

# Lead in Natural Waters by Graphite Furnace Atomic Absorption using EPA Method 200.9

## Key Words

- Atomic Absorption
- EPA 200.9
- Environment
- Lead
- Omega cuvette
- Water
- Zeeman GFAAS



## Key Benefits

- Advanced spectrometer hardware and automated software wizards ensure the Thermo Scientific iCE 3000 Series Atomic Absorption Spectrometers meet the requirements of EPA Method 200.9 with ease.
- Graphite furnace television allows real-time visualization of the inside of the cuvette, ensuring repeatable sample deposition time after time.
- Software wizards enable controlled and automated optimization of the ash and atomize temperatures.
- In-built QC test functionality allows Method stipulated assessment of laboratory performance to be easily included in the analysis sequence.

## Summary

The Thermo Scientific iCE 3000 Series Atomic Absorption Spectrometers offer the ideal solution of the analysis of natural waters by graphite furnace atomic absorption using EPA Method 200.9. The compact spectrometers are designed with ease of use in mind and feature a range of software wizards to aid every step of the method development process. In addition, enhanced QC test functionality ensures Method requirements are implemented. This Application note details full method development and spectrometer optimization; determination of the linear dynamic range and method detection limit and demonstrates analyte recovery and data quality through the analysis of spiked samples.

## Introduction

Lead is known to cause a variety of adverse health effects when people are exposed to it for relatively short periods. These effects may include interference with red blood cell chemistry and delays in normal physical and mental development in babies and young children, including slight deficits in attention span, hearing and learning abilities. Longer term exposure has the potential to cause stroke and kidney disease, and certain forms of cancer.

Lead is rarely found in source waters, but rivers may be contaminated by lead mining and smelting operations. Lead contamination of drinking water by lead plumbing or fixtures is by far the greatest cause for concern, as all water is corrosive to metal plumbing to some degree. Up until the early 1930's, it was common practice to use lead piping for domestic plumbing systems, and, although these have now largely been replaced by copper pipework, the solder used to join the copper pipes and fittings contained large amounts of lead.

Lead has no known beneficial effects, and so the Maximum Contaminant Level Goal for lead has been set to zero by the US Environmental Protection Agency. Since lead cannot be removed by the water processing system, the EPA requires that the water systems control the corrosiveness of their water if the lead level exceeds the Action Level, which is currently set to 15 µg/L.

The determination of lead in drinking and natural waters is analytically challenging, as the normal levels are near the detection limits of common elemental analysis instruments. Lead determinations suffer from a variety of chemical and physical interferences, and sample collection, transport and laboratory treatment must be rigorously controlled to avoid contamination. Graphite Furnace Atomic Absorption Spectrometry is a cost-effective technology that does have the sensitivity necessary to perform these measurements.

## EPA Method 200.9

The Environmental Protection Agency has published Method 200.9 "Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption". This method has been approved for use in compliance monitoring programs in both the Clean Water Act and the Safe Drinking Water Act. The documented Method is available in electronic form from the US Governments National Environmental Methods Index web site at:

<http://www.nemi.gov>

This Method provides procedures for the determination of dissolved and total recoverable elements by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) in ground water, surface water, drinking water, storm runoff, and industrial and domestic wastewater. It is also applicable to the determination of total recoverable elements in sediments, soils and sludges. It is currently at Revision 2.2.

Method 200.9 applies to a list of 16 elements, which includes lead. This publication discusses the application of the Thermo Scientific AA spectrometer with the Zeeman Graphite Furnace and Graphite Furnace Autosampler to the measurement of lead in natural and drinking waters following the Method 200.9 procedures.

### Graphite Furnace Atomic Absorption Spectrometer

Section 6.1 of revision 2.2 of Method 200.9 specifies the attributes of the Graphite Furnace Spectrometer that are required. For this work, the Thermo Scientific AA Series spectrometer was fitted with the Zeeman Graphite Furnace and Graphite Furnace Autosampler was used. The system was controlled by the SOLAAR Atomic Absorption Data Station software.

Section 6.1. of the method sets out the characteristics of the spectrometer, graphite furnace system and delayed atomization device that are required to implement the method. Details of the design and operation of the Zeeman Graphite Furnace are given in reference (1), which shows that the equipment meets the requirements set out in the method. The delayed atomization device used for this work was the Thermo Scientific Omega platform cuvette. The characteristics of the Omega cuvette design are described in detail in reference (2). The Method requires that the spectrometer must be fitted with an adequate background correction system capable of removing undesirable non-specific absorbance over the spectral region of interest and provide an analytical condition not subject to the occurrence of inter-element spectral overlap interferences. The AA spectrometer is fitted with background correction system using the Zeeman effect, which is capable of meeting these requirements. The characteristics of the background correction systems fitted to the spectrometer are described in detail in reference (3).

