

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

Key Words

- Atomic Absorption
- EPA 200.9
- Environment
- Selenium
- Water
- Zeeman
- GFAAS

Introduction

Selenium is a metal found in natural deposits with ores containing other elements. Selenium is widely used in electronic and photocopier components, but it is also used in glass, pigments, rubber, metal alloys, textiles, petroleum, medical therapeutic agents and photographic emulsions.

Selenium at low levels is an essential human nutrient, but at higher levels, human exposure to selenium can cause both short and long term health effects. Short term effects include changes to hair and finger nails, damage to the peripheral nervous system, and increased fatigue and irritability. Long term exposure to selenium has been linked to loss of hair and fingernails, damage to kidney and liver tissues, and damage to the nervous and circulatory systems.

The Maximum Contaminant Level Goal (MCLG) for this element has been set to 50 µg/L (parts per billion, ppb) by the US Environmental Protection Agency (EPA). Based on this MCLG, the EPA has set the Maximum Contaminant Level (MCL, a legally enforceable standard) at 50 µg/L, because the EPA believes that, given present technology and resources, this is the lowest level to which water systems can reasonably be required to remove this contaminant, should it occur in drinking water. The EPA has set the selenium standard for drinking water at this level to protect consumers served by public water systems from the effects of long-term, chronic exposure to selenium.

The determination of selenium in drinking and natural waters is analytically challenging, as the concentration levels required are near the detection limits of common elemental analysis instruments. In addition, selenium exists naturally in a variety of chemical forms, including both organic and inorganic compounds, and different oxidation states. These can result in a variety of chemical and physical interferences in the analysis. Graphite Furnace Atomic Absorption Spectrometry (GFAAS) is a cost-effective technology that does have the sensitivity and relative freedom from interference effects 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://web1.er.usgs.gov/nemi/method_summary.jsp?param_method_id=4797

This Method provides procedures for the determination of dissolved and total recoverable elements by Graphite Furnace Atomic Absorption Spectrometry 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, although a draft of Revision 3 is also available.

Method 200.9 applies to a list of 16 elements, which includes selenium. This publication discusses the application of the Thermo Scientific AA Spectrometers with Zeeman Graphite Furnace and Graphite Furnace Autosampler to the measurement of selenium in natural and drinking waters following the Method 200.9 procedures. It is a companion document to references (i) and (ii), which discuss the measurement of lead and arsenic concentrations using Method 200.9 methodology with the same equipment.

Graphite Furnace Atomic Absorption Spectrometer

The details, and performance and features of the AA Series spectrometer and accessories used are discussed in the context of the EPA Method 200.9 in reference (i), where the suitability of the instrument for this work is confirmed.

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 selenium master standard solution containing 1000 mg/L of selenium 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 selenium 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 (iii)), and the preparation of a suitable modifier solution is described in reference (i).

Samples

Riverine and Estuarine Water Reference Materials for Trace Metals (SLRS1, SLRS2 and SLEW1) were obtained from the National Research Council Canada, Ottawa, Canada K1A 0R6. These samples have unknown natural concentrations of selenium, and so were spiked with various concentrations of selenium and used for the method development experiments described below. The estuarine water SLEW1 provides a particularly challenging sample, as the salinity is 11.6 parts per thousand, which has the potential to generate large background signals and significant interferences.

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. The concentrations of the major matrix components in these samples were determined by ICP-OES analysis. These samples were also used for method development and spike recovery experiments.

The concentrations of the major matrix elements in these samples, and the certified selenium concentrations, where available, are shown in Table 1.

Sample	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Se (µg/L)
SLRS 1	25.1	5.99	10.4	1.3	Unknown
SLRS 2	5.70	1.51	1.86	0.69	Unknown
SLEW 1	Unknown	Unknown	4480	Unknown	Unknown
NIST 1640	7.045	5.819	29.35	0.994	21.96
Tap water	95	2.5	7.9	1.3	Unknown
Drinking water	96	2.4	8.5	1.7	Unknown
Mineral water	103	2.6	10.1	2	Unknown

Table 1: Sample Composition

Set up and Optimisation

Spectrometer

The default spectrometer parameters provided by the SOLAAR software for Graphite Furnace selenium measurements were used, except that the Transient Area signal measurement was selected, 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.

