower levels for As will mean that some water-supply systems will need to make changes in how they treat their drinking water. For this study, nine water samples were analyzed using U.S. EPA Method 200.9 and the PerkinElmer® AAnalyst™ 800.

Both the PerkinElmer AAnalyst 800 and AAnalyst 600 are completely automated, multielement AA spectrometers. They each have an eight-lamp turret as well as identical optical systems and detectors. The difference between the two instruments is that the AAnalyst 800 has the ability to perform flame atomic absorption as well as

graphite furnace atomic absorption (GFAA) measurements. Although the data cited in this note were acquired using an AAnalyst 800, the same results would be expected on an AAnalyst 600 furnace-only instrument.

The AAnalyst 600 and 800 feature longitudinal Zeeman-effect background correction and a high-efficiency optical design with a unique, high-quantum efficiency optical system for outstanding signal-to-noise ratios. The patented transversely heated graphite atomizer (THGA) design in the AAnalyst 600 and 800 instruments features an integrated platform and a uniform temperature distribution along its entire length, which eliminates many common interferences found in GFAA.

## Experimental

The AAnalyst 800 furnace program is listed in Table 1. A 20 µL sample volume was used with a 5 µL volume of a Pd and Mg(NO<sub>3</sub>)<sub>2</sub> mixed matrix modifier.

Instrument parameters are listed in Table 2. The integration time and baseline offset correction (BOC) times were optimized for the As determination. The BOC is measured just before atomization to establish the baseline for peak-area measurement, which improves accuracy and precision. Research has shown that increasing the BOC time and minimizing the integration time for the atomized signal can improve detection limits.<sup>2</sup> Up to a factor of two improvement in the detection limit of As is possible by optimizing the BOC and read times.<sup>3</sup>

## Reagents

Mg(NO<sub>3</sub>)<sub>2</sub>: PE Pure part number B0190634

Pd: PE Pure part number B0190635

Calibration standard: GFAAS mixed standard PE Pure part number N9300244

QCS Standard: Quality control standard PE Pure part number N9300281

## Procedure

The EPA Method 200.9 Rev 2.2 was followed for this analysis. Prior to sample analysis, an initial demonstration of performance was done to establish the linear range, instrument detection limit (IDL), accuracy of the calibration with a quality control standard (QCS) and the method detection limit (MDL). The IDL was determined by running ten replicates of a blank solution and was found to be 0.3 µg/L.

Table 1. Graphite Furnace Program.

Step	Temp. (°C)	Ramp Time (s)	Hold Time (s)	Internal Gas Flow (mL/min)	Gas Type
1	110	1	20	250	Argon
2	130	20	30	250	Argon
3	1100	10	40	250	Argon
4	2100	0	5	0	Argon
5	2450	1	5	250	Argon

Table 2. Instrument Parameters.

Model	AAAnalyst 800
THGA	Standard tube
Element	As
Lamp	EDL
Current (mA)	380
Wavelength (nm)	193.7
Slit Width (nm)	0.7 L
Read Time (s)	2.0
Delay Time (s)	0.5
BOC Time (s)	5.0
Replicates	2
Sample volume (µL)	20
Matrix Modifier (in 5 µL)	5 µg Pd + 3 µg Mg(NO <sub>3</sub> ) <sub>2</sub>

In section 9.2.2 of the method, a procedure for determining the linear dynamic range (LDR) is described. Standards of 1, 5, 10, 50, 75, 100, 150 and 200 µg/L were analyzed to determine the linear range. Using the lower four standards, the 100 µg/L standard was within 0.5% of its true value. The 150 µg/L standard was at -4.7% and the 200 µg/L standard was 9% low. While the 200 µg/L standard was considered linear by the method (within ±10%), it was found that, if it or the 150 µg/L standard were included in the calibration, there would be a large bias effect on the intercept of the calibration curve. Thus, to maintain accuracy at low levels, the 100 µg/L standard should be considered the upper linear range. For this study, the sample concentrations were expected to be low and the calibration consisted of four standards at 1, 5, 10 and 50 µg/L.

The method QCS is a second-source standard used to check the accuracy of the calibration standards. This QCS was prepared at 40 µg/L and the resulting recovery was 99%. A laboratory fortified blank (LFB), also at 40 µg/L, resulted in a recovery of 103% and the instrument performance check (IPC) standard at 20 µg/L was recovered at 103%.

## Results

The MDL was determined by running seven separate solutions of a 0.6 µg/L standard as part of an analytical run with full quality control. The seven results are listed in Table 3. The MDL was calculated to be 0.2 µg/L. Figure 1 shows the calibration standards used to create the curve for the MDL determinations.