The method specifies the use of single element hollow cathode lamps, or single element electrodeless discharge lamps with the associated power supplies. The latter are not required with the efficient optical design of the spectrometers, and a Thermo Scientific single element coded lead hollow cathode lamp was used.

The Method specifies that an alternate internal gas containing 5 % hydrogen in argon must be used as a continuous gas flow environment during the Dry and Ash furnace cycles. A suitable gas mixture was obtained from BOC, and connected to the alternate gas inlet of the Graphite Furnace. This alternate gas was selected for the Dry and Ash phases of the furnace program.

The Method specifies the use of a Graphite Furnace Autosampler capable of adding matrix modifier solutions to the furnace, adding a single addition of analyte, and completing methods of standard additions when required. The Thermo Scientific Graphite Furnace Autosampler provides all of these facilities (see reference 4).

## Reagents and Standards

### Deionised water

Deionised water used throughout this work was obtained from a Millipore Deioniser system. The conductivity of the water used was >18 Mohms/cm.

### Nitric acid

High purity concentrated nitric acid (Trace Analysis Grade) was obtained from Fisher Scientific UK, Bishop Meadow Road, Loughborough LE11 5RG, UK. This was used without further purification.

### Standard solutions

A lead master standard solution containing 1000 mg/L of lead was obtained from Fisher Scientific UK. This was diluted with 1 % v/v (approximately 0.1 M) nitric acid to provide the working standards required.

The calibration blank solution used throughout was a 1 % v/v solution of nitric acid.

The method requires that the accuracy of the standards used is confirmed by comparison with a second standard obtained from an independent source. For this work, a multi-element standard containing 10.0 mg/L of lead was obtained from Analytical Reference Materials International, 700 Corporate Circle, Suite A, Golden, CO 80401-5635, USA.

### Matrix modifier

The Method specifies the use of a matrix modifier containing both palladium and magnesium, following the recommendations of Welz, Schlemmer and Mudakavi (reference 5). The modifier was prepared from palladium nitrate and magnesium nitrate solutions each containing 20 g/L of the metal, obtained from Spex Certiprep, 203 Norcross Ave., Metuchen, NJ 08840, USA. The final matrix modifier solution used for this work contained 3 g/L of palladium and 0.33 g/L of magnesium. 5 µL of this solution were added to each injection, providing 15 µg of palladium and 1.65 µg of magnesium, equivalent to 10 µg of Mg(NO<sub>3</sub>)<sub>2</sub>, with each sample injection.

As the study progressed, it became clear that lead contamination originating from the palladium solution contributed significantly to the blank lead signals. It was estimated that this contamination was equivalent to approximately 1.1 µg/L of lead in the sample. Since the modifier is added to every measurement, including all the blanks and standards, the effect of this contamination is eliminated by the normal calibration procedure, and so does not affect the measured sample concentrations.

### Samples

Riverine and Estuarine Water Reference Materials for Trace Metals (SLRS1, SLRS2 and SLEW1) were obtained from the National Research Council (NRC) Canada, Ottawa, Canada, K1A 0R6. These samples have very low natural concentrations of lead (around 0.1 µg/L) that are below the typical Method Detection Limits of the 200.9 procedures, and were spiked with various concentrations of lead and used for the method development experiments described below.

Standard Reference Material 1640, Trace Elements in Natural Water, was obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA. This was used as received, to confirm the accuracy of the final procedure.

Samples of laboratory tap water, mains drinking water, and mineral water from a drinks dispenser were obtained locally, and were acidified with 1 % v/v of nitric acid. These samples were also used for method development and spike recovery experiments.

## Set up and Optimization

### Spectrometer

The default spectrometer parameters provided by the SOLAAR software for Graphite Furnace lead measurements were used, except that the wavelength was changed from the default value of 217.0 nm to the alternate lead line at 283.3 nm, and Transient Area signal measurement was selected, both as recommended in the Method.

Each measurement was performed in duplicate, and so the Number of Resamples parameter was set to 2.

The final set of Spectrometer parameters used is shown in Figure 1.