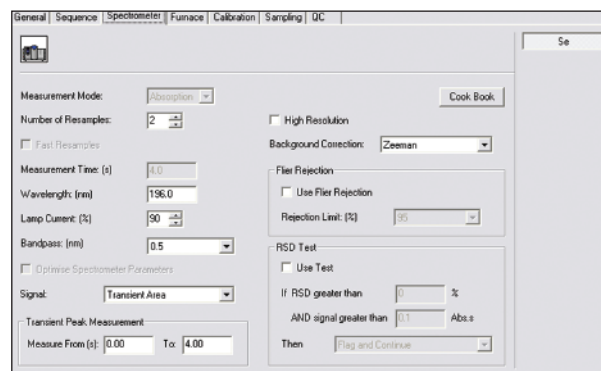


Figure 1: Spectrometer parameters

Graphite Furnace Autosampler

Injection

The height of the Furnace auto-sampler capillary tip in the cuvette was adjusted while observing the injection using the Graphite Furnace TeleVision (GFTV) accessory fitted to the spectrometer, as described in reference (i).

Sampling

The Furnace Autosampler Sampling parameters were set up as described in reference (i).

The final set of Sampling parameters used is shown in Figure 2.

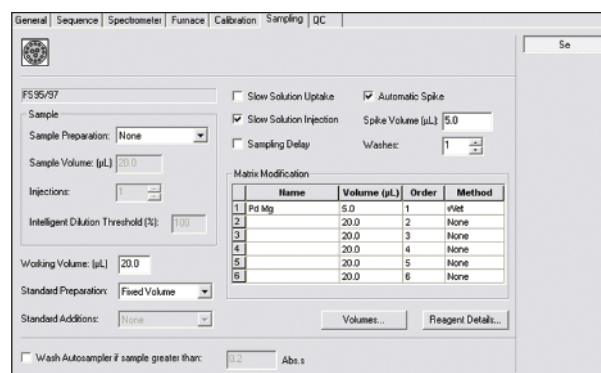


Figure 2: Sampling parameters

Graphite Furnace Program

Dry phase

Optimisation of the Dry phase of the Furnace Program using the GFTV image was described in reference (i).

Ash phase

Table 2 of the Method recommends an Ash (Char) temperature of 1000 °C for selenium, but also suggests that this should be optimised for individual instruments. The automatic Ash Atomise function provided in the SOLAAR software was therefore used to optimise the Ash phase temperature.

A typical, automatically generated Ash plot for a spiked sample of the drinking water is shown in Figure 3. This plot shows that Ash (Char) temperatures up to 1350 °C can be used without significant loss of the analyte. However, it also reveals a small decrease in the signal that takes place above 1100 °C. This decrease is not present in the Ash plot for the calibration standard, and so slightly low recovery of the analyte from this sample will be seen if Ash phase temperatures above 1100 °C are used. For this work, therefore, the Ash phase temperature of 1000 °C that is suggested in Table 2 of the Method was used.

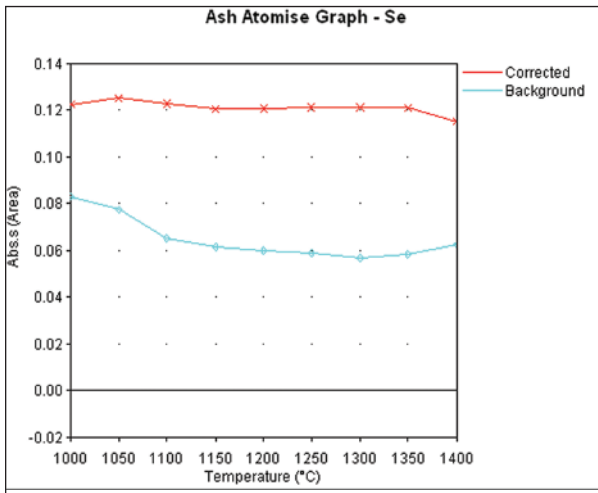


Figure 3: Automatic Ash Atomize plot for a spiked Drinking Water sample

The change in the background signal from the spiked Drinking Water sample with the time of the Ash phase was investigated, and the results are shown in Figure 4.

