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Validation Report for the Determination of Major and Trace Anions by Ion Chromatography (DX-600)

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The Dionex DX600 ion chromatograph

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Contents

FIGURES

TABLES

1. Method Overview

1.1 INSTRUMENTATION

The Ion Chromatograph used is a Dionex DX-600 instrument with suppressed conductivity and UV detection. Suppression and separation are performed by a Dionex column set consisting of an anion self-regenerating suppressor (ASRS), an AG14 guard column and an AS14 analytical column. The system is controlled and data collected by a dedicated PC through dedicated software (Chromeleon v6.40), which controls all functions associated with the instrument. A summary of typical instrument operating conditions is given in Table 1.

Table 1 Summary of Instrumental and Analytical Parameters

Parameter	Standard Operating Condition
Guard column	Dionex AG14
Analytical column	Dionex AS14
Eluent	3.5mM Na_2CO_3/1.0mM $NaHCO_3$
Eluent feed pressure	6 to 9 psi
Eluent degas	>20 minutes with He gas
Sample loop	Nominal 100 µl
Pump pressure	1000 to 3000 psi
Background conductivity	10 to 30 µS
UV absorbance	205 nm
Pump rate	1.2 ml min^{-1}

1.2 THEORY

A known quantity of sample is injected into a stable flow of mobile phase maintained by the instrument's pump. The eluent and sample mixture pass though the suppressor, which reduces the conductivity of the eluent and increases the conductivity of the analyte by the electrolytic exchange of sodium and hydrogen ions across a cation membrane. Highly conducting sodium carbonate and sodium bicarbonate are converted into poorly conducting carbonic acids by the replacement of sodium for hydrogen; poorly conducting anionic salts in the sample are converted into more conductive anionic salts, thus improving the conductivity detector background/response ratio. The now 'suppressed' eluent and sample mixture passes through the guard column, the function of which is to protect the analytical column from contamination or damage. The mixture then passes though the analytical column. The various anions are differentially retarded on the column according to size and charge, which dictate their affinity for the stationary and mobile phases. The conductivities and UV absorbances of the separated anions eluted from the column are detected as transient peaks using both electrochemical and UV absorbance detectors. Quantification is subsequently achieved by comparing their areas to those of standards with known concentrations using the dedicated instrument software.

1.3 ANALYTICAL METHOD

The instrumental operating conditions are given in Table 1.

The instrument is calibrated at the beginning of every analytical run using twelve standards, two of which are prepared manually, the other ten are prepared on line by the instrument. QC and blank samples are analysed at the start and end of each run and after not less than every 20 samples.

Further details of the analytical method, including the concentration ranges for the standards, details of their preparation, etc are given in BGS Technical Procedure AGN 2.3.6; *Determination of major and trace anions by ion chromatography*.

2 Scope

The scope of this validation report is the determination of F^-, Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-} and SO_4^{2-} by electrochemical detection and NO_2^-, Br^- and NO_3^- by UV absorbance detection in natural waters, including pore-waters, and synthetic or experimental fluids, including hydrothermal fluids and aqueous leachates. The scope assumes that the solutions are diluted to a total anion concentration no greater than 1000 mgl^{-1}.

The validation has been performed on a range of matrices representing this scope (see section 3.1 for further details).

3 Method Validation Procedure and Criteria

Method validation was carried out as a planned activity, according to BGS Operating Procedure AGN 1.6, based on the method of Cheeseman and Wilson (1989).

3.1. PREPARATION AND MEASUREMENT OF VALIDATION SOLUTIONS

3.1.1 Test Solutions for Cheeseman and Wilson Validation Exercise

3.1.1.1 Blank

Because peaks are generally not observed in deionised water, the standard deviation on the repeated measurement of a true 'blank' solution could not be used as the basis for determining limits of detection. Vanatta and Coleman (1997) recommend that limits of quantification are instead based on repeated analysis of a low concentration standard. This approach is considered acceptable so long as the concentrations in the standard used as a 'blank' are not more than five times the concentrations of the calculated limits of detection. The 'pseudo blank' used for the validation exercise is given in Table 2.

Table 2 Pseudo Blank Concentrations

Anion	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	HPO_4^-	SO_4^{2-}
	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$
'Pseudo blank' concentration	0.005	0.025	0.010	0.020	0.010	0.050	0.050

3.1.1.2 High and Low Standards

Two standards representing 20% and 80% of the upper calibration limit were used (calibration standards 8 and 11).

3.1.1.3 Sample Matrices and Spike Tests

Validation data were acquired for three test matrices representative of the scope of the method:

(i) Keyworth tap water (low salinity matrix).

(ii) Atlantic Ocean sea water (high salinity matrix).

A bulk solution for this matrix was prepared by diluting the neat sea water (purchased from Ocean Scientific International) by a factor of 50 with deionised water in order to reduce the total anion concentration below 1000 mgl^{-1}. At this dilution, Cl^- still falls outside the calibration range, however, further dilution was deemed unnecessary as the resulting sample would essentially contain just Cl^-, the validation of which is covered in the low and contaminated matrices.

(iii) Contaminated Groundwater (waste matrix).

This is a typical contaminated landfill leachate filtered through a nominal 0.2 μm filter. To bring all species within analytical range, the leachate was diluted by a factor of 10 with deionised water and used as the matrix for validation.

A total volume of 4 l of the low and high validation solutions were prepared. The contaminated ground water was prepared from an actual landfill leachate sample of which there was only enough to prepare approximately 2.5 l; unfortunately, this matrix was consumed before all five validation runs could be completed. Data for the waste matrix are still included within the validation report, although it should be noted that the statistics are based only on three batches of four samples.

Each of the matrix samples described above were analysed neat and with the addition of a spike. Each spiked matrix was prepared volumetrically by adding 0.5 ml of spike and making up to 50 ml with the relevant matrix. Spike stock and relevant 'in sample' concentrations are given in Table 3.

Table 3 Summary of Spike and Spiked Sample Concentrations

Anion	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	HPO_4^-	SO_4^{2-}
	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$
Spike conc.	250	1000	250	250	1000	500	5000
Spike sample conc.	2.50	10.0	2.50	2.50	10.0	5.00	50.0

The solutions analysed in the validation process are given in Table 4. All validation samples were prepared from stock solutions on a daily basis. All the validation solutions were taken through the normal analytical procedure and analysed four times in random order on at least five separate runs (with the exception of the contaminated matrix and spike, which was consumed after just three successful runs). Normal instrument shutdown was carried out between each run.

Table 4 Validation Solutions Analysed for Each Anion.

Validation Solution	Description of Solution
Blank	Pseudo blank described in Table 2
Low Standard	20% of calibration range
High Standard	80% of calibration range
Low Matrix Sample	Keyworth tap water
Low Matrix Spiked Sample	Keyworth tap water + spike
High Matrix Sample	As described in 3.1.1.3 (ii)
High Matrix Spike Sample	High matrix + spike
Contaminated Matrix	As described in 3.1.1.3 (iii)
Contaminated Matrix Spike Sample	Contaminated Matrix + Spike

3.1.2 Aquacheck Proficiency Testing

In addition to the Cheeseman and Wilson test solutions specified in 3.1.1, a number of Aquacheck proficiency testing samples were also analysed on various runs.

3.2 VALIDATION CALCULATIONS

The results for each of the validation runs have been compiled into an Excel validation spreadsheet. Data for each species have subsequently been transferred into separate Cheeseman and Wilson spreadsheets. Separate spreadsheets are available for each species in each matrix for each relevant detector. Calculations performed automatically within the spreadsheets give rise to data for:

Limit of detection;

Standard deviation;

Percent bias;

Percent recovery of spiked samples;

Degrees of freedom;

Uncertainty (derived from estimated bias and precision).

3.3. ACCEPTANCE CRITERIA

Acceptance criteria were established as part of the validation plan before commencing the validation exercise. The criteria were based on desirable performance targets for the technique rather than any specific regulatory requirements.

3.3.1 Accuracy and Bias

Based on the Cheeseman and Wilson exercise, the absolute value of the percentage bias on the high and low standards should be <5%, and the percentage spike recovery should be between 95 to 105% for all matrices. Supporting data from analysis of Aquacheck samples should be within 10% of accepted reference values, with a bias of no more than 8%.

3.3.2 Precision (Repeatability and Reproducibility)

The precision, based on the total standard deviation (S_t) for the high and low standards and the spiked and unspiked samples should be less than either 5% or the minimum target concentration, whichever is the largest. Supporting data from analysis of the QC solution should be within 10% at the 3s level.

3.3.3 Limit of Detection and Target Concentrations

There is no requirement for the method to meet any statutory concentration limits, therefore, the minimum target concentration is interpreted as being a target Limit of Quantification (LoQ). The limit of detection should be less than four times the LoQ's given in Table 5. Supporting data from the analysis of deionised water blanks and serial dilution of low standards will be used to support these limits.

Table 5 Target Quantification Limits.

Anion	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	HPO_4^-	SO_4^{2-}
	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
Target LoQ	0.010	0.050	0.010	0.020	0.010	0.10	0.100

3.3.4 Measurement of Uncertainty

The expanded uncertainty for all determinands (using a coverage factor of 2) should be better than 10% at concentrations an order of magnitude or more above the target limit of quantification.

4. Calibration Range and Linearity

Calibration was performed according to the regime described in AGN 2.3.6. The upper calibration limits for each anion are given in Table 6.

Table 6 Upper Calibration Limits

Anion	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	HPO_4^-	SO_4^{2-}
	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
Maximum concentration	5.00	100	50.0	5.00	5.00	10.0	200

In total, nine separate analytical runs were carried out as part of the validation exercise. Each calibration was inspected to ensure its quality (R-squared values must be better than 99.7% and the offset must be less than ±0.05). Over the calibration ranges used for the species under consideration, there is a small departure from linearity. A linear fit is, therefore, inappropriate. As part of the validation runs, either one of two calibration fits were used at the discretion of the qualified operator. These are both quadratic fits, either with (YQuad) or without (Y0QOff) forced fit though the intercept. This approach gave acceptable R-squared and offset performance for all calibrations carried out as part of the validation exercise, as summarised for the ECD and

AD detectors in Tables 7 and 8 respectively. Example calibration graphs for ECD and AD nitrite are given in Figures 1 and 2 respectively.

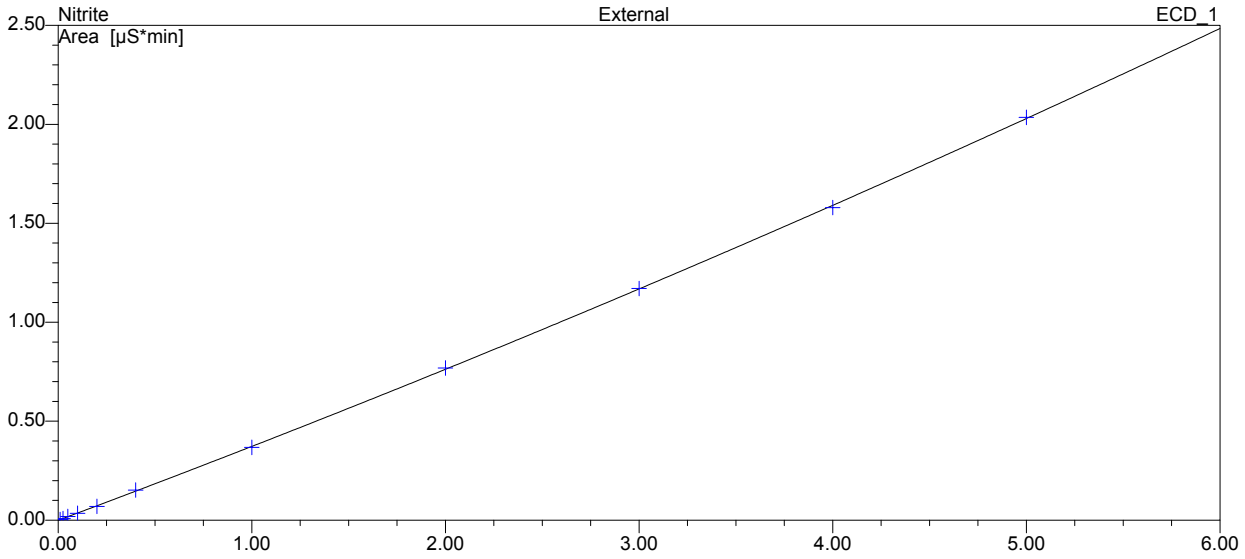

Figure 1 An ECD example calibration plot for nitrite using a 'Y0QOff' fit with an R-squared value of 99.990% and an offset of –0.0007.