Figure 1: Final Spectrometer parameters

### Graphite Furnace Autosampler

#### Injection

The height of the Furnace Autosampler capillary tip in the cuvette was adjusted while observing the injection using the Graphite Furnace TeleVision (GFTV) accessory fitted to the spectrometer. The GFTV accessory provides a high definition, real time image of the inside of the cuvette, and is described in detail in reference (6). The final capillary tip position and resulting sample injection, are shown in figures 2 and 3.



Figure 2: Optimized Capillary Tip position

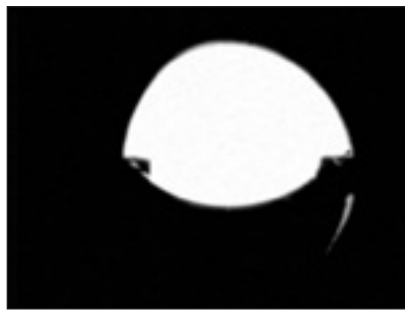


Figure 3: Optimized sample injection

### Sampling

The Omega platform cuvettes are capable of handling sample volumes up to 50  $\mu\text{L}$ . The final total injected volume used in this work was 30  $\mu\text{L}$ ; nevertheless, it was found to be beneficial to select the *Slow Solution Injection* function. This causes the sample to be deposited into the cuvette more slowly than usual, and ensures that the liquid spreads out along the length of the platform, and does not overflow the platform sides.

The *Working Volume* (the volume of sample injected into the cuvette) was set to 20  $\mu\text{L}$ , in accordance with the recommendation made in Table 2 of the 200.9 Method.

The Furnace Autosampler was used to add 5  $\mu\text{L}$  of the palladium/magnesium modifier solution automatically to each injection. The *Wet Injection* technique was used, where both the sample and modifier are picked up in the capillary tip, and are injected together into the cuvette.

The Furnace Autosampler was also used to automatically dilute a single working standard to provide three measurements to define the calibration curve. The *Fixed Volume* method was used, so that the total volume of liquid injected into the cuvette for each standard measurement remained constant.

Finally, the Automatic Spike function was used, with a spike volume of 5  $\mu\text{L}$ , to perform the spike recovery experiments described below.

The final set of Sampling parameters used is shown in figure 4.

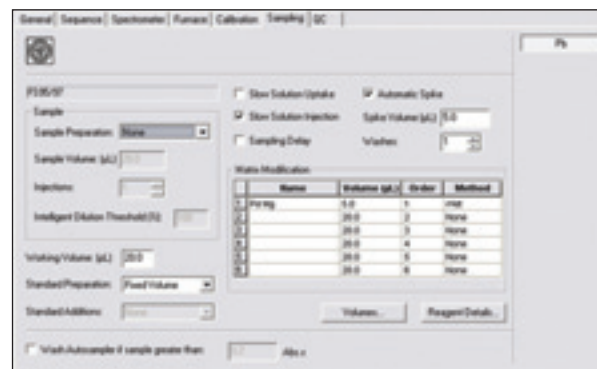


Figure 4: Final Sampling parameters

## Graphite Furnace

### Dry phase

First, the Dry phase of the Furnace Program was optimized, again using the GFTV image to evaluate the effects of changing the Dry parameters.

It was found to be beneficial to pre-warm the cuvette to 70 °C before injecting the sample. When combined with a ramp of 100 °C/s to the final drying temperature of 130 °C, this gave both smoother injections and more rapid drying, and a dry time of 25 s was found to be sufficient. With these drying parameters, relative standard deviations for the standard measurements of well under 1 % could be routinely achieved.

### Ash and Atomize phases

The notes associated with Table 2 of the 200.9 Method recommend that the hydrogen in argon gas mixture should be used for the Dry and Ash phases of the Furnace Program, and so this was selected. They also recommend that a cool-down step between the Ash and the Atomize phases should be used. The spectrometer automatically provides an auto-zero operation between the Ash and the Atomize phases of the Furnace Program, during which the cuvette is not heated, so that no signals are generated and the baseline absorbance can be set accurately. This function also provides the recommended cool-down step, and an additional cool-down phase was not found to be beneficial, and was not used.

Table 2 of the Method recommends Ash (Char) and Atomization temperatures of 1250 °C and 2000 °C respectively for lead, but also suggests that these should be optimized for individual instruments. The automatic Ash Atomize function provided in the SOLAAR software was therefore used to optimize these parameters.

A typical, automatically generated Ash Atomize plot for a sample of the SLRS1 riverine water spiked with sufficient lead to give an easily measurable signal is shown in 5. Ash Atomize plots were generated for the other samples that were also measured, but all were similar.

