Application Note: 40851

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

Key Words

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

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

Arsenic occurs naturally in rocks and soil, water, air, and plants and animals. It can be further released into the environment through natural activities such as volcanic action, erosion of rocks and forest fires, or through human actions. Because it occurs naturally in the environment and as a by-product of some agricultural and industrial activities, it can enter drinking water through the ground or as runoff into surface water sources.

Human exposure to arsenic can cause both short and long term health effects. Long term exposure to arsenic has been linked to cancer of the bladder, lungs, skin, kidneys, nasal passages, liver and prostate. Non-cancer effects can include thickening and discoloration of the skin, stomach pain, nausea, vomiting, diarrhoea, numbness in hands and feet, partial paralysis, and blindness.

Short term exposure to high doses of arsenic can cause other adverse health effects, but such effects are unlikely to occur from U.S. public water supplies that are in compliance with the arsenic standard.

Arsenic has no known beneficial effects, and so the Maximum Contaminant Level Goal for this element has been set to zero by the US Environmental Protection Agency (EPA). On January 22, 2001 the EPA adopted a new standard for arsenic in drinking water at 10 parts per billion (ppb, µg/L), replacing the old standard of 50 ppb. This change removed approval from ICP method 200.7 and SM3120B for regulatory drinking water measurement of arsenic, leaving GFAAS as one of the two remaining approved techniques (in addition to ICP-MS). The rule became effective on February 22, 2002. The EPA has set the arsenic standard for drinking water at this level to protect consumers served by public water systems from the effects of long-term, chronic exposure to arsenic.

The determination of arsenic in drinking and natural waters is analytically challenging, as the concentration levels required by the revised standard are near the detection limits of common elemental analysis instruments. In addition, arsenic 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 is a cost-effective technology that does have the sensitivity and relative freedom from interference effects necessary to perform these measurements.

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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 arsenic. This publication discusses the application of the Thermo Scientific AA Spectrometer with Zeeman Graphite Furnace and Graphite Furnace Autosampler to the measurement of arsenic in natural and drinking waters following the Method 200.9 procedures. It is a companion document to reference (i), which discusses the measurement of lead 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

An arsenic master standard solution containing 1000 mg/L of arsenic 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 arsenic 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 (ii)), 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 OR6. These samples have low natural concentrations of arsenic, and were spiked with various concentrations of arsenic 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 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 arsenic concentrations, where available, are shown in Table 1.

Sample	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	As (µg/L)
SLRS 1	25.1	5.99	10.4	1.3	0.55
SLRS 2	5.70	1.51	1.86	0.69	0.77
SLEW 1	Unknown	Unknown	4480	Unknown	0.76
NIST 1640	7.045	5.819	29.35	0.994	26.67
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 Optimization

Spectrometer

The default spectrometer parameters provided by the SOLAAR software for Graphite Furnace arsenic 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.

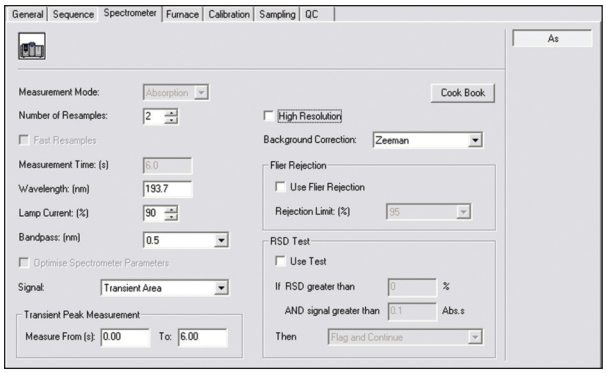

Figure 1: Spectrometer parameters

Graphite Furnace Autosampler

Injection

The height of the Furnace Autosampler 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). The final capillary tip position and resulting sample injection, are shown in Figure 2.

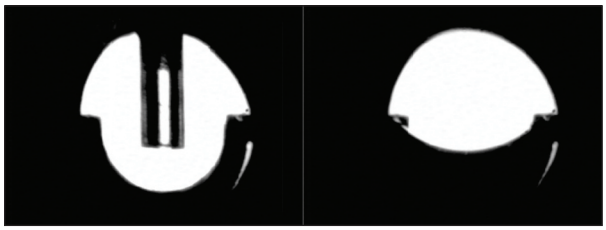

Figure 2: Optimized Capillary Tip position and Sample Injection

Sampling

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

Although the Furnace Autosampler automatically includes a wash cycle after every injection, it has an additional facility that will cause a second wash cycle to be performed if the previous signal exceeds a specified value. This was found to be useful to improve the on-going Calibration Blank QC measurements described below. A trigger value of 0.3 abs.s was used, equivalent to a concentration of approximately 60 µg/L.