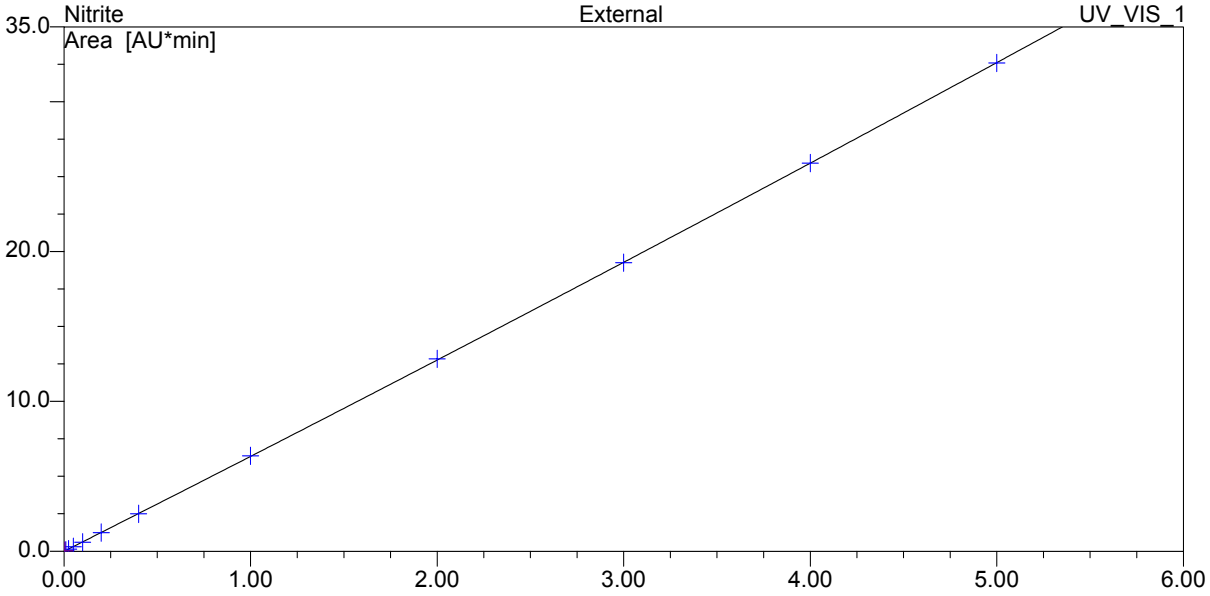

Figure 2 An AD example calibration plot for nitrite using a 'Y0QOff' fit with an R-squared value of 99.996% and an offset of –0.0028.

Table 7 R-Squared and Offset Data for Validation Calibrations for ECD.

Run Date	Fit	R-Squared %	Offset	Run Date	Fit	R-Squared %	Offset	Run Date	Fit	R-Squared %	Offset
Fluoride				Bromide				Phosphate			
29-Jan	Y0QOff	99.994	-0.0002	29-Jan	Y0QOff	99.955	0.0003	29-Jan	Y0QOff	99.969	-0.0025
30-Jan	Y0QOff	99.996	-0.0001	30-Jan	Y0QOff	99.990	-0.0005	30-Jan	Y0QOff	99.993	-0.0011
31-Jan	Y0QOff	99.985	-0.0009	31-Jan	Y0QOff	99.993	0.0000	31-Jan	Y0QOff	99.970	-0.0010
14-Feb	Y0QOff	99.969	-0.0011	14-Feb	Y0QOff	99.986	0.0005	14-Feb	Y0QOff	99.998	-0.0030
01-Apr	Y0QOff	99.969	-0.0006	01-Apr	Y0QOff	99.994	-0.0005	01-Apr	Y0QOff	99.980	0.0014
02-Apr	Y0QOff	99.977	-0.0001	02-Apr	Y0QOff	99.978	-0.0011	02-Apr	YQuad	99.860	0.0000
04-Apr	Y0QOff	99.996	-0.0009	04-Apr	Y0QOff	99.980	-0.0002	04-Apr	YQuad	99.958	0.0000
07-Apr	Y0QOff	99.973	-0.0005	07-Apr	YQuad	99.991	0.0000	07-Apr	YQuad	99.899	0.0000
08-Apr	Y0QOff	99.975	0.0001	08-Apr	Y0QOff	99.981	0.0003	08-Apr	Y0QOff	99.991	-0.0006
	Mean	*99.982*	*-0.0005*		*Mean*	*99.983*	*-0.0001*		*Mean*	*99.958*	*-0.0008*
	RSD	*0.010*	*0.0004*		*RSD*	*0.009*	*0.0004*		*RSD*	*0.035*	*0.0010*
Chloride				Nitrate				Sulphate			
29-Jan	YQuad	99.904	0.0000	29-Jan	Y0QOff	99.979	-0.0026	29-Jan	YQuad	99.878	0.0000
30-Jan	Y0QOff	99.914	-0.0100	30-Jan	Y0QOff	99.979	-0.0024	30-Jan	Y0QOff	99.900	-0.0375
31-Jan	Y0QOff	99.910	-0.0096	31-Jan	Y0QOff	99.982	-0.0018	31-Jan	YQuad	99.887	0.0000
14-Feb	Y0QOff	99.909	-0.0010	14-Feb	YQuad	99.893	0.0000	14-Feb	Y0QOff	99.882	-0.0379
01-Apr	YQuad	99.898	0.0000	01-Apr	Y0QOff	99.982	-0.0025	01-Apr	YQuad	99.885	0.0000
02-Apr	YQuad	99.873	0.0000	02-Apr	YQuad	99.979	0.0000	02-Apr	YQuad	99.879	0.0000
04-Apr	YQuad	99.896	0.0000	04-Apr	Y0QOff	99.981	-0.0022	04-Apr	YQuad	99.885	0.0000
07-Apr	YQuad	99.905	0.0000	07-Apr	YQuad	99.985	0.0000	07-Apr	YQuad	99.896	0.0000
08-Apr	Y0QOff	99.919	-0.0128	08-Apr	YQuad	99.967	0.0000	08-Apr	YQuad	99.909	0.0000
	Mean	*99.903*	*-0.0037*		*Mean*	*99.970*	*-0.0013*		*Mean*	*99.889*	*-0.0084*
	RSD	*0.009*	*0.0047*		*RSD*	*0.018*	*0.0011*		*RSD*	*0.008*	*0.0130*
Nitrite											
29-Jan	Y0QOff	99.923	-0.0013								
30-Jan	Y0QOff	99.990	-0.0007								
31-Jan	Y0QOff	99.987	-0.0001								
14-Feb	Y0QOff	99.961	-0.0009								
01-Apr	Y0QOff	99.987	0.0001								
02-Apr	Y0QOff	99.989	0.0002								
04-Apr	Y0QOff	99.971	-0.0010								
07-Apr	YQuad	99.993	0.0000								
08-Apr	Y0QOff	99.994	-0.0001								
	Mean	*99.977*	*-0.0004*								
	RSD	*0.017*	*0.0005*								

Table 8 R-Squared and offset data for validation calibrations for AD.

Run Date	Fit	R-Squared %	Offset	Run Date	Fit	R-Squared %	Offset	Run Date	Fit	R-Squared %	Offset
Nitrite				Bromide				Nitrate			
29-Jan	Y0QOff	99.990	-0.0037	29-Jan	Y0QOff	99.965	-0.0064	29-Jan	Y0QOff	99.998	-0.0213
30-Jan	Y0QOff	99.996	-0.0028	30-Jan	Y0QOff	99.995	0.0005	30-Jan	Y0QOff	99.995	-0.0095
31-Jan	Y0QOff	99.995	-0.0055	31-Jan	Y0QOff	99.964	-0.0077	31-Jan	Y0QOff	99.998	-0.0007
14-Feb	Y0QOff	99.973	-0.0249	14-Feb	Y0QOff	99.993	-0.0069	14-Feb	YQuad	99.831	0.0000
01-Apr	Y0QOff	99.975	0.0034	01-Apr	Y0QOff	99.990	-0.0014	01-Apr	Y0QOff	99.991	0.0053
02-Apr	Y0QOff	99.981	0.0037	02-Apr	Y0QOff	99.975	0.0010	02-Apr	YQuad	99.994	0.0000
04-Apr	Y0QOff	99.990	0.0114	04-Apr	Y0QOff	99.986	-0.0019	04-Apr	Y0QOff	99.996	0.0078
07-Apr	YQuad	99.903	0.0000	07-Apr	YQuad	99.959	0.0000	07-Apr	YQuad	99.994	0.0000
08-Apr	Y0QOff	99.982	0.0050	08-Apr	Y0QOff	99.969	0.0000	08-Apr	YQuad	99.986	0.0000
	Mean	*99.976*	*-0.0015*		*Mean*	*99.977*	*-0.0025*		*Mean*	*99.976*	*-0.0020*
	RSD	*0.017*	*0.0069*		*RSD*	*0.012*	*0.0030*		*RSD*	*0.032*	*0.0059*

5 Accuracy, Bias and Spike Recovery Tests

No Certified Reference Materials (CRMs) are relevant to the determination of anions in waters. However, the accuracy of the determinations by ion chromatography can be assessed from consideration of the method validation experiments described in Section 3 and data from the Aquacheck proficiency testing scheme for waters.

5.1 METHOD VALIDATION TESTS

The data obtained for the method validation tests are summarised in Appendix 1. For each species for each relevant detector, up to three separate summary sheets are provided, covering the low salinity, high salinity and waste matrices. For chloride, no data are available for the high salinity matrix, in which the chloride concentration was designed to exceed the normal calibration range. For nitrite by electrochemical detection, no data are available for the high salinity matrix because of interference from the high chloride; data are available from the absorbance detector.

In all cases, the default statistics have been calculated using total standard deviations (S_t), i.e. the standard deviation on all 20 data points gathered for each species. Additionally, for nitrite by ED in the waste matrix, nitrite by AD in the waste and high matrices and nitrate by AD in the high salinity matrix, further summary sheets are included using statistics calculated using the 'within batch' standard deviation (S_b). This statistic calculates the average standard deviation based on the standard deviations of the four samples within each batch, and is useful in cases where there may be evidence of sample instability.

Data for the pseudo blank and low and high standards are also included in the summaries. It should be noted that these data are repeated in each species' summary sheets, and are not actually determined separately for each matrix.

5.1.1 Bias

Calibration bias may be estimated from data for the 20% and 80% calibration solutions. Additionally, because a pseudo blank of known concentration was used, it is also possible to calculate an estimated bias from these data. A summary of the bias data is given in Table 9.

For the 20% and 80% standards, the percentage bias data are all well within the target value of ±8%. Indeed, all are within ±3% and all but chloride and sulphate are within ±1%.

The percentage bias on the pseudo blank data are, understandably, much higher since the concentrations of the species in the pseudo blank (see Table 2) are all actually below the target limits of quantification (see Table 5). Nevertheless, these data are all considered highly acceptable, and lend supporting evidence as to the suitability of the limits of quantification (see Section 8).

Table 9 Bias Data from Validation Tests

Anion	Bias of Pseudo Blank	Bias of 20% standard	Bias of 80% standard	Mean
	%	%	%	*%*
F^-	-18.40	0.38	0.43	*0.41*
Cl^-	40.44	3.12	1.54	*2.33*
NO_2^- (ECD)	-8.10	1.24	0.56	*0.90*
Br^- (ECD)	3.20	1.09	0.28	*0.69*
NO_3^- (ECD)	41.85	0.94	0.97	*0.96*
HPO_4^{2-}	-18.43	0.72	0.12	*0.42*
SO_4^{2-}	-11.76	2.49	1.14	*1.82*
NO_2^- (AD)	-18.80	0.32	0.07	*0.20*
Br^- (AD)	-0.17	0.78	0.22	*0.50*
NO_3^- (AD)	26.40	0.54	0.60	*0.57*

5.1.2 Spike Recovery

Spike tests were carried out as described in Section 3.1.3.3. Summary data taken from the Cheeseman and Wilson calculations are given in Table 10.

Spike recoveries are conventionally calculated relative to the spike concentration. However, this method can lead to misleading results if the amount of spike added is relatively small compared to the concentration in the original matrix. Two types of recoveries have, therefore, been calculated. The first is calculated relative to the spike concentration (the conventional spike recovery) and are reported for all data except chloride and nitrite (by ECD) in the high matrix, for which no validation data are available because of the high concentration of Cl. The second set of recoveries are calculated relative to the sample concentration, and are reported for all species in which the concentration in the original matrix are at least one order of magnitude above the limit of quantification. It should be noted that the spike recoveries with respect to the sample are not a strict measure of accuracy, since the concentration in the original matrix is not an absolute value. Both sets of calculated recoveries are included in Table 10.