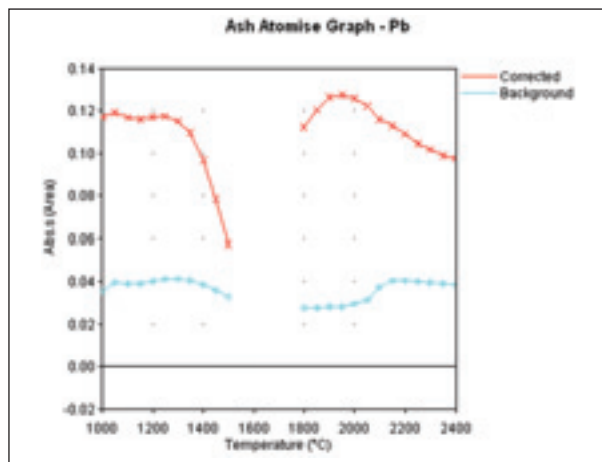


Figure 5: Automatic Ash Atomize plot for spiked SLRS1 sample

The plot shows that the Atomize temperature of 2000 °C recommended in Table 2 of the Method is indeed the optimum temperature. However, the plot also shows that an Ash (Char) temperature up to 1350 °C can be used without

loss of the analyte. Paragraph 10.2 of the Method suggests that the Ash temperature should be set to at least 100 °C below the maximum that can be used without analyte loss, and for this work, a final Ash temperature of 1200 °C was used.

The estuarine water sample SLEW1 showed the largest background signal of any of the samples investigated, and so the Ash time was selected to minimize this. A final time of 20 seconds was used, with a fast ramp of 1000 °C/s from the Dry phase.

The signals from the SLRS1 and SLRS2 riverine water samples showed some tailing that was not present in the other samples, or in the standards, and so a final atomization time of 6s was used to ensure that all the signal from these samples was captured. A typical signal from the spiked SLEW1 sample is shown in 6.

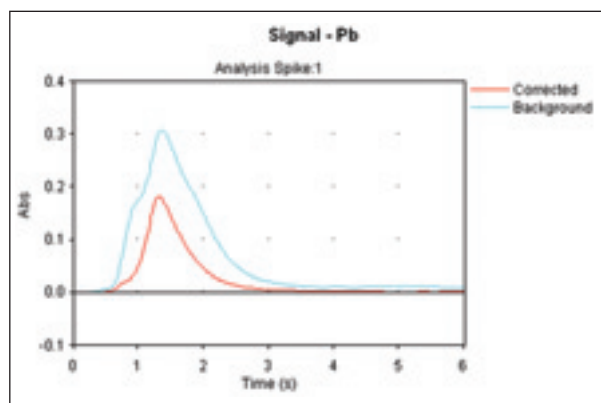


Figure 6: Signal from spiked SLEW1 sample

The final set of Graphite Furnace parameters used is shown in Figure 7.

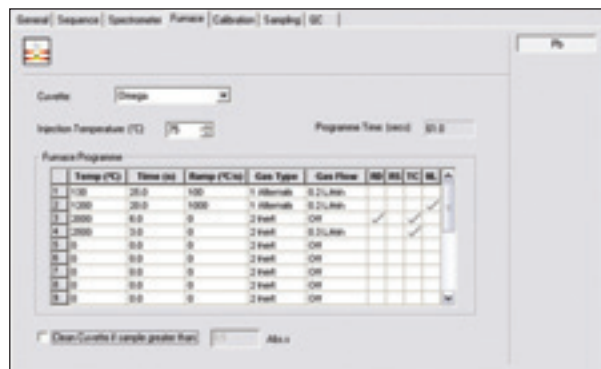


Figure 7: Optimized Furnace Program

## Initial Demonstration of Performance

Each laboratory using the 200.9 Method is required to operate a formal Quality Control (QC) program, which must include an initial demonstration of laboratory capability. This is described in section 9.2 of the Method.

The initial demonstration of performance is used to characterize the instrument performance (determination of linear dynamic range, and the analysis of quality control samples) and the laboratory performance (determination of method detection limits) prior to samples being analyzed by the Method.



### Linear Dynamic Range

GFAAS calibration graphs are inherently curved, and the 200.9 Method provides a procedure for ensuring that this does not introduce significant errors, by defining a procedure in paragraph 9.2.2 for measuring the Linear Dynamic Range (LDR) of the instrument. Measured sample analyte concentrations that exceed the upper limit of the LDR must be diluted and re-analyzed, or analyzed by another approved method.