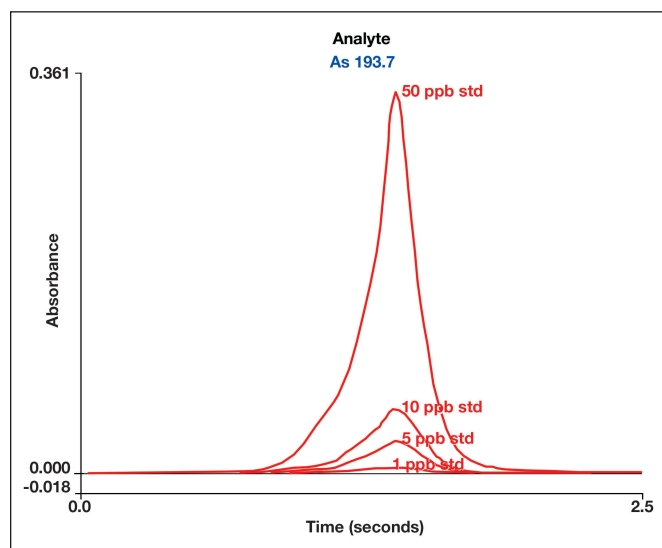


Figure 1. As calibration curve peak plots.

Nine drinking-water samples were acquired from eight cities across the western region of the United States and one from the mid-western region. A PerkinElmer Optima™ 4300 ICP optical emission spectrometer was used to characterize the mineral levels in the water samples. Table 4 lists the values for the major elements in the water samples.

The As analysis for these samples was performed using the AAnalyst 800 GFAA and the results are listed in Table 5. One sample was spiked at 40 µg/L as the laboratory fortified matrix (LFM), and a duplicate of the sample

was also included in the analytical run. All samples, except for one, were well below the new MCL of 10 µg/L. Samples from two cities were at or below the MDL and samples from two other cities were at two times the MDL. The sample chosen for the duplicate was at the MDL as was the duplicate and the 40 µg/L spike for that sample recovered at 110%. To determine accuracy and

precision at the practical quantifiable limit (PQL), a 1 µg/L standard was analyzed with five replicates. This sample read 1.06 µg/L, or within 6% of the true value, with 11% RSD. The U.S. EPA acceptance limit, given in 40 CFR Parts 9, 141 and 142, is 30% at the 3 µg/L PQL.

## Conclusion

The PerkinElmer AAnalyst 600 and 800 Zeeman-furnace atomic absorption spectrometers are capable of meeting the new MCL of 10 µg/L for As in drinking water. The MDL was determined to be 0.2 µg/L, which is more than an order of magnitude lower than the 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.

## References

- 66 FR Part 6976 – Appendix B, Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring; Final Rule, Environmental Protection Agency, August 2002.
- L'vov, BL et al., Spectrochim Acta, 49B, p 1609 (1994).
- Presentation at 37th Rocky Mountain Conference, Denver, CO, July 1995.

Table 3. MDL Results.

Sample	Result (µg/L)
MDL 1	0.69
MDL 2	0.57
MDL 3	0.53
MDL 4	0.61
MDL 5	0.50
MDL 6	0.62
MDL 7	0.53
Average	0.58
Standard Deviation	0.066
MDL 3.14 x SD	0.2

Table 4. ICP Results (mg/L).

Sample	Ca 315.887	K 766.490	Mg 279.079	Na 589.592	S 180.669	Si 251.611
Tap Water 1	0.962	5.05	1.09	60	8.9	0.651
Tap Water 2	2.33	0.564	1.16	73.1	12.75	5.25
Tap Water 3	58.8	5.04	24.8	124	73.09	4.66
Tap Water 4	28.7	0.56	5.01	4.95	3.249	5.52
Tap Water 5	12.7	3.12	3.64	73	14.56	25.9
Tap Water 6	73	4.3	26.4	85.7	81.01	4.05
Tap Water 7	21.1	1.35	3.47	10.4	12.09	1.78
Tap Water 8	43.8	1.99	2.68	50	22.19	15.9
Tap Water 9	19	2.4	4.71	18	21.43	2.88

Table 5. Water Results.

Sample ID	As results (µg/L)
Tap Water 1	1.2
Tap Water 2	0.4
Tap Water 3	1.5
Tap Water 4	0.4
Tap Water 5	23.4
Tap Water 6	1.8
Tap Water 7	0.2
Tap Water 8	1.2
Tap Water 9	0.2
Tap Water 9 Duplicate	< 0.2

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