The final set of Sampling parameters used is shown in Figure 3.

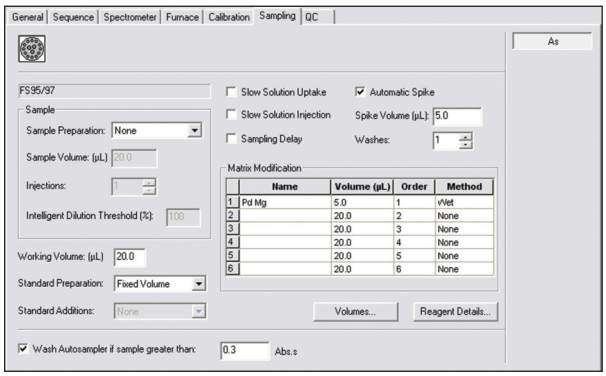

Figure 3: Sampling parameters

Graphite Furnace Program

Dry phase

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

Ash and Atomize phases

Table 2 of the Method recommends Ash (Char) and Atomisation temperatures of 1300 ºC and 2200 ºC respectively for arsenic, 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 Atomise plot for a sample of the NIST 1640 water CRM is shown in Figure 4. This plot also shows that Ash (Char) temperatures up to 1550 ºC can be used without loss of the analyte.

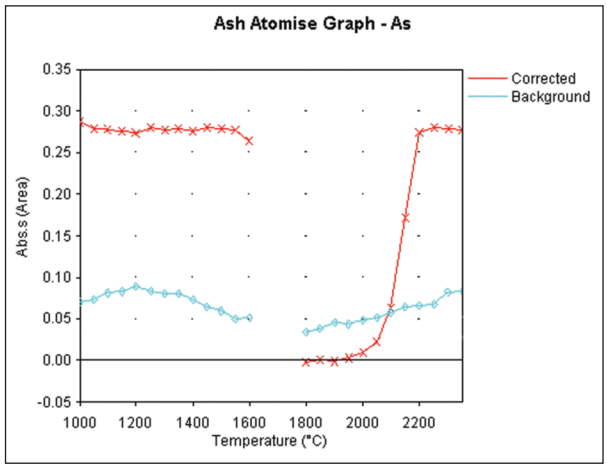

Figure 4: Automatic Ash Atomize plot for NIST 1640 water CRM

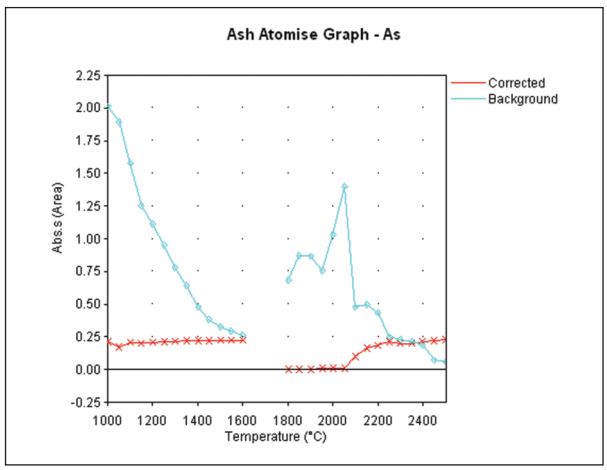

Figure 5: Automatic Ash Atomize plot for spiked SLEW1 sample

The Ash Atomize plot for the high matrix SLEW1 sample is shown in Figure 5. This shows that, as expected from the high salinity of this sample, there is a very high background signal, which decreases as the ash temperature increases. Although the Zeeman background correction system that is fitted to the spectrometer is perfectly capable of handling these large background signals, it is preferable to select conditions to minimize the background signal in order to reduce the severity of gas phase interferences resulting from the co-volatilisation of the analyte and the residual matrix.

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 1350 °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 30 seconds was used, with a fast ramp of 1000 °C/s from the Dry phase.

The plots show that an Atomize temperature of 2250 °C is the optimum for these samples, slightly higher than the 2200 °C value suggested in the Method. Although the area of the signal remained approximately constant as the atomize phase temperature was increased above 2250 °C, the signal peaks became significantly narrower and higher at the higher atomization temperatures, and as little as 100 °C change increased the signal peak height by 40 % (Figure 6). There are benefits from working with the lower, broader peaks generated using the minimum usable atomization temperature, particularly in extending the linear dynamic range (LDR), and so an atomization temperature of 2250 °C was used. At this temperature, an atomization time of 6 s was required to ensure that the entire signal was captured.