The conventional spike recoveries for all species (except chloride in the waste matrix) are within the target ±5% value. The chloride spike recovery in the waste matrix gives a value of 86.57%, which may still be considered acceptable given that the concentrations in the matrix samples are not absolute values, hence leading to an additional source of uncertainty. It should also be noted that, in this case, the concentration of chloride in the original matrix is very high (~78 mg l^{-1}) compared to the concentration of the spike (10 mg l^{-1}) and that the percentage recovery relative to the sample gives a perfectly acceptable value of 98.25%. Similarly, all other recoveries calculated with respect to the matrix rather than the spike are within the target ±5% value set for the conventional recovery tests.

Table 10 Spike and Sample Recoveries for Each Matrix

		Mean Matrix Concentration			Percentage Spike Recovery			Percentage Sample Recovery		
Anion	Spike Concentration	Low Matrix	High Matrix	Waste Matrix	Low Matrix	High Matrix	Waste Matrix	Low Matrix	High Matrix	Waste Matrix
	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	%	%	%	%	%	%
F^-	2.50	0.035	0.029	0.090	100.27	96.26	97.93	n/a	n/a	n/a
Cl^-	10.0	34.1	n/a	77.7	102.58	n/a	86.57	100.76	n/a	98.25
NO_2^- (ECD)	2.50	0.000	n/a	2.62	99.06	n/a	95.42	n/a	n/a	95.58
Br^- (ECD)	2.50	0.030	1.33	2.60	100.74	101.56	96.61	n/a	102.98	96.71
NO_3^- (ECD)	10.0	17.3	0.021	25.5	103.03	99.76	95.65	101.77	n/a	98.27
HPO_4^{2-}	5.00	2.56	0.000	0.289	97.47	97.68	98.47	95.01	n/a	n/a
SO_4^{2-}	50.0	71.5	58.0	105	101.36	104.84	95.07	100.96	104.22	97.64
NO_2^- (AD)	2.50	0.001	0.001	2.58	99.93	95.28	97.11	n/a	n/a	97.14
Br^- (AD)	2.50	0.034	1.47	2.58	99.53	100.05	97.90	n/a	100.08	97.94
NO_3^- (AD)	10.0	17.2	0.012	24.8	101.97	102.07	97.24	101.16	n/a	98.88

5.2 AQUACHECK PROFICIENCY TESTING

Accuracy may also be assessed by consideration of Z-scores from proficiency testing schemes, such as Aquacheck. The Aquacheck distributions consist of alternating matrices of a low TDS clean water, a relatively high TDS saline potable water and artificial waste water, with major element compositions representative of the scope of the method.

As part of the validation exercise, a number of Aquacheck samples were included within the analytical runs. These included clean water distributions 237 and 241, saline potable water distributions 238 and 242, and waste distributions 239 and 243. Clean waters were analysed for F^-, Cl^-, NO_2^-, NO_3^-, HPO_4^{2-} and SO_4^{2-}; saline potable waters for Cl^-, Br^- and SO_4^{2-}; and waste waters for Cl^-, NO_2^-, NO_3^- and HPO_4^{2-}. Summary data for each determinand are given in Tables 11 to 20.

Overall, the quality of the data is exceptionally good. All pass the Aquacheck Z-score criteria of ±2 and the validation target accuracy and bias (±10% and ±8% respectively) with only a few exceptions.

For fluoride, two results exceed the ±10% target. For distribution 237 the single failure (10.73) is considered a one-off. The data for distribution 241 are all high relative to the reference value, with one result having a mean difference of 19.12%. However, there is a significant difference between the reference values and the 'mean of all labs', against which the validation data are in much better agreement. The overall bias, even including the two failed data, is within the target ±8% limit.

For chloride, all data are well within the ±10% target values, with the exception of a one-off failure for distribution 239 (-10.25%). The overall bias is –2.45%.

For nitrite, by both electrochemical and absorbance detection, data for distribution 237 all fail target criteria. This appears to be anomalous, and is probably related to deterioration or contamination of the sample, which is relatively old (see also nitrate and sulphate). Data for more recent distributions 239 and 243 pass all target criteria, with an average bias (excluding distribution 237) better than ±1% for both detectors.

For bromide, data for the absorbance detector meet all criteria, with a bias of less than 3%, even though the concentrations in the samples are within four times the limit of quantification. The data for the electrochemical detector fail the ±10% criteria for three of the seven samples tested, but are all within ±20%, which is excellent given that the concentrations are within three times the limit of quantification.

For nitrate, by both electrochemical and absorbance detection, data for distribution 237 all fail target criteria. This appears to be anomalous, and is probably related to deterioration of the sample, which is relatively old (see also nitrite and sulphate). Data for more recent distributions 239, 241 and 243 pass all target criteria, with an average bias (excluding distribution 237) better than ±6% for both detectors.

For phosphate, all data pass target criteria, with an overall bias of 1.99%

For sulphate, data for distribution 237 all fail target criteria. This appears to be anomalous, and is probably related to deterioration of the sample, which is relatively old (see also nitrite and nitrate). Data for more recent distributions 238, 241 and 242 pass all target criteria, with an average bias (excluding distribution 237) better than ±4%.

Table 11 Fluoride Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
237	1.151	1.160	1.130	1.81	0.18
237	1.170	1.160	1.130	3.54	0.35
237	1.186	1.160	1.130	4.98	0.50
237	1.165	1.160	1.130	3.08	0.31
237	1.213	1.160	1.130	7.32	0.73
237	1.251	1.160	1.130	10.73	1.07
241	1.198	1.235	1.090	9.93	0.99
241	1.298	1.235	1.090	19.12	1.91
241	1.160	1.235	1.090	6.42	0.64
			Mean	*7.44*	*0.74*

Table 12 Chloride Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
237	8.921	9.438	9.450	-5.48	-0.52
237	9.086	9.438	9.450	-3.73	-0.35
237	9.081	9.438	9.450	-3.79	-0.36
237	9.085	9.438	9.450	-3.74	-0.35
237	9.054	9.438	9.450	-4.07	-0.38
237	9.098	9.438	9.450	-3.60	-0.34
238	281.289	280.600	280.000	0.46	0.05
238	293.930	280.600	280.000	4.97	0.50
239	9.674	10.080	10.080	-4.03	-0.40
239	9.796	10.080	10.080	-2.82	-0.28
239	9.790	10.080	10.080	-2.88	-0.29
239	10.006	10.080	10.080	-0.73	-0.07
239	9.902	10.080	10.080	-1.77	-0.18
239	10.196	10.080	10.080	1.15	0.12
239	9.047	10.080	10.080	-10.25	-1.03
241	25.582	25.400	25.400	0.71	0.07
241	26.044	25.400	25.400	2.54	0.25
241	24.356	25.400	25.400	-4.11	-0.41
242	137.778	142.800	135.000	2.06	0.21
243	31.481	29.830	29.800	5.64	0.56
			Mean	*-2.45*	*-0.24*

Table 13 ECD Nitrite Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
237	0.436	0.352	0.348	25.32	2.53
237	0.324	0.352	0.348	-6.95	-0.70
237	0.395	0.352	0.348	13.39	1.34
237	0.413	0.352	0.348	18.74	1.87
237	0.421	0.352	0.348	21.06	2.11
237	0.382	0.352	0.348	9.89	0.99
239	2.347	2.308	2.332	0.64	0.06
239	2.392	2.308	2.332	2.55	0.26
239	2.318	2.308	2.332	-0.60	-0.06
239	2.404	2.308	2.332	3.08	0.31
239	2.445	2.308	2.332	4.86	0.49
239	2.350	2.308	2.332	0.77	0.08
239	2.466	2.308	2.332	5.74	0.57
239	2.250	2.308	2.332	-3.51	-0.35
243	5.464	5.186	5.255	3.97	0.40
			Mean	4.96	0.50
		Mean (excluding Distribution 237)		*-0.21*	*-0.02*

Table 14 ECD Bromide Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
238	0.036	0.043	0.042	-14.45	-1.45
238	0.050	0.043	0.042	17.30	1.73
238	0.039	0.043	0.042	-8.29	-0.83
238	0.050	0.043	0.042	18.72	1.87
238	0.042	0.043	0.042	-1.66	-0.17
242	0.064	0.068	0.064	-0.98	-0.10
242	0.067	0.068	0.064	3.88	0.39
			Mean	*2.07*	*0.21*

Table 15 ECD Nitrate Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
237	0.279	0.576	0.577	-51.55	-2.97
237	0.319	0.576	0.577	-44.62	-2.57
237	0.321	0.576	0.577	-44.17	-2.54
237	0.311	0.576	0.577	-45.94	-2.65
237	0.361	0.576	0.577	-37.28	-2.15
239	22.878	22.147	21.559	6.12	0.61
239	22.758	22.147	21.559	5.56	0.56
239	22.686	22.147	21.559	5.23	0.52
239	22.851	22.147	21.559	6.00	0.60
239	22.861	22.147	21.559	6.04	0.60
239	23.606	22.147	21.559	9.50	0.95
239	23.516	22.147	21.559	9.08	0.91
239	22.260	22.147	21.559	3.25	0.33
241	15.883	15.310	15.400	3.74	0.37
241	16.300	15.310	15.400	6.46	0.65
241	15.057	15.310	15.400	-1.65	-0.17
243	13.275	13.130	12.882	3.05	0.31
			Mean	*-9.48*	*-0.39*
		Mean (excluding Distribution 237)		*5.20*	*0.52*

Table 16 Phosphate Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
237	4.444	4.363	4.369	1.71	0.17
237	4.390	4.363	4.369	0.47	0.05
237	4.448	4.363	4.369	1.79	0.18
237	4.174	4.363	4.369	-4.47	-0.45
237	4.505	4.363	4.369	3.12	0.31
237	4.512	4.363	4.369	3.28	0.33
239	0.016	0.017	0.016	0.21	0.02
239	0.017	0.017	0.016	2.68	0.27
239	0.016	0.017	0.016	1.23	0.12
239	0.017	0.017	0.016	3.15	0.32
239	0.017	0.017	0.016	4.31	0.43
239	0.017	0.017	0.016	4.08	0.41
241	2.999	3.092	2.876	4.28	0.43
243	0.015	0.015	0.015	2.05	0.20
			Mean	*1.99*	*0.20*

Table 17 Sulphate Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
237	7.205	8.310	8.310	-13.29	-1.10
237	7.217	8.310	8.310	-13.15	-1.09
237	7.339	8.310	8.310	-11.68	-0.97
237	7.317	8.310	8.310	-11.96	-0.99
237	7.430	8.310	8.310	-10.59	-0.88
237	7.537	8.310	8.310	-9.31	-0.77
238	330.476	327.900	328.000	0.79	0.08
238	350.947	327.900	328.000	7.03	0.70
241	26.622	27.400	27.400	-2.84	-0.28
241	27.576	27.400	27.400	0.64	0.06
241	24.813	27.400	27.400	-9.44	-0.94
242	232.745	248.700	249.000	-6.42	-0.64
			Mean	*-6.97*	*-0.61*
		Mean (excluding Distribution 237)		*-3.45*	*-0.33*

Table 18 AD Nitrite Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
237	0.439	0.352	0.348	26.09	2.61
237	0.417	0.352	0.348	19.77	1.98
237	0.415	0.352	0.348	19.34	1.93
237	0.431	0.352	0.348	23.76	2.38
237	0.418	0.352	0.348	20.00	2.00
237	0.417	0.352	0.348	19.89	1.99
239	2.246	2.308	2.332	-3.67	-0.37
239	2.323	2.308	2.332	-0.37	-0.04
239	2.407	2.308	2.332	3.21	0.32
239	2.423	2.308	2.332	3.92	0.39
239	2.328	2.308	2.332	-0.16	-0.02
239	2.457	2.308	2.332	5.38	0.54
239	2.159	2.308	2.332	-7.40	-0.74
			Mean	*9.98*	*1.00*
		Mean (excluding Distribution 237)		*0.13*	*0.01*

Table 19 AD Bromide Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
238	0.044	0.043	0.042	4.74	0.47
238	0.040	0.043	0.042	-4.98	-0.50
238	0.045	0.043	0.042	7.11	0.71
238	0.042	0.043	0.042	-1.42	-0.14
238	0.045	0.043	0.042	7.35	0.73
242	0.067	0.068	0.064	4.66	0.47
			Mean	*2.91*	*0.29*

Table 20 AD Nitrate Aquacheck Data

Dist	Mean	Mean of all labs	Reference Value	Difference	Z-scores
	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	%	
237	0.348	0.576	0.577	-39.53	-2.28
237	0.365	0.576	0.577	-36.62	-2.11
237	0.349	0.576	0.577	-39.33	-2.26
237	0.342	0.576	0.577	-40.68	-2.34
237	0.400	0.576	0.577	-30.48	-1.76
239	21.878	22.147	21.559	1.48	0.15
239	22.466	22.147	21.559	4.21	0.42
239	22.438	22.147	21.559	4.08	0.41
239	22.557	22.147	21.559	4.63	0.46
239	22.681	22.147	21.559	5.21	0.52
239	22.098	22.147	21.559	2.50	0.25
241	15.856	15.310	15.400	3.57	0.36
241	15.480	15.310	15.400	1.11	0.11
			Mean	*-12.30*	*-0.62*
		Mean (excluding Distribution 237)		*3.35*	*0.33*

6. Precision

The overall precision of the method can be assessed by consideration of data obtained from the method validation tests described in Section 3 and data collected from QC samples.