The upper limit of the LDR is established by determining the signal responses from a minimum of six different concentration standards across the range, two of which must be close to the upper limit of the LDR. The upper limit of the LDR should be an observed signal no more than 10 % below the level extrapolated from the four lower standards.

To determine the LDR for lead measured using the optimised parameters described above, a standard solution containing 200 µg/L of lead was prepared. It was expected that the upper limit of the LDR would be below this concentration.

The automatic Standard Preparation facility of the Graphite Furnace Autosampler was then used to prepare a 10 point calibration, by making equally spaced dilutions of the 200 µg/L standard. The signal responses from these were measured, and the data was exported from SOLAAR to a spreadsheet for further analysis.

The results obtained are shown in Table 1 and Figure 8.

Standard concentration (µg/L)	Signal response (abs.s)	Estimated signal response (abs.s)	Error in estimation (abs.s)	Relative error
0	0.01127			
20	0.10846			
40	0.20670			
60	0.28850			
80	0.36786			
100	0.44481	0.46312	0.01831	4 %
120	0.51199	0.55225	0.04026	7 %
140	0.57910	0.64137	0.06227	10 %
160	0.63994	0.73049	0.09055	12 %
180	0.69455	0.81961	0.12506	15 %
200	0.74170	0.90873	0.16703	18 %

Table 1: LDR Results

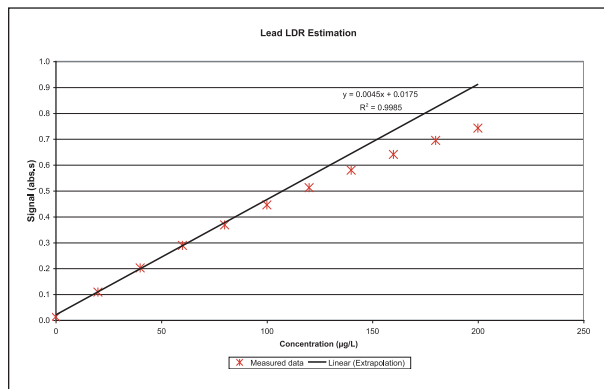


Figure 8: LDR Estimation

The results show that, as expected, the calibration is significantly curved at the higher signal values. A least squares linear fit to the blank and first four calibration points gave an excellent straight line, with a correlation coefficient (R<sup>2</sup> value) of 0.9985. The signal response for the 140 µg/L standard is 10 % down from the value estimated by extrapolating this line, and so this point is the upper limit of the LDR.

### Calibration parameters

Based on the results of the LDR estimation, a top standard concentration of 100 µg/L was used. Even though this is well below the upper limit of the LDR defined by the Method, the calibration graph shows a small amount of curvature. The Furnace Autosampler was used to automatically dilute the 100 µg/L standard to provide three calibration points, and the Segmented Curve calibration algorithm provided in the SOLAAR software was used to eliminate the effects of the curvature.

The final calibration parameters used are shown in Figure 9, and a typical calibration graph measured with these parameters is shown in Figure 10.



Figure 9: Final Calibration Parameters

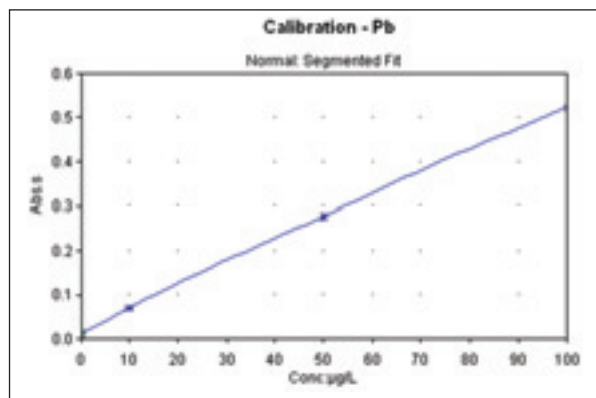


Figure 10: Typical calibration graph

### Quality Control Sample

Paragraph 9.2.3 of the Method requires that the calibration standards and acceptable instrument performance must be verified by the preparation and analysis of a Quality Control Sample (QCS).

The preparation and characteristics of the QCS are set out in Section 7.12 of the Method. The QCS must be obtained from an outside source that is different from the source of the standard stock solutions, but must be prepared in the same acid matrix as the calibration standards. The concentration of the QCS should be chosen so that the signal response is approximately 0.1 abs.s.