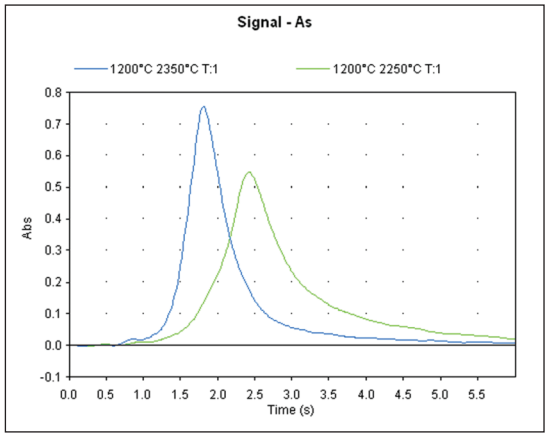

Figure 6: Arsenic signals at different Atomization Temperatures

Although the default furnace program automatically includes a Cuvette Clean phase, there is an additional facility that will cause a full Cuvette Clean cycle to be performed if the previous signal exceeds a specified value. This was found to be useful to improve the on-going Calibration Blank QC measurements described below. The trigger value was set to 0.3 abs.s, equivalent to a concentration of approximately 60 µg/L.

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

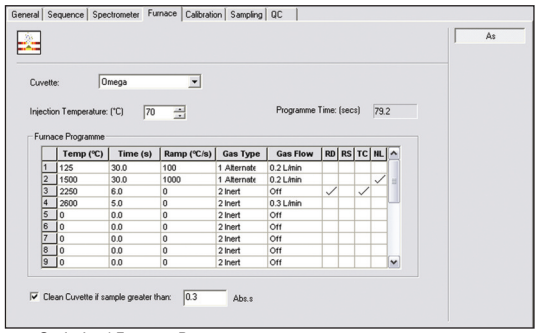

Figure 7: Optimized Furnace Program

Initial Demonstration of Performance

Each laboratory using the 200.9 Method is required to operate a formal Quality Control (QC) program, 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 Autosampler are described in reference (i). A master standard solution containing 200 µg/L of arsenic was used.

The results obtained are shown in Table 2 and Figure 8.

Standard concentration (µg/L)	Signal response (abs.s)	Estimated signal response (abs.s)	Error in estimation (abs.s)	Relative error
0	0.00137			
20	0.14969			
40	0.28474			
60	0.41777			
80	0.54436			
100	0.64355	0.68580	0.04225	6 %
120	0.74585	0.82121	0.07536	9 %
140	0.82665	0.95662	0.12997	14 %
160	0.92893	1.09202	0.16309	15 %
180	1.0118	1.22743	0.21563	18 %
200	1.09035	1.36283	0.27248	20 %

Table 2: LDR Results

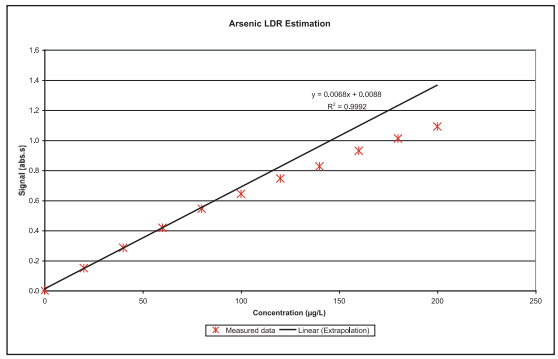

Figure 8: LDR Estimation

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^2 value) of 0.9992. The signal response for the 120 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.

Although the peak area signal used to calculate the sample concentration results remains reasonably constant for any sample as the atomization temperature is increased above the minimum value, the peak height increases sharply with increasing atomisation temperature, as shown in Figure 6. The curvature of the calibration plot depends strongly on the height of the signal, even though it is the area that is actually being measured. Higher atomization temperatures, that generate tall, narrow peaks, therefore, reduce the upper limit of the LDR.

For this work, the minimum atomization temperature was used, giving lower broad peaks that in turn maximise 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 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 9, and a typical calibration graph measured with these parameters is shown in Figure 10.