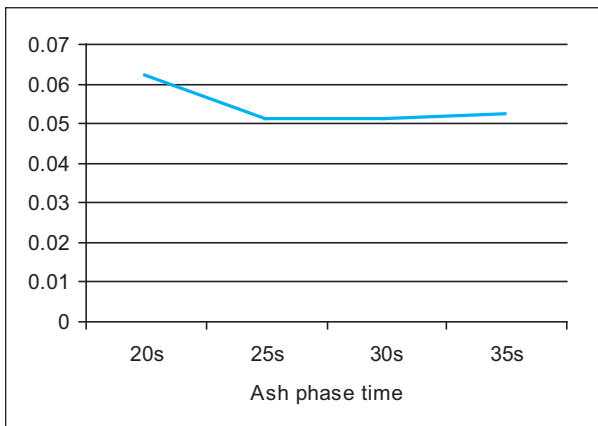


Figure 4: Ash phase time optimization results.

From these results, an Ash phase time of 30 seconds was selected.

As discussed in reference (i), the 200.9 Method specifies the use of an internal cuvette gas containing 5 % hydrogen in argon for the Dry and Ash phases of the furnace program, to assist in the removal of halide ions, and to reduce the palladium contained in the modifier to the metallic form, which stabilises the analytes most efficiently. However, it has been shown in reference (iii) that the presence of hydrogen in the cuvette during the atomization phase

depresses the selenium signal. Section 4.4 of the Method therefore recommends that an additional furnace program phase to purge residual hydrogen from the cuvette with pure argon should be used before the Atomize phase.

The signal from a selenium standard solution measured without using hydrogen in any phase was compared with the signals from measurements using the hydrogen in argon mixture for the Dry and Ash phases, with a Purge phase at the same temperature as the Ash phase, and of varying duration. The results are shown in Figure 5.

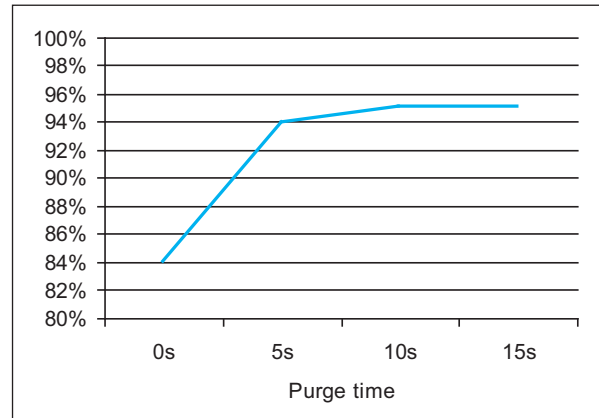


Figure 5: Purge phase optimisation results

A 10 second Purge phase restores around 95 % of the signal, but it was not possible to eliminate the signal suppression caused by the hydrogen entirely.

Atomize phase

The Method recommends an atomization temperature of 2000 °C for selenium. However, detailed investigations using the automatic Ash Atomize facilities provided by the SOLAAR software revealed that this temperature was rather low. More importantly, the optimum atomization temperature was found to vary significantly between the different samples, and between the samples and the standard solutions. This is shown in Figure 6, where the atomize plots for a simple standard solution, a spiked drinking water sample, and the NIST1640 CRM sample are compared.