For this work, the QCS was prepared from a Test Standard supplied by Analytical Reference Materials International. This contained 10 mg/L of lead, and was diluted with 1 % nitric acid to give a QCS containing 20.0 µg/L.

Three separate samples of the QCS were analyzed, and the results are shown in Table 2.

Sample	Measured concentration (µg/L)
QCS 1	20.27
QCS 2	19.77
QCS 3	19.44
Mean	19.8
Relative standard deviation	2.1%
Recovery	99.1%

Table 2: QCS Analysis Results

The signal response recorded for the QCS measurements was approximately 0.11 abs.s. The Method requires that the determined concentration of the QCS should be within ±10 % of the stated value, and so these results confirm that the calibration standards and instrument performance are within specification.

### Method Detection Limit

The Method requires that the Method Detection Limit (MDL) must be established for all analytes, and the procedure for doing this is described in paragraph 9.2.4. This paragraph references the US Code of Federal Regulation 40, Chapter 1, part 136, Appendix B, which describes the procedure in more detail.

The MDL must be estimated using a sample of reagent water (blank) spiked with a concentration of the analyte equivalent to 2-3 times the Instrumental Detection Limit (IDL).

The SOLAAR software provides an automated procedure (a 'Wizard') that will perform an experiment to estimate the detection limit for any element, measured using any parameter set. The Check Instrument Performance Wizard estimates the detection limit using the IUPAC definition of detection limits (reference 7). It will also estimate the Characteristic Concentration, and performs some statistical checks on the data to confirm the absence of some common problems encountered in detection limit measurements.

The Wizard was used to estimate the IDL of the Spectrometer and Zeeman Graphite Furnace used with the optimized parameters described above. The Detection Limit

Blank solution used was the 1 % nitric acid blank used throughout this work.

The results of four separate runs of the Wizard, performed at various times throughout this investigation are shown in Table 3.

Run	Characteristic Concentration (µg/L)	Instrumental Detection Limit (µg/L)	Drift factor	Warnings
1	0.8142	0.2913	0.5	Possible contamination
2	0.9394	0.3256	0.1	Possible contamination.
3	1.0723	0.4726	0.0	Possible contamination.
4	0.8951	0.4336	0.4	Possible contamination
Mean	0.930	0.381		

Table 3: IDL Results

The Drift factor estimates the contribution that any time dependent variations of the results make to the calculated detection limit - values less than 1 indicate that time dependent variations are not significant. The Wizard has correctly recognized that a contamination problem is present. This is due to the contamination of the palladium solution used to prepare the matrix modifier. This introduces a small baseline signal common to all measurements, the effect of which is eliminated by the calibration procedure. The IDL therefore has been shown to be 0.38 µg/L.

The procedure described in the Method requires that the laboratory blank (1 % nitric acid) should be fortified with the analyte at a level of 2-3 times the estimated IDL, then analyzed seven times. The MDL is calculated from the concentration results by calculating the standard deviation, and multiplying it by Student's t value for a 99 % confidence level and standard deviation estimate with 6 degrees of freedom, which is 3.14. Paragraph 9.2.4 of the Method recommends that the relative standard deviation of the seven replicate results should be greater than 10 %, confirming that the analyte concentration in the fortified blank is not inappropriately high for the MDL measurement. It also suggests that an average of at least three values determined in separate experiments may be a more appropriate estimate of the MDL. The laboratory blank (1 % nitric acid solution) was therefore fortified with 1.0 µg/L of lead, and analyzed seven times. This analysis was repeated on a different day, with different solutions. Later, the MDL was again determined twice more, using a laboratory blank solution fortified with 0.5 µg/L of lead. The results of these analyses are summarized in Table 4

Run	Actual concentration (µg/L)	Mean measured concentration (µg/L, n=7)	Standard deviation (µg/L, n=7)	Relative standard deviation	Method Detection Limit (µg/L)
1	1.0	0.99	0.11	11.6%	0.36
2	1.0	1.09	0.17	15.9%	0.54
3	0.5	0.30	0.16	55.0%	0.51
4	0.5	0.48	0.11	22.7%	0.34
Mean					0.44

Table 4: MDL Results

All four of the MDL estimates meet the criteria set out in the Method, and so the mean value of 0.44 µg/L can be considered to be representative of the performance of the laboratory and the instrument.

Table 2 of the Method shows some typical single laboratory MDL's; the MDL value shown for lead is 0.7 µg/L. The Thermo Scientific Spectrometer and Zeeman Graphite Furnace system therefore comfortably exceeds this value.