The data obtained for the method validation tests are summarised in Appendix 1. Standard deviation data (expressed as a percentage relative to the mean concentration) are available for the 20% and 80% standards, the low salinity, high salinity and waste matrices (both with and without spike) and the pseudo blank.

The QC data established as part of the validation and subsequent analytical runs are summarised in Figures 3 to 12.

All of the relative standard deviation data (expressed at 1s) are summarised in Table 21.

Table 21 Summary of Relative Standard Deviation Data for Validation Samples and Quality Control Samples

		Validation Data								QC Data
Anion	Blank	Standard		Low Matrix		High Matrix		Waste Matrix		
		20%	80%	Sample	Spike	Sample	Spike	Sample	Spike	
F^-	21.59	1.316	1.278	4.079	3.170	120.5	3.183	4.507	4.038	1.782
Cl^-	21.67	1.164	0.6389	0.7247	0.7095	n/a	n/a	0.5839	0.4529	1.568
NO_2^- (ECD)	20.36	1.445	1.143	n/a	2.316	n/a	n/a	6.791	2.583	1.713
NO_2^- (ECD)*	n/a	n/a	n/a	n/a	n/a	n/a	n/a	2.209	2.036	n/a
Br^- (ECD)	10.56	0.9523	0.7554	19.36	1.786	2.222	2.347	4.083	1.796	1.592
NO_3^- (ECD)	30.72	1.686	1.221	1.236	2.262	309.3	1.716	2.892	0.8221	1.680
HPO_4^{2-}	23.14	1.010	0.6508	2.006	2.210	n/a	2.157	5.330	4.097	2.890
SO_4^{2-}	15.70	0.9205	0.5966	0.7282	0.7661	0.9485	1.067	0.848	0.740	1.453
NO_2^- (AD)	14.79	1.398	0.7496	190.1	2.550	183.0	3.341	1.579	1.938	1.491
NO_2^- (AD)*	n/a	n/a	n/a	n/a	n/a	51.39	2.088	n/a	n/a	n/a
Br^- (AD)	8.618	2.197	0.8050	8.959	2.577	1.300	1.576	2.045	1.661	1.255
NO_3^- (AD)	22.28	1.656	0.6697	0.5724	1.590	148.4	3.205	1.1280	1.125	0.7700
NO_3^- (AD)*	n/a	n/a	n/a	n/a	n/a	35.71	2.055	n/a	n/a	n/a

*Standard deviations calculated using 'within-batch' data

Overall, the quality of the data is exceptionally good. All are within the validation target criteria of 5% and the QC chart criteria of 10% at 3s (3.33% at 1s) with only a few exceptions.

The relative standard deviations on the pseudo blank data are, understandably, poorer than 10% in most cases since the concentrations of the species in the pseudo blank (see Table 2) are all below the target limits of quantification (see Table 5). Nevertheless, these data are all considered highly acceptable, and lend supporting evidence as to the suitability of the limits of quantification (see Section 8).

The data for nitrite and bromide in the low salinity matrix, fluoride, nitrite and nitrate in the high salinity matrix and phosphate in the waste matrix are all within three times the respective limits of quantification. As for the pseudo blank, it is, therefore, understandable that the data fail to meet the target value.

For nitrite by ED in the waste matrix, a relative standard deviation of 6.79 is obtained despite the concentration being well above the limit of quantification (~3 mg l^{-1}). This indicates there is some evidence of instability of nitrite in the waste matrix. As explained in Section 5.1, the relative standard deviation obtained using 'within batch' standard deviation (2.21%) is within the target value.