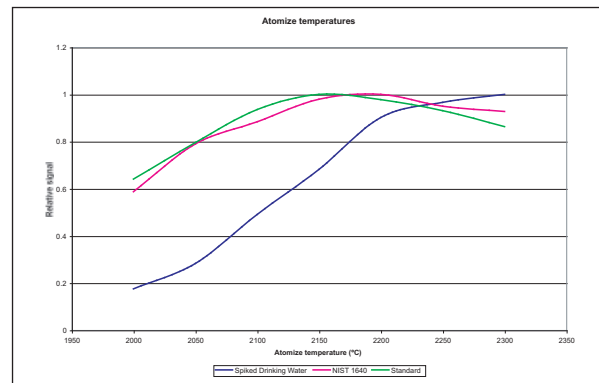


Figure 6: Atomize plots for different samples

Figure 6 shows that the optimum atomize temperatures for the standard and NIST 1640 samples are 2150 °C and 2200 °C respectively, but the spiked Drinking Water sample requires at least 2300 °C. This implies that it is not possible to choose a single optimum temperature that is suitable for all types of sample, and a compromise atomize temperature of 2250 °C was finally selected. With this temperature, an atomize time of 4 s was found to be sufficient to capture the entire signal.

A typical selenium signal from the NIST 1640 CRM measured under these conditions is shown in Figure 7.

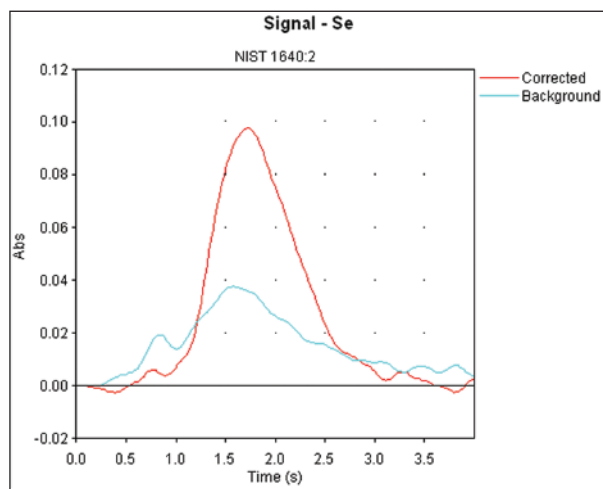


Figure 7: Selenium signal with final atomization parameters

The final set of Graphite Furnace parameters used is shown in Figure 8.

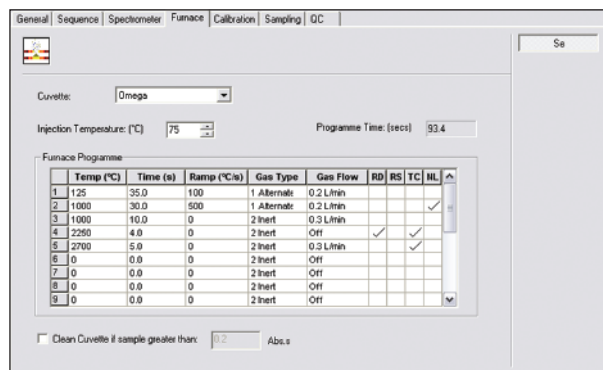


Figure 8: Optimised Furnace Program

Initial Demonstration of Performance

Each laboratory using the 200.9 Method is required to operate a formal Quality Control (QC) program, including an Initial Demonstration of Performance. This is discussed in detail in reference (i).

Linear Dynamic Range

The details of the experiments used to determine the Linear Dynamic Range (LDR) using the automatic standard preparation facilities provided by the Furnace auto-sampler are described in reference (i).

A master standard solution containing 300 µg/L of selenium was used.

The results obtained are shown in Table 2 and Figure 9.

Standard concentration (µg/L)	Signal response (abs.s)	Estimated signal response (abs.s)	Error in estimation (abs.s)	Relative error
0	0.00578			
30	0.12799			
60	0.25166			
90	0.37402			
120	0.48452			
150	0.60954	0.60985	0.00031	0 %
180	0.70851	0.73020	0.02169	3 %
210	0.81261	0.85055	0.03794	4 %
240	0.90727	0.97090	0.06363	7 %
270	0.99318	1.09125	0.09807	9 %
300	1.03934	1.21160	0.14226	12 %