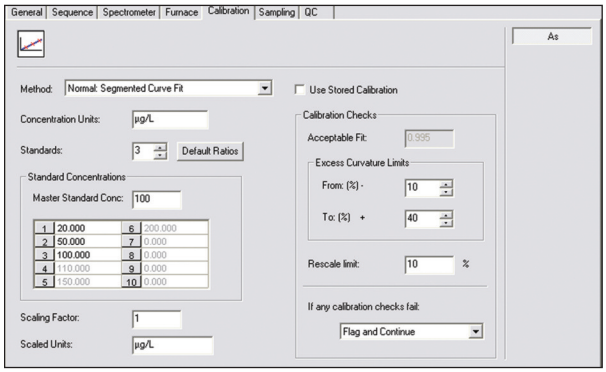

Figure 9: Calibration parameters

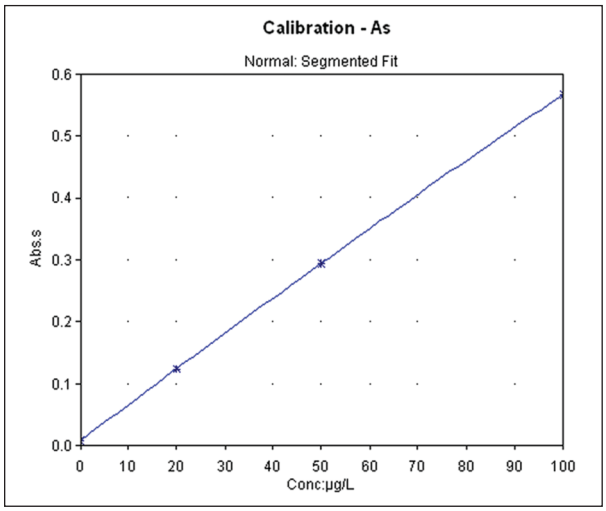

Figure 10: Typical calibration graph

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 arsenic, 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 analyzed at various times throughout this work, and the results are shown in Table 3.

Sample	Measured concentration (µg/L)
QCS 1	20.0
QCS 2	20.4
QCS 3	19.3
QCS 4	20.0
QCS 5	19.5
Mean	19.8
Relative standard deviation	2.3 %
Recovery	99.0 %

Table 3: QCS Analysis Results

The signal response recorded for the QCS measurements was approximately 0.13 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 ±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 results of three separate runs of the Wizard, performed at various times throughout this investigation are shown in Table 4.

Run	Characteristic Concentration (µg/L)	Instrumental Detection Limit (µg/L)	Drift factor	Warnings
1	0.7	1.5	0.1	None
2	0.6	1.4	0.6	None
3	0.7	1.2	0.2	None
Mean	0.67	1.4		

Table 4: 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 did not generate any warnings, indicating that its internal statistical tests were satisfied. The IDL for arsenic measured under the conditions described has therefore been shown to be 1.4 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 2-3 times the estimated IDL. For initial estimates of the MDL, the laboratory blank was therefore fortified with 2.5 µg/L of arsenic. 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. For these measurements, the relative standard deviation of the seven measurements was consistently lower than 10 %, and so a new set of solutions fortified to 1.0 µg/L was used. The results of a typical set of 7 replicate analyses of these solutions is shown in Table 5.

Sample	Measured Concentration (µg/L)
MDL1	1.18
MDL2	0.77
MDL3	0.70
MDL4	1.16
MDL5	0.91
MDL6	0.98
MDL7	1.24
Mean	0.99
Method Detection Limit	0.66
Relative Standard Deviation	21.2 %

Table 5: MDL Results

The MDL was estimated five 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 0.6 µg/L, which can be considered to be representative of the performance of the laboratory and the instrument. The relative standard deviation of the MDL from all the estimates was 12 %.

Table 2 of the Method shows some typical single laboratory MDLs; the MDL value given for arsenic is 0.5 µg/L. However, MDL values themselves will show variations, as they are calculated using statistics based on small numbers of replicates.

The upper limit of the LDR for arsenic has been shown to be 120 µg/L. Recovery of the arsenic contained in the QCS sample was 99.0 %, and the Method Detection Limit was found to be 0.6 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 arsenic.

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 analysed, and are discussed in detail in reference (i).

Several 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.

The QC results obtained during a typical run are shown in Table 6.

QC Test	Measured Result (µg/L)	Expected Result (µg/L)	Pass Criteria	Test Result
Initial IPC	51.2	50.0	±5 % (47.5 - 52.5 µg/L)	PASS
Calibration blank	0.6	0	±IDL (±1.2 µg/L)	PASS
LRB	nd	0	<2.2*MDL (<1.3 µg/L)	PASS
LFB	19.3	20.0	85 - 115 % (17 - 23 µg/L)	PASS
Continuing IPC 1	53.0	50.0	±10 % (45 - 55 µg/L)	PASS
Calibration blank	nd	0	±IDL (±1.2 µg/L)	PASS
Continuing IPC 2	51.9	50	±10 % (45 - 55 µg/L)	PASS
Calibration blank	0.7	0	±IDL (±1.2 µg/L)	PASS
Final IPC	50.7	50	±10 % (45 - 55 µg/L)	PASS
Calibration blank	nd	0	±IDL (±1.2 µg/L)	PASS

nd = not detected. The measured result was below the MDL of 0.6 µg/L.