The upper limit of the LDR for lead has been shown to be 140 µg/L. Recovery of the lead contained in the QCS sample was 99.1 %, and the Method Detection Limit was found to be 0.44 µg/L. The results obtained confirm that the Thermo Scientific GFAAS instrument meets or exceeds the requirements set out for the Initial Demonstration of Performance in the EPA 200.9 Method for the determination of lead.

### Assessing Laboratory Performance

Section 9.3 of the Method sets out a number of QC procedures intended to assess the laboratory performance. These must be followed for each batch of samples that are analyzed.

Four typical batches of samples were analyzed during this work, using the analysis parameters developed as described above, and the specified QC procedures were included in the Analysis Sequence. The QC procedures were implemented using the automatic QC Test functionality provided in the SOLAAR software.

#### Laboratory Reagent Blank

Paragraph 9.3.1 of the Method specifies that one Laboratory Reagent Blank (LRB) must be analyzed with every batch of 20 or fewer samples. Preparation of the LRB is described in paragraph 7.10.2 of the Method. For this work, a 1 % v/v nitric acid solution was used for the LRB.

LRB concentration values that exceed the MDL should be suspected. When the LRB concentration constitutes 10 % or more of the analyte concentration measured in a sample, or is 2.2 times the MDL, whichever is greater, the source of the contamination must be traced and removed so that acceptable LRB concentrations are obtained. Fresh aliquots of the sample(s) must then be prepared, and the analysis must be repeated.

Typical LRB concentrations measured in this work were close to zero, and in only one case exceeded the measured MDL of 0.44 µg/L.

#### Laboratory Fortified Blank

Paragraph 9.3.2 of the Method specifies that one Laboratory Fortified Blank (LFB) must be analyzed with every batch of 20 or fewer samples. Preparation of the LFB is described in paragraph 7.10.3 of the Method. For this work, the LFB was prepared by fortifying the LRB solution with 20 µg/L of lead.

If the recovery of the analyte falls outside the required control limits of 85-115 %, that analyte is judged to be out of control, and the source of the problem should be identified and resolved before continuing the analysis.

The LFB test was set up as QC Check 3 in the SOLAAR software. The recoveries of the LFB ranged from 94 % to 105 % over four separate analytical runs carried out over a

three week period. The QC Control Chart facility in SOLAAR was used to plot this data, together with the control limits, as shown in Figure 11.

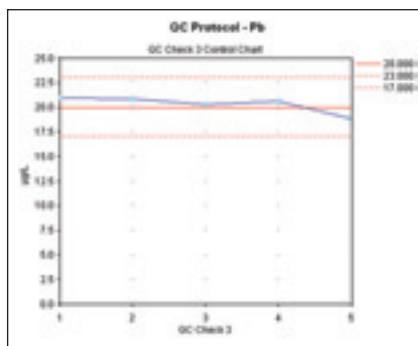


Figure 11: LFB Control Chart

For these four runs, the LFB concentration is comfortably within the limits, and analysis is clearly in control.

#### Instrument Performance Check

Paragraph 9.3.4 of the Method specifies that Initial and Continuing Instrument Performance Checks must be performed. For all determinations, the laboratory must analyze the Instrument Performance Check (IPC) solution and the Calibration Blank immediately following each calibration, after every 10th sample, and at the end of the sample run. Preparation of the IPC solution is described in Section 7.11 of the Method, and for this work, a standard solution containing 50 µg/L of lead in 1 % v/v nitric acid was used.

The concentration result for the Calibration Blank must always be less than the IDL, but greater than a negative signal in concentration units equal to the IDL.

Analysis of the IPC solution immediately following the calibration must verify that the instrument is within ±5 % of calibration, and subsequent analyses of the IPC solution must be within ±10 % of the calibration.

The Calibration Blank check was implemented as a QC Calibration Blank Test in the SOLAAR software, and was performed 13 times during the sample analysis runs. 7 of the 13 Test results were outside the limits required, with both the positive and negative limits exceeded. This is a consequence of the palladium modifier contamination described above. The Calibration Blank concentration result is calculated as the difference between the signal response for the true Calibration Blank measurement, and the signal response for the Calibration Blank Test measurement - these signals were typically in the region of 0.01 abs.s, while the signal response equivalent to the IDL concentration was of the order of 0.002 abs.s.

The concentration is therefore calculated from the small difference between two relatively large signals, so that the noise on the signals has a large effect on the final result.

The Initial Instrument Performance Check was implemented as a QC Check Test, and was performed six times during different sample runs over the course of this work. The overall mean recovery was 102.7 %, and the relative standard deviation across the six measurements was 2.0 %.