Table 2: LDR Results

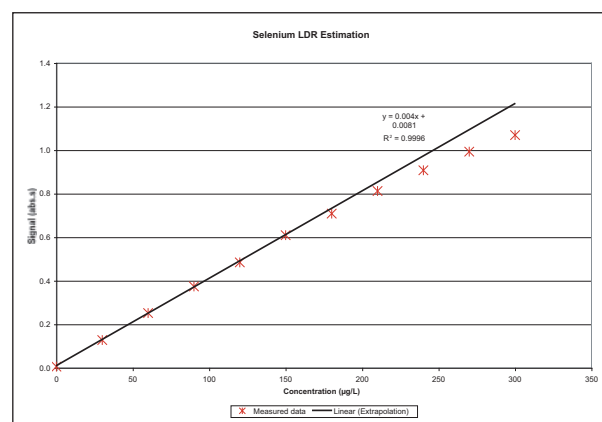


Figure 9: LDR Estimation

The results show that the calibration is slightly 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^2 value) of 0.9996. The signal response for the 270 µg/L standard is 9 % down from the value estimated by extrapolating this line, and so the upper limit of the LDR is at this level.

Calibration parameters

Based on the results of the LDR estimation and the MCL that is required to be measured, a top standard concentration of 100 µg/L was used. This is well below the upper limit of the LDR defined by the Method, and the calibration graph shows a very small amount of curvature. The Furnace auto-sampler was used to automatically dilute a 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 residual curvature.

The final calibration parameters used are shown in Figure 10, and a typical calibration graph measured with these parameters is shown in Figure 11.

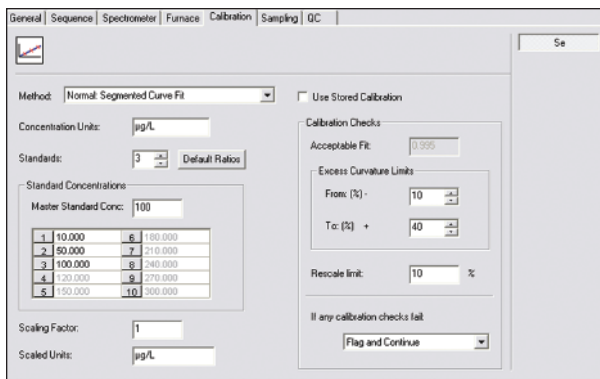


Figure 10: Calibration parameters

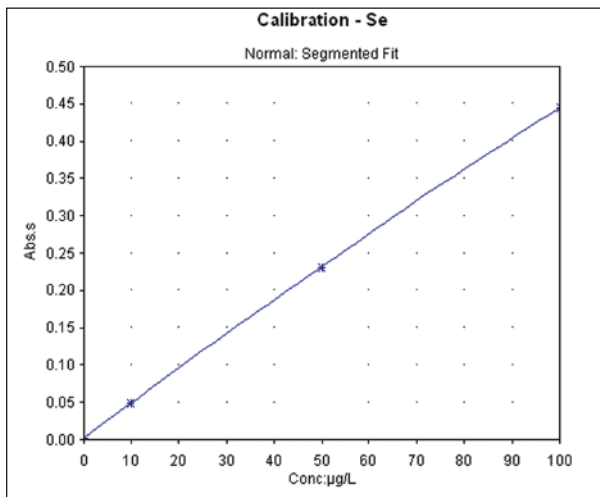


Figure 11: Typical calibration graph

Quality Control Sample

The Method specifies that the calibration standards and acceptable instrument performance must be verified by the preparation and analysis of a Quality Control Sample (QCS). The QCS used in this work contained 20.0 µg/L of selenium, and was prepared from a Test Standard supplied by Analytical Reference Materials International, as described in reference (i).

Five separate samples of the QCS were analysed at various times throughout this work, and the results are shown in Table 3.

Sample	Measured concentration (µg/L)
QCS 1	22.0
QCS 2	21.0
QCS 3	20.9
QCS 4	20.7
QCS 5	20.7
Mean	21.1
Relative standard deviation	2.6 %
Recovery	105.3 %

Table 3: QCS Analysis Results

The signal response recorded for the QCS measurements was approximately 0.08 abs.s. The Method requires that the analytical signal measured for the QCS should be approximately 0.1 abs.s, and the measured

concentration should be within $\pm 10\%$ of the stated value. These results confirm that the calibration standards and instrument performance are acceptable.

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 detail in reference (i).