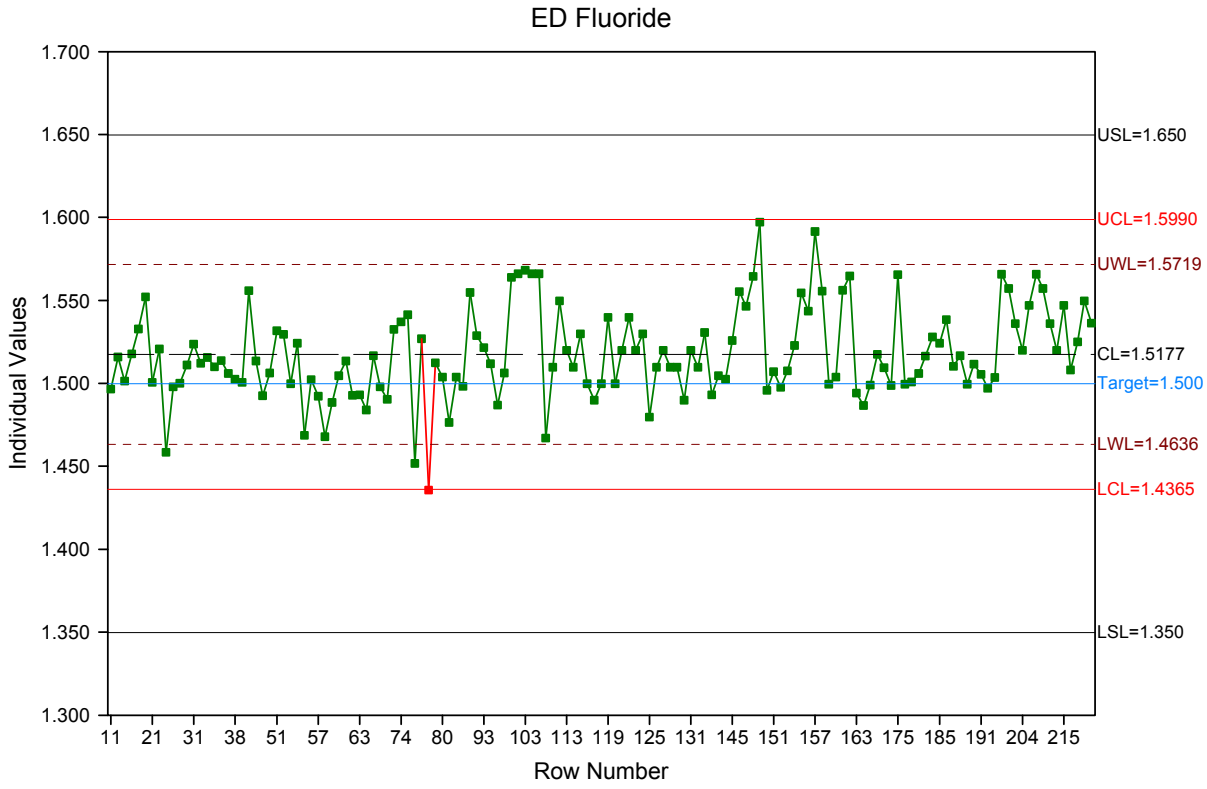

Figure 3 Fluoride QC Data

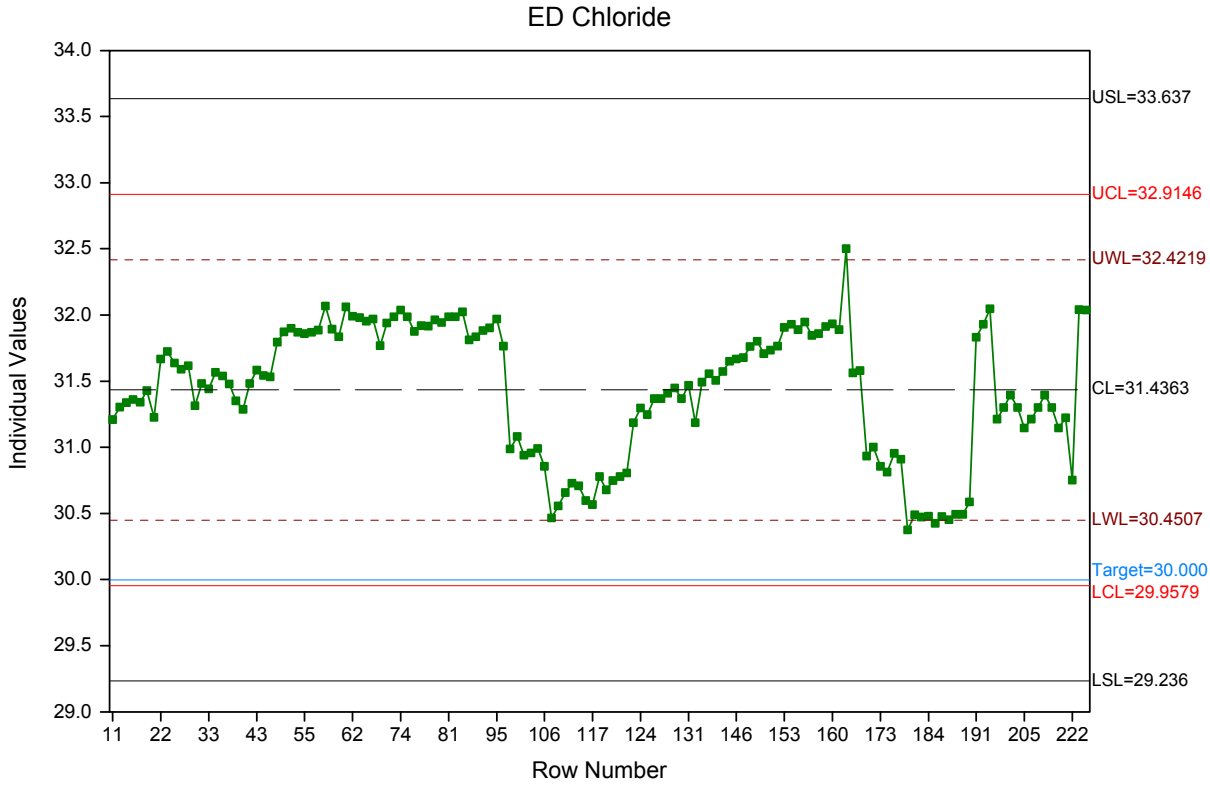

Figure 4 Chloride QC Data

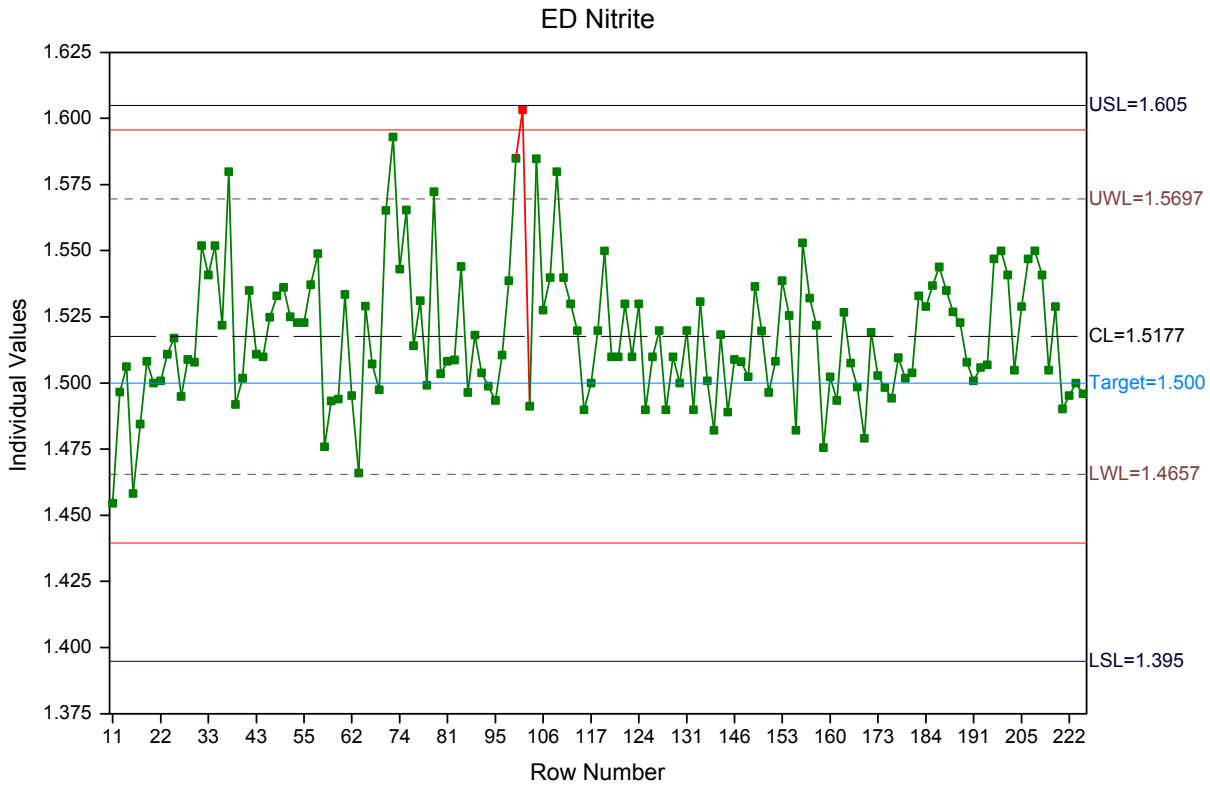

Figure 5 Nitrite QC Data by ECD

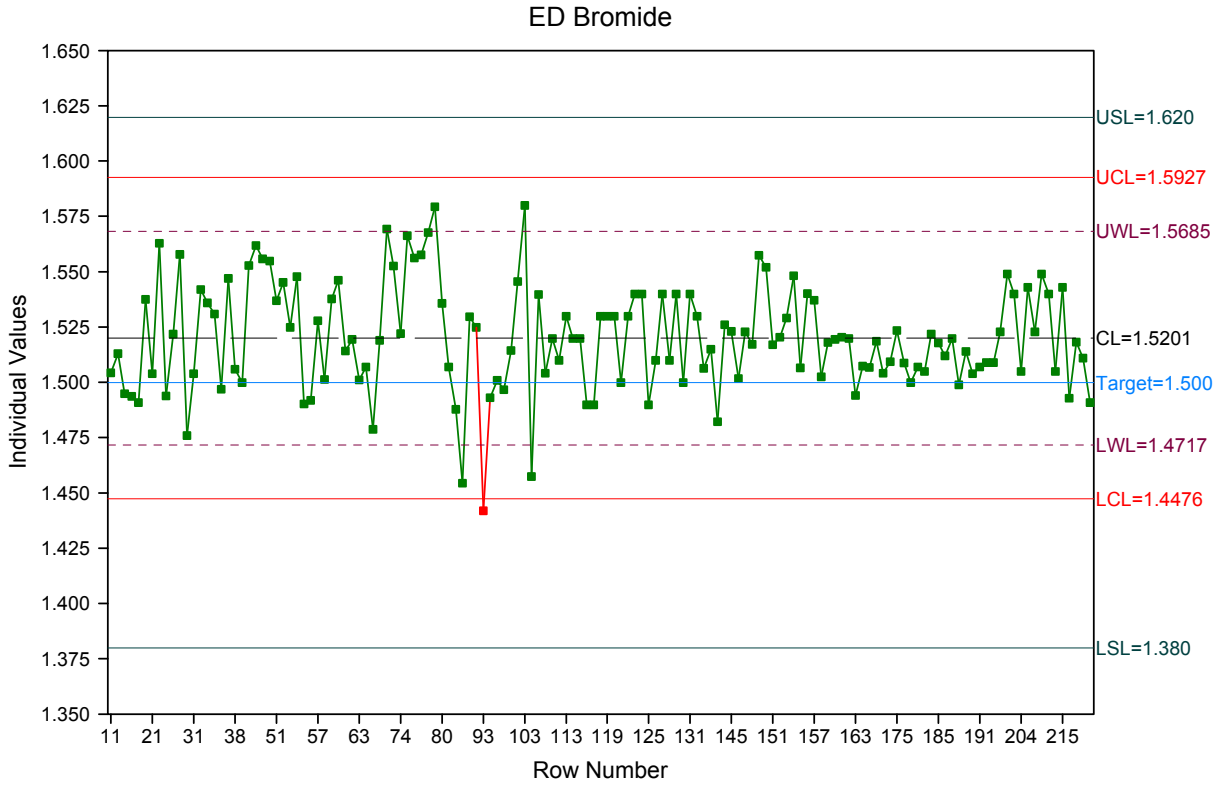

Figure 6 Bromide QC Data by ECD

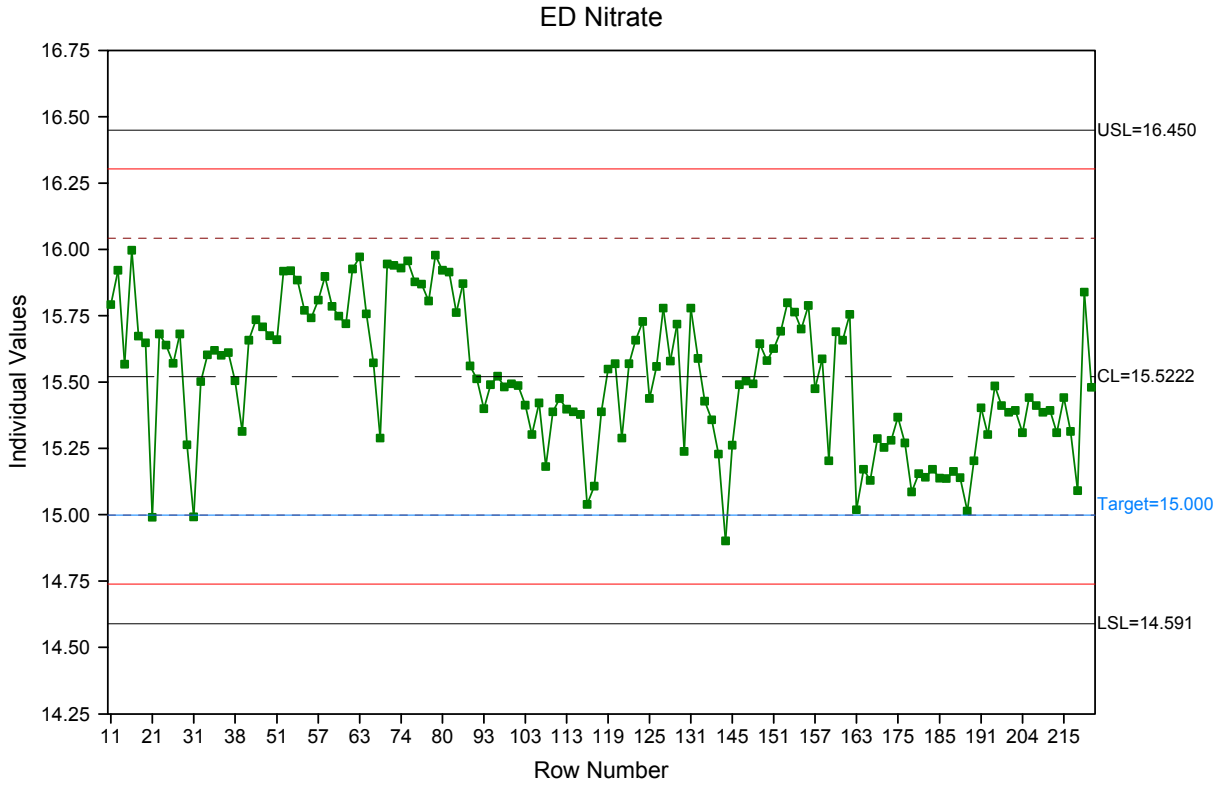

Figure 7 Nitrate QC Data by ECD

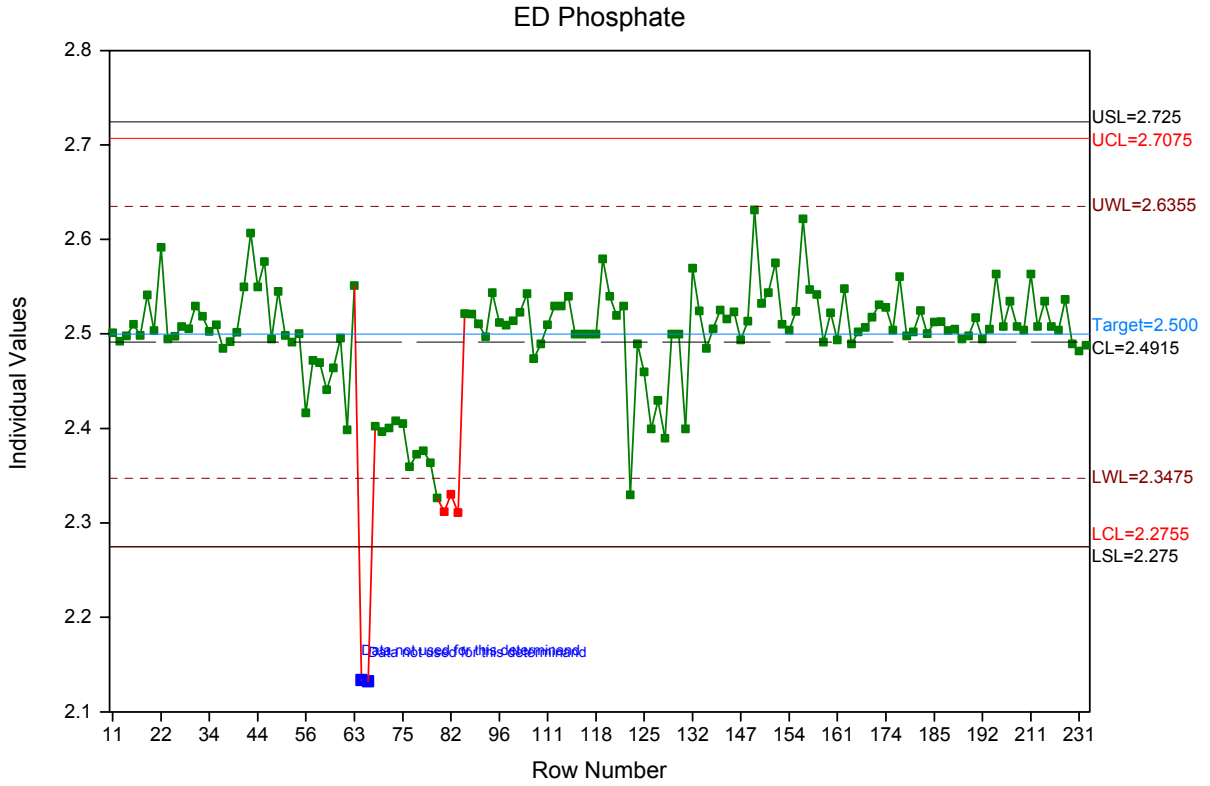

Figure 8 Phosphate QC Data

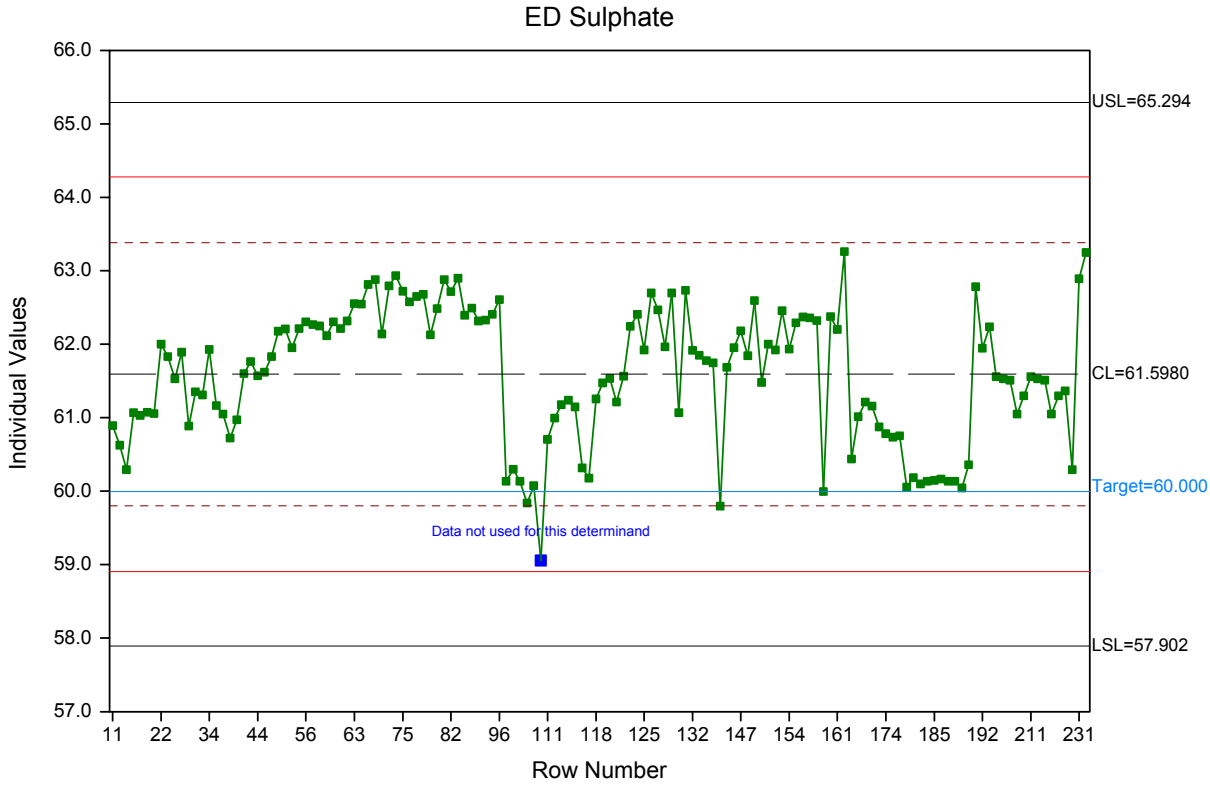

Figure 9 Sulphate QC Data

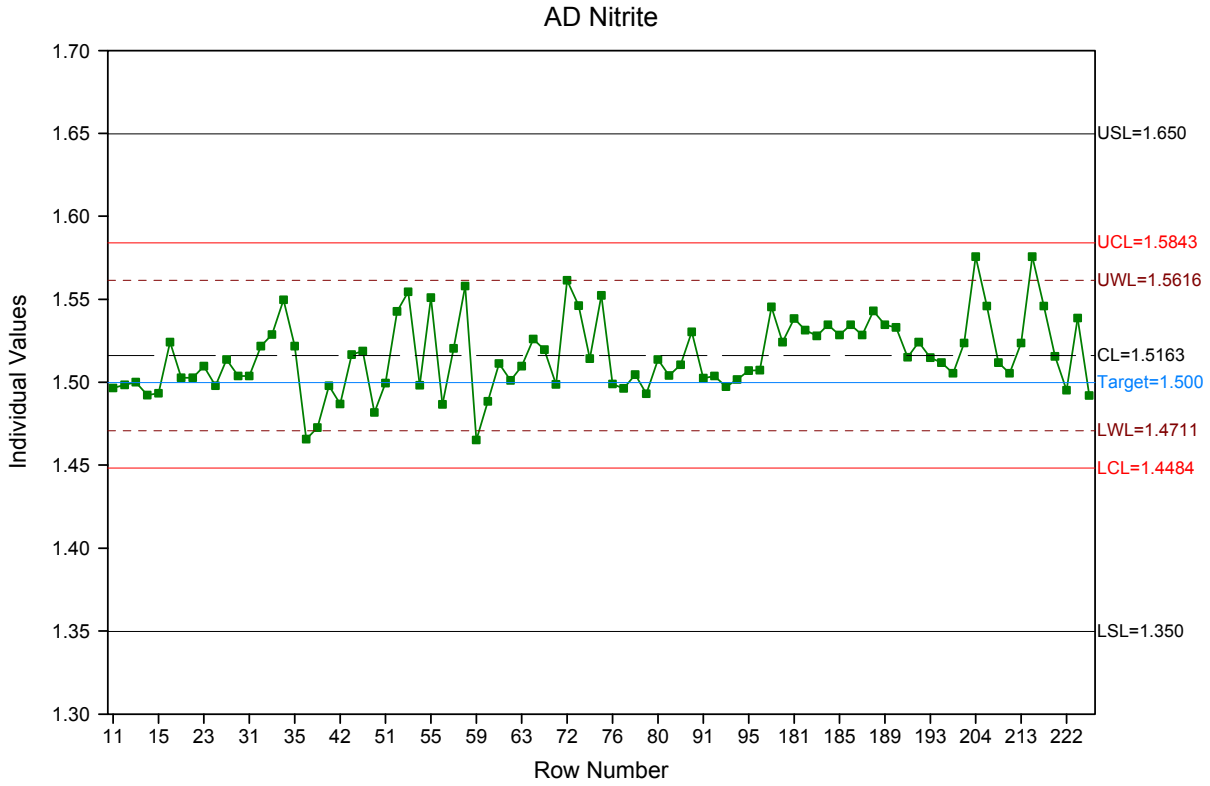

Figure 10 Nitrite QC Data by AD

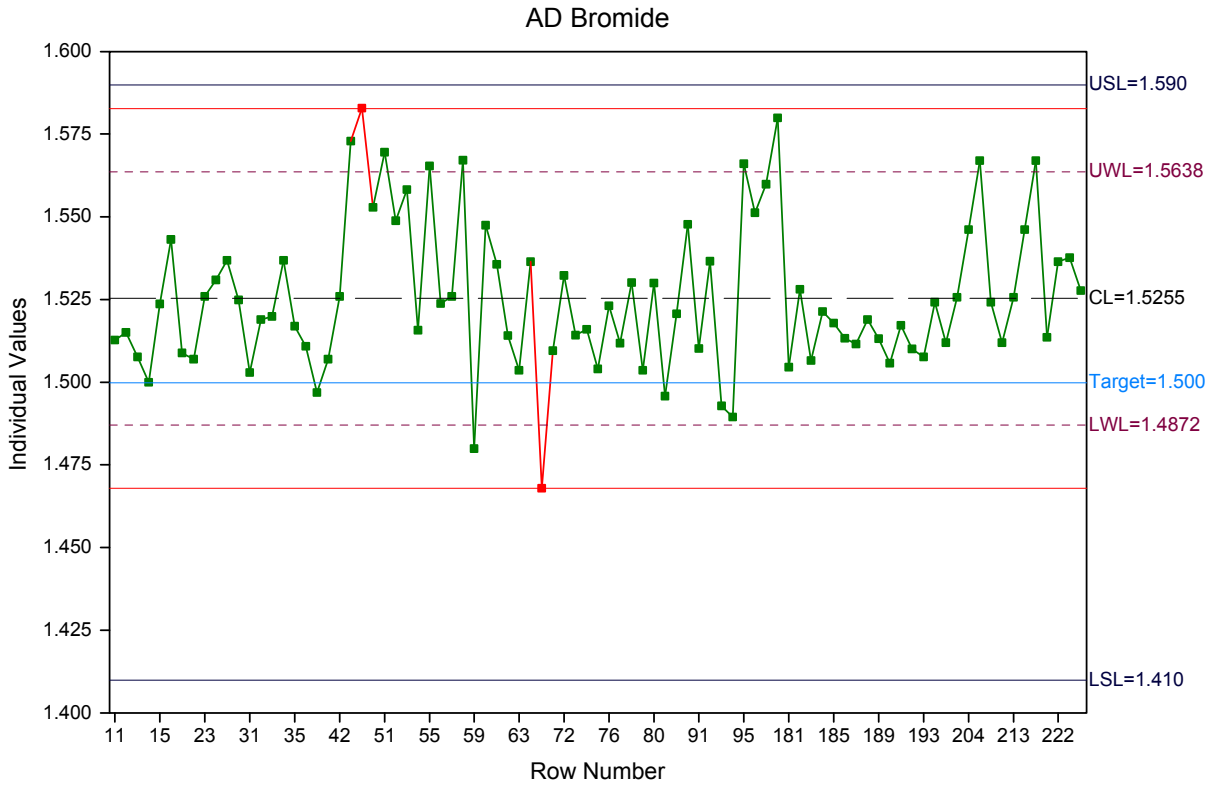

Figure 11 Bromide QC Data by AD

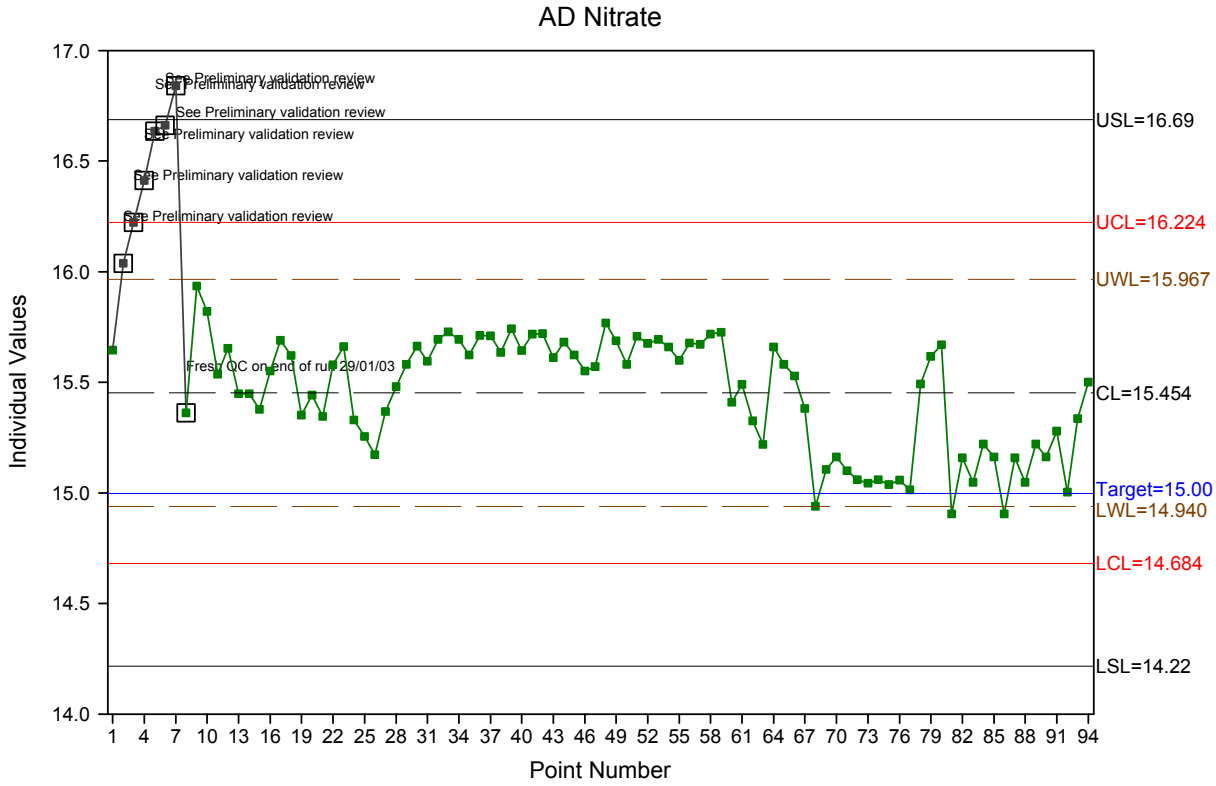

Figure 12 Nitrate QC Data by AD

7. Ruggedness

The validation exercise was designed to be particularly thorough, using three contrasting test matrices typical of the samples routinely analysed by the laboratory. The instrument was completely shut down and restarted between validation runs and the validation data were collected over a period of approximately four months. The bias, recovery, accuracy and precision data obtained for these matrices all pass target criteria, and go some way towards demonstrating the ruggedness of the method.

For ion chromatography, it is important that different sample matrices give rise to acceptable chromatograms, with good peak separation and resolution and stable retention times. Good peak separation and resolution is clearly achieved for the standards, as seen in the chromatograms for the 80% standard (Figures 13 and 14, for ED and AD chromatograms respectively).

For the low salinity matrix both without (Figures 15 and 16) and with spike (Figures 17 and 18), similarly good quality chromatograms are obtained. For the high salinity matrix, peak separation and resolution are still good both without (Figures 19 and 20) and with spike (Figures 21 and 22). Although this matrix has a chloride concentration in the order of 400 mg l^{-1}, the high salt content does not effect peak retention times or separation, with the exception of nitrite by ECD, which is absorbed within the chloride peak. The nitrite peak on the absorbance detector is unaffected by the high chloride. For the waste matrix, again, both without (Figures 23 and 24) and with spike (Figures 25 and 26) the chromatograms are still of excellent quality with good peak separation and resolution.

Overall, the validation data and good quality chromatograms for the range of matrices covered indicate that the technique is rugged. The only potential problem is the determination of nitrite by ED in the presence of chloride; as a result, absorbance data should be used preferentially for nitrite. If ED data have to be used for any reason, care should be taken to ensure that no chloride-nitrite co-elution has occurred and that nitrite data are reliable.