The Continuing Instrument Performance Check was performed nine times over the course of this work. All the results were within the specified limits; the mean recovery was 98.5 %, and the relative standard deviation across all nine results was 4.9 %.

The results obtained for the on-going QC procedures specified in the Method generally indicate that the laboratory performance is in control. The procedures reveal a problem with a contaminated reagent used to make up the Matrix Modifier solution, which particularly affects the on-going Calibration Blank tests. This is not, however, relevant to the use of the Thermo Scientific instrument for the EPA 200.9 Method.

### Analyte Recovery and Data Quality

Section 9.4 of the Method defines a series of procedures for determining the analyte recovery of Laboratory Fortified Matrix (LFM) samples. Spike recoveries must be in the range 70 - 130 %. The Method also specifies that the background absorbance signal from the samples must be <1.0 A.s before the results can be considered to be reliable.

For this work, all the samples analyzed were also automatically spiked using the Furnace Autosampler facilities. The spike increased the sample concentration by an amount equivalent to 2.5 µg/L in the original sample. The results obtained are shown in Table 5.

Sample	Background signal (A.s)	Measured concentration (µg/L)	Measured spike concentration (µg/L)	Spike Recovery
SLRS 1	0.039	nd*	24.1	96.4 %
SLRS 2	0.038	nd*	23.4	93.6 %
SLEW 1	0.36	nd*	23.3	93.2 %
Tap water	0.028	0.8	25.4	98.4 %
Drinking water	0.035	nd*	24.7	98.8 %
Mineral water	0.034	nd*	24.7	98.8 %

\* nd = not detected. The measured result was below the MDL of 0.44µg/L.

Table 5: Spiked Sample results

The background signals recorded for these samples are all well below the 1.0 A.s limit, and so the results can be considered to be reliable. All the spike recoveries are comfortably within the acceptable range, and so this implementation of the Method has been shown to give excellent spike recoveries with the samples examined.

The Method goes on to define procedures that should be

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used when the spike recoveries fall outside the acceptable limits. As all the recoveries from the samples examined in this work were well within the acceptable limits, these procedures were not investigated further.

As a further check on the Data Quality, a sample of the NIST 1640 Certified Reference Material (Trace Elements in Natural Water) was analyzed. The lead concentration in this material is certified at 27.89 ± 0.14 µg/L. The measured result obtained was 27.03 µg/L, 96.9 % of the Certified value.

The Analyte Recovery criteria set out in the 200.9 Method have been easily achieved with a range of samples analyzed using the Thermo Scientific AA Spectrometer. The Data Quality of the measurement system has been further confirmed by the excellent recovery of the analyte from a Certified Reference Material.

### Conclusions

The Thermo Scientific iCE 3000 Series Atomic Absorption Spectrometers fitted with Zeeman Graphite Furnace and Graphite Furnace Autosamplers are entirely suitable for the determination of lead concentrations in natural water samples using the EPA 200.9 methodology. The Method Development Tools provided, particularly the Graphite Furnace TeleVision accessory and the automatic Ash Atomize experiment, allow the instrument parameters to be quickly and reliably optimized.

The analytical performance of the system meets all the performance criteria set out in the Method, and the comprehensive QC Tests facilities provided in the SOLAAR software facilitates adherence to the the detailed Quality Control requirements.

### References

- 1) Design Features of the GF95 Graphite Furnace Accessory. Thermo Scientific publication number PS40701.
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- 3) Design Considerations for High Performance Background Correction Systems for Atomic Absorption Spectrometry. Thermo Scientific publication number PS40690.
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- 5) Palladium Nitrate-Magnesium Nitrate Modifier for Electrothermal Atomic Absorption Spectrometry. Welz, Schlemmer and Mudakavi, Journal of Analytical Atomic Spectrometry, vol. 7, p1257, 1992.
- 6) Graphite Furnace TeleVision - the Ultimate Graphite Furnace Development Tool. Thermo Scientific publication number AN40840.
- 7) G.L. Long and J.D. Winefordner, Limit of detection: a closer look at the IUPAC definition, Analytical Chemistry, 55 (1983) 712A-724A.

*The method of sample treatment described in this publication should be performed only by a competent chemist or technician trained in the use of safe techniques in analytical chemistry. Users should acquaint themselves with particular hazards which may be incurred when toxic materials are being analysed and handled in the instruments, and the instrument must be used in accordance with the operating and safety instructions given in the Operators manual.*

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