Table 6: Typical QC Results from a sample run

The database filtering functions provided by the SOLAAR software were used to automatically collate the results for the Continuing Instrument Performance Check for the sample runs performed over a four week period, and present them as QC Control Chart, shown in Figure 11.

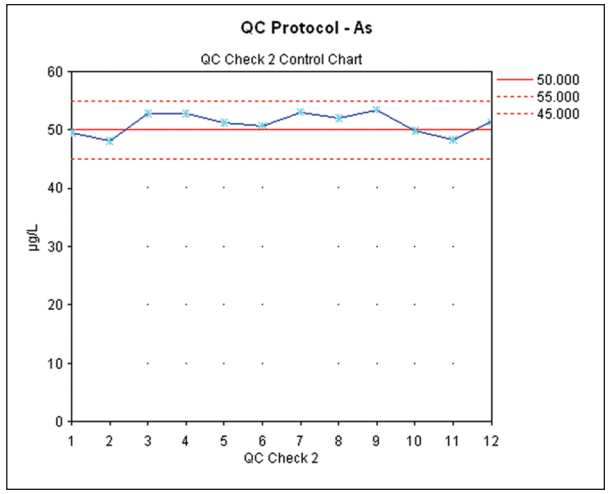

Figure 11: Continuing IPC results over 4 weeks

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 samples analysed were assessed by automatically spiking the samples using the Furnace Autosampler 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 7.

Sample	Background signal (abs.s)	Measured sample concentration (µg/L)	Measured LFM sample concentration (µg/L)	Analyte Recovery
SLRS 1	0.04	nd	23.0	92 %
SLRS 2	0.04	nd	25.0	100 %
SLEW 1	0.30	nd	19.8	79 %
Tap water	0.07	nd	22.8	91 %
Drinking water	0.06	nd	22.1	88 %
Mineral water	0.07	0.7	23.3	93 %

nd = not detected. The measured result was below the MDL of 0.6 µg/L.

Table 7: 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. All the recoveries are within the acceptable range, and so this implementation of the Method has been shown to give acceptable analyte recoveries for the samples examined.

The Method goes on to define procedures that should be used when the analyte recoveries fall outside the acceptable limits. Although the recovery from the SLEW1 LFM sample is within the limits specified in the Method, it is significantly poorer than the recovery from the other samples investigated. The SLEW1 sample, and an LFM prepared from it, were therefore analyzed using the Method of Standard Additions (MSA), as defined in Section 11.5 of the Method. The LRB, LFB and QCS samples were also measured using the MSA in the same run.

Sample	Background signal (abs.s)	Measure concentration (µg/L)	Measured spike concentration (µg/L)	Recovery
LRB		nd		
LFB		20.2		104 %
QCS		19.6		99.2 %
SLEW1	0.15	nd	25.1	100.4 %

nd = not detected. The measured result was below the MDL of 0.6 µg/L.

Table 8: Results using MSA calibration

The Standard Additions calibration graph for the SLEW1 LFM is shown in Figure 12.

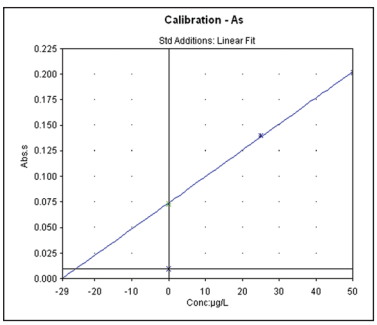

Figure 12: SLEW1 LFM using MSA calibration

As a further check on the Data Quality, a sample of the NIST 1640 Certified Reference Material (Trace Elements in Natural Water) was analyzed five times over a period of four weeks. The arsenic concentration in this material is certified at 26.67 ± 0.41 µg/Kg. The mean measured result obtained was 25.0 µg/L, with a relative standard deviation of 4.6 %. This is 94 % 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 Atomic Absorption Spectrometer. The recovery was close to the lower limit of the criteria for one 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 iCE 3000 Series Atomic Absorption Spectrometers fitted with Zeeman Graphite Furnace and Graphite Furnace Autosamplers are entirely suitable for the determination of arsenic 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 wizard, 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 Thermo Scientific 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) Palladium Nitrate-Magnesium Nitrate Modifier for Electrothermal Atomic Absorption Spectrometry. Welz, Schlemmer and Mudakavi, Journal of Analytical Atomic Spectrometry, vol. 7, p1257, 1992.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

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