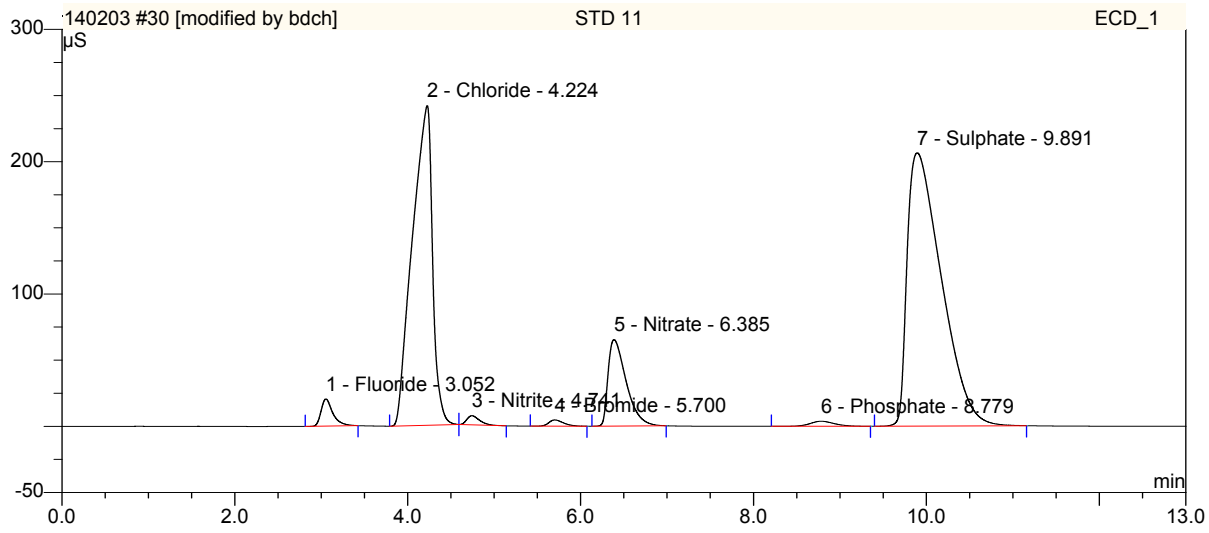

Figure 13 Example 80% Standard ECD Chromatogram

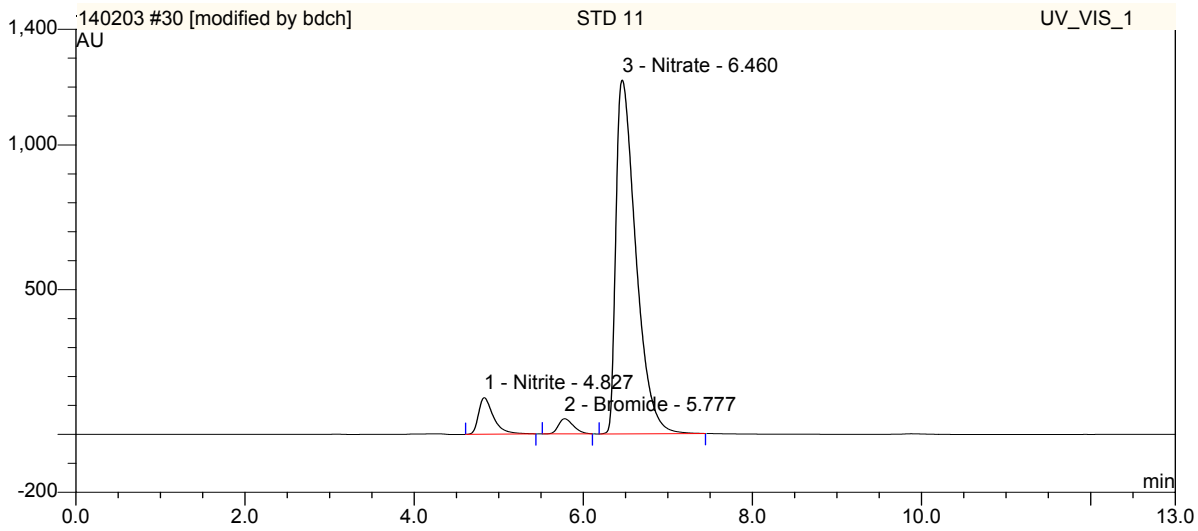

Figure 14 Example 80% Standard AD Chromatogram

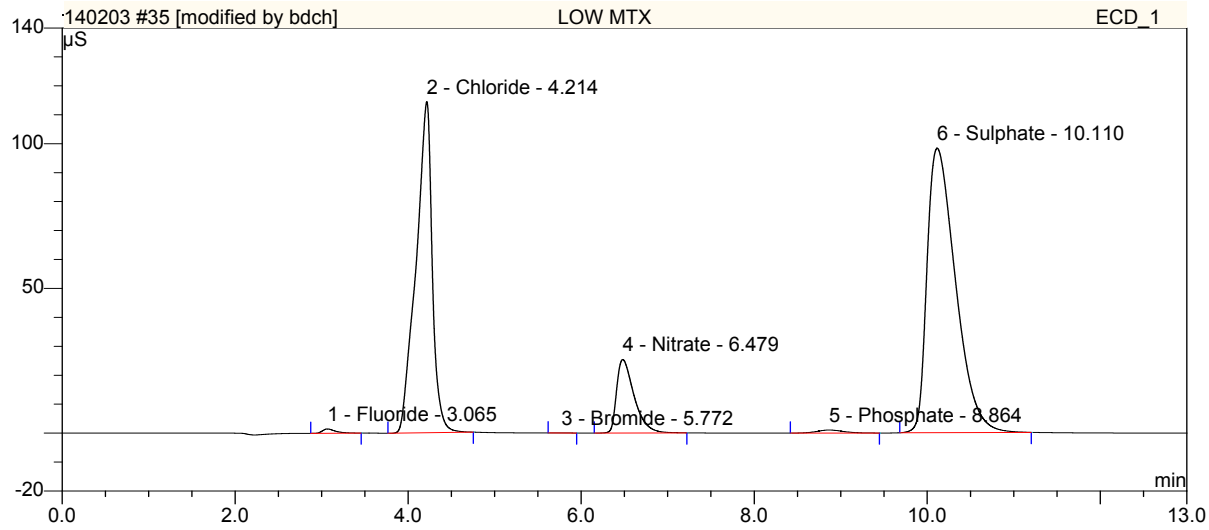

Figure 15 Example Low Salinity Matrix Neat Sample ECD Chromatogram

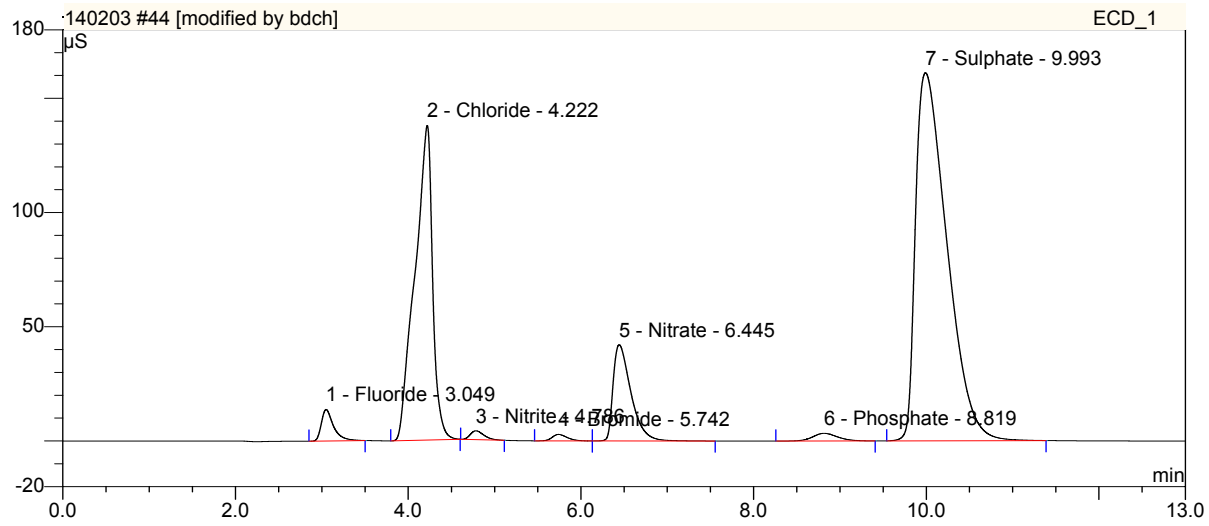

Figure 16 Example Low Salinity Matrix Plus Spike ECD Chromatogram

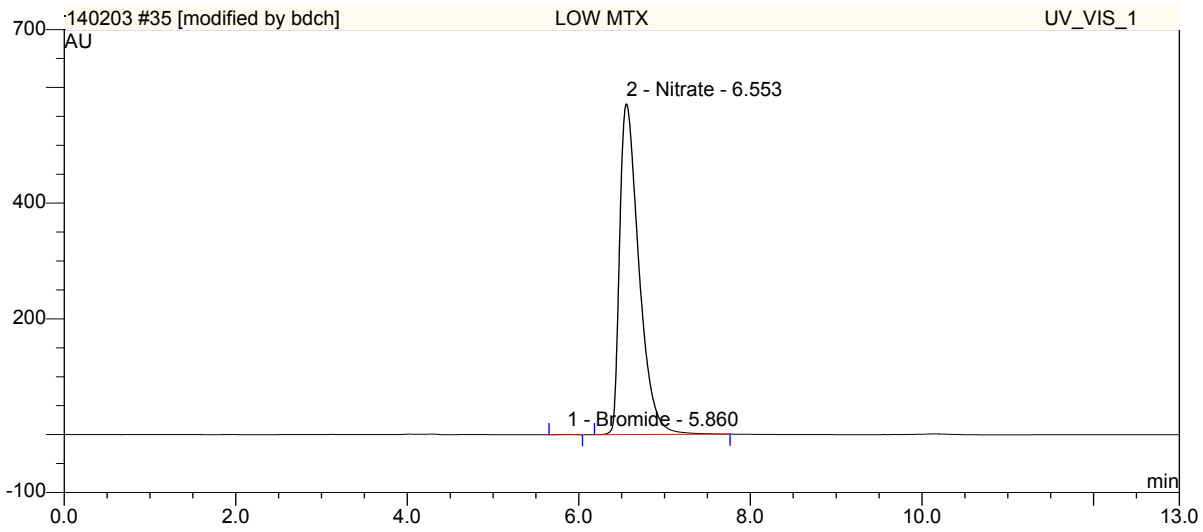

Figure 17 Example Low Salinity Matrix Neat Sample AD Chromatogram

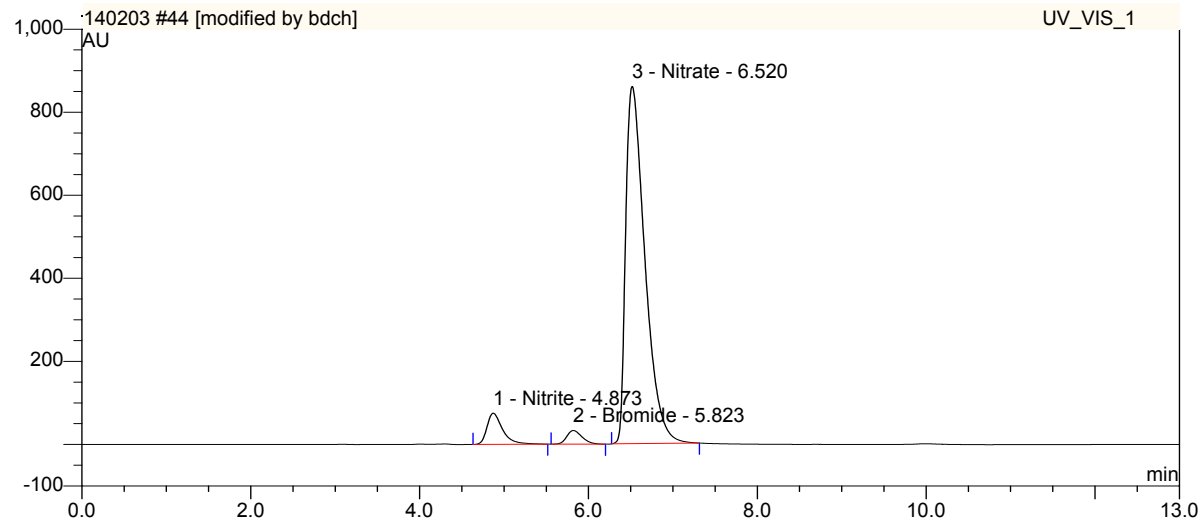

Figure 18 Example Low Salinity Matrix Plus Spike AD Chromatogram

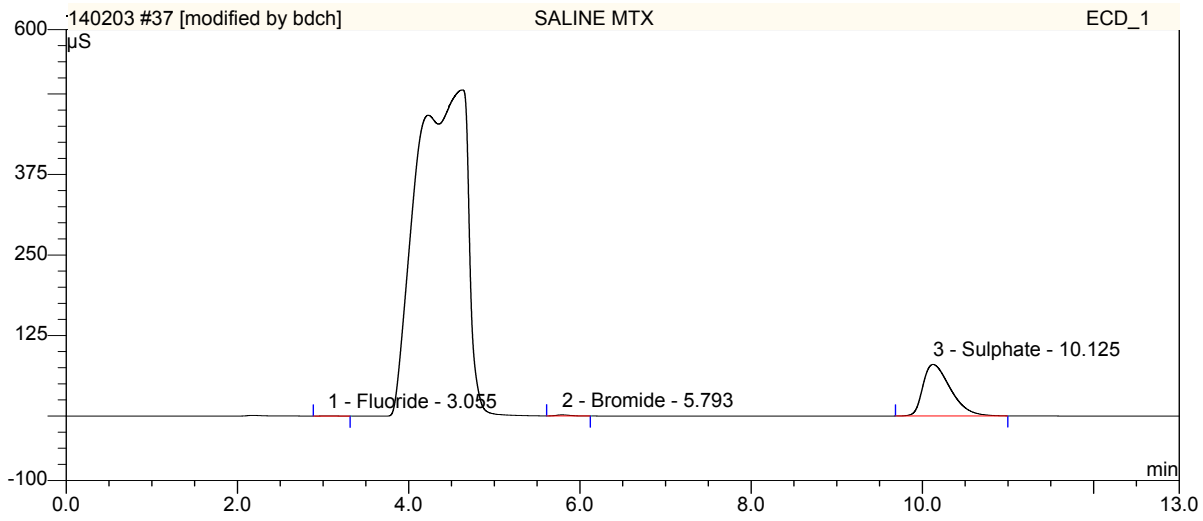

Figure 19 Example High Salinity Matrix Neat Sample ECD Chromatogram

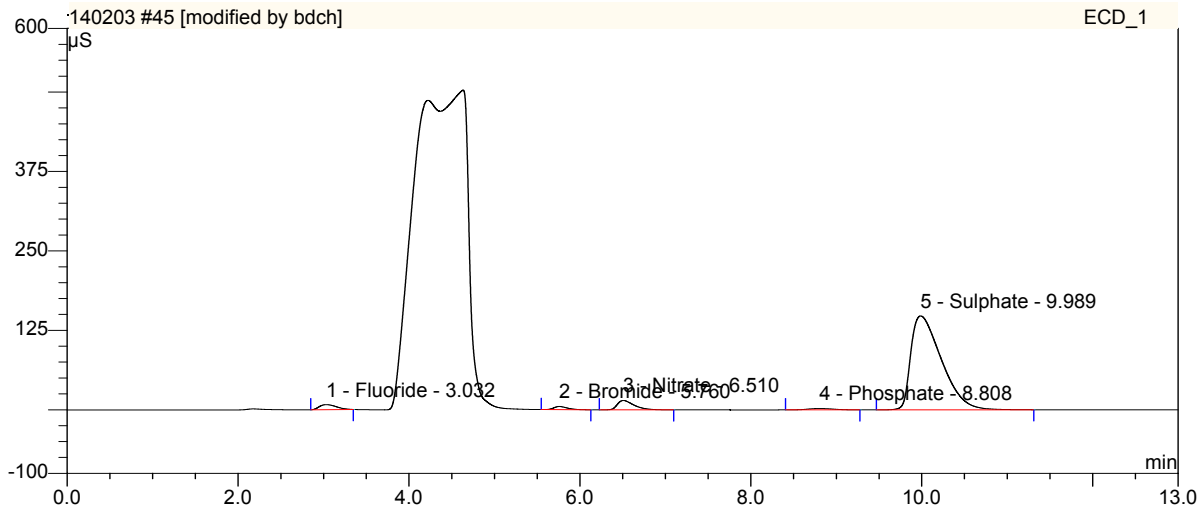

Figure 20 Example High Salinity Matrix Plus Spike ECD Chromatogram

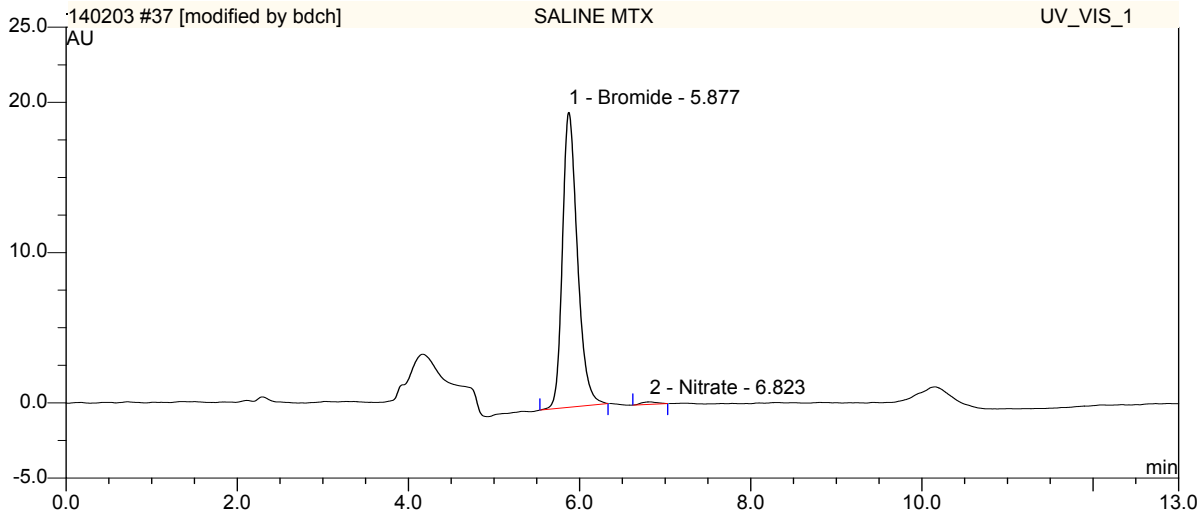

Figure 21 Example High Salinity Matrix Neat Sample AD Chromatogram

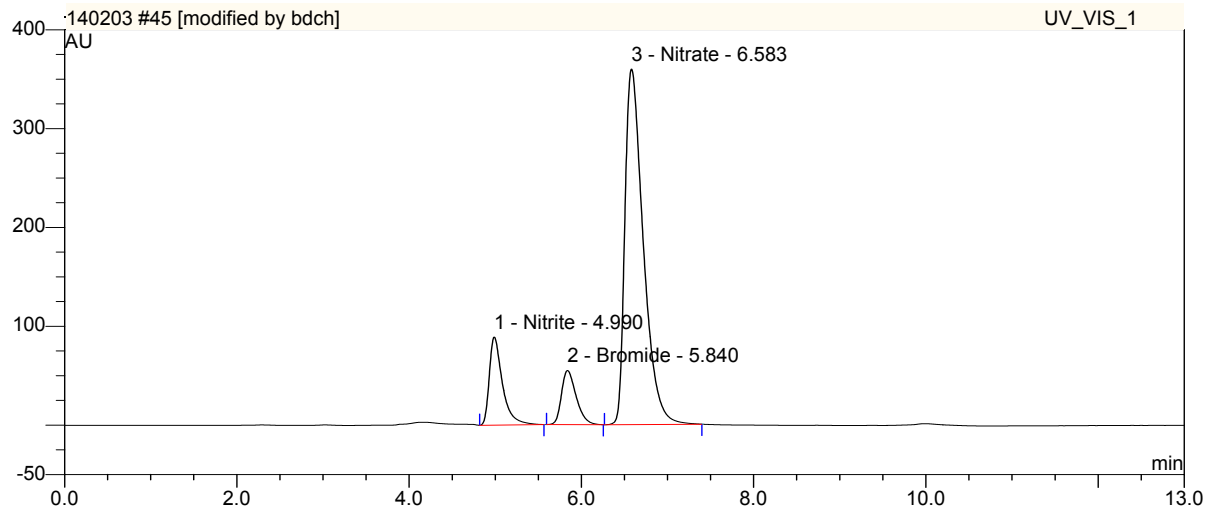

Figure 22 Example High Salinity Matrix Plus Spike AD Chromatogram

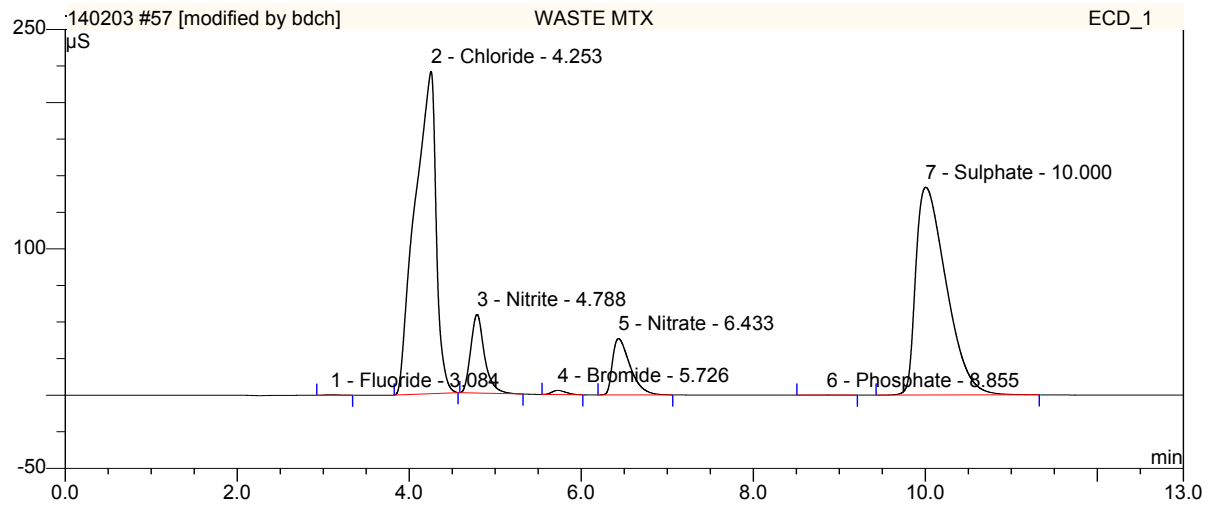

Figure 23 Example Waste Matrix Neat Sample ECD Chromatogram

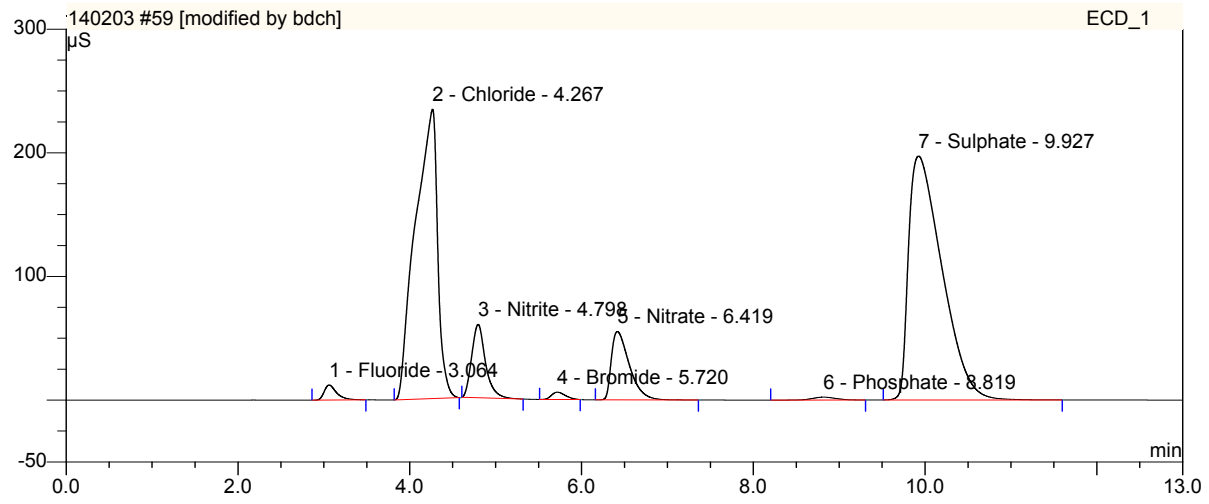

Figure 24 Example Waste Matrix Plus Spike ECD Chromatogram