The Check Instrument Performance Wizard provided in the SOLAAR software was first used to estimate the Instrumental Detection Limit. The Wizard reported an IDL of 1.9 µg/L, with a characteristic concentration of 0.8 µg/L, a Drift factor of 0 and no warnings. The IDL for selenium measured under the conditions described has therefore has been shown to be 1.9 µg/L.

The procedure for estimating the MDL requires that the laboratory blank (1 % nitric acid) should be fortified with the analyte at a level of 1-3 times the estimated IDL. For initial estimates of the MDL, the laboratory blank was therefore fortified with 2.0 µg/L of selenium. The Method requires that the relative standard deviation of the seven replicate results used to calculate the MDL should be greater than 10 %, to confirm that the analyte concentration in the fortified blank is not inappropriately high. The result of a typical set of 7 replicate analyses of these solutions is shown in Table 4.

Sample	Measured Concentration (µg/L)
MDL1	2.39
MDL2	2.61
MDL3	2.62
MDL4	3.08
MDL5	2.50
MDL6	2.65
MDL7	2.17
Mean	2.6
Method Detection Limit	0.9
Relative Standard Deviation	10.8 %

Table 4: MDL Results

The MDL was estimated four times during this work, as part of other analytical runs. All estimates met the criteria set out in the Method. The mean value of all the estimates was 1.2 µg/L, which can be considered to be representative of the performance of the laboratory and the instrument. The relative standard deviation of these four MDL estimates was 30 %.

The upper limit of the LDR for selenium has been shown to be 270 µg/L. Recovery of the selenium contained in the QCS sample was 105.3 %, and the Method Detection Limit was found to be 1.2 µg/L.

These 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 selenium.

Assessing Laboratory Performance

Section 9.3 of the Method sets out a number of QC procedures intended to assess the laboratory performance. These must followed for each batch of samples that are analysed, and are discussed in detail in reference (i).

Several typical batches of samples were analysed 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. All QC Tests routinely passed the acceptance criteria.

The database filtering functions provided by the SOLAAR software were used to automatically collate the results for the Continuing Instrument Performance Check results for the sample runs performed over a three week period, and present them as QC Control Chart, shown in Figure 12.

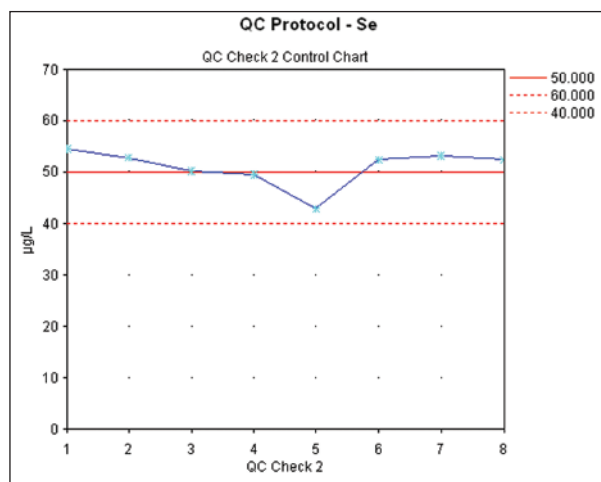


Figure 12: Continuing IPC results over 3 weeks

All the results are comfortably within the control limits, and show that the analysis is under control.

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. Analyte recoveries must be in the range 70 – 130 %. The Method also specifies that the background absorbance signal from the samples must be <1.0 abs.s before the results can be considered to be reliable.

For this work, analyte recoveries for all the sample analysed were assessed by automatically spiking the samples using the Furnace auto-sampler facilities. The spike increased the sample concentration by an amount equivalent to 25 µg/L in the original sample. Typical results obtained are shown in Table 5.

Sample	Background signal (abs.s)	Measured sample concentration (µg/L)	Measured LFM sample concentration (µg/L)	Analyte Recovery
SLRS 1	0.06	1.6	25.3	95 %
SLRS 2	0.07	nd	23.8	95 %
SLEW 1	0.55	1.5	10.4	36 %
Tap water	0.08	nd	23.6	94 %
Drinking water	0.08	1.4	23.1	87 %
Mineral water	0.07	nd	22.9	92 %

nd = not detected. The measured result was below the MDL of 1.2 µg/L.

Table 5: LFM results

The background signals recorded for these samples are all well below the 1.0 abs.s limit, and so the results can be considered to be reliable. The recoveries for all samples except the high salinity estuarine water sample SLEW1 are within the acceptable range, and so this implementation of the Method has been shown to give acceptable analyte recoveries for the range of low salinity water samples examined.

The Method goes on to define procedures that should be used when the analyte recoveries fall outside the acceptable limits. The SLEW1 sample, and an LFM prepared from it with a spike concentration of 20 µg/L, were therefore analysed using the Method of Standard Additions (MSA), as defined in Section 11.5 of the Method. The results obtained are shown in Table 6.

Sample	Background signal (abs.s)	Measured concentration (µg/L)	Recovery
SLEW1	0.48	nd	
SLEW1 LFM	0.38	20.7	103.5 %

nd = not detected. The measured result was below the MDL of 1.2 µg/L.

Table 6: Results using MSA calibration

The Standard Additions calibration graph for the SLEW1 LFM is shown in Figure 13.

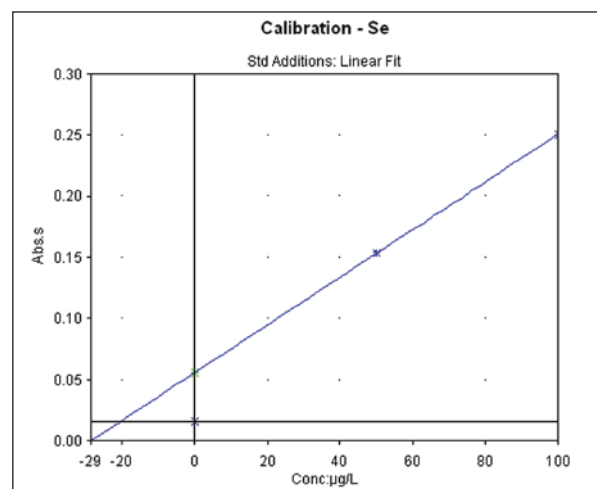


Figure 13: SLEW1 LRM using MSA calibration

As a further check on the Data Quality, a sample of the NIST 1640 Certified Reference Material (Trace Elements in Natural Water) was analysed five times over a period of three weeks. The selenium concentration in this material is certified at 21.96 ± 0.51 $\mu\text{g}/\text{Kg}$. The mean measured result obtained was 23.3 $\mu\text{g}/\text{L}$. This is 106 % of the Certified value.

The Analyte Recovery criteria set out in the 200.9 Method have been easily achieved with a range of low salinity samples analysed using the Thermo Scientific instrument. The recovery was below the lower limit of the criteria for one high salinity sample investigated, but calibration using the Method of Standard Additions resulted in full recovery. The Data Quality of the measurement system has been further confirmed by the acceptable recovery of the analyte from a Certified Reference Material.

Conclusions

The Thermo Scientific AA Spectrometer fitted with a Zeeman Graphite Furnace and Graphite Furnace auto-sampler is entirely suitable for the determination of selenium 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 optimised.

The analytical performance of the system meets the performance criteria set out in the Method, and the comprehensive QC Tests facilities provided in the SOLAAR software permit the detailed Quality Control requirements of the Method to be quickly and simply set up. The flexible Calibration functions, together with Furnace Autosampler facilities, allow the Method of Standard Additions calibration strategy to be easily implemented if necessary.

References

- i) *Lead in Natural Waters by Graphite Furnace Atomic Absorption using EPA Method 200.9. Thermo Scientific publication number AN40849*
- ii) *Arsenic in Natural Waters by Graphite Furnace Atomic Absorption using EPA Method 200.9. Thermo Scientific publication number AN40849*
- iii) *Palladium Nitrate-Magnesium Nitrate Modifier for Electrothermal Atomic Absorption Spectrometry. Welz, Schlemmer and Mudakavi, Journal of Analytical Atomic Spectrometry, vol. 7, p1257, 1992.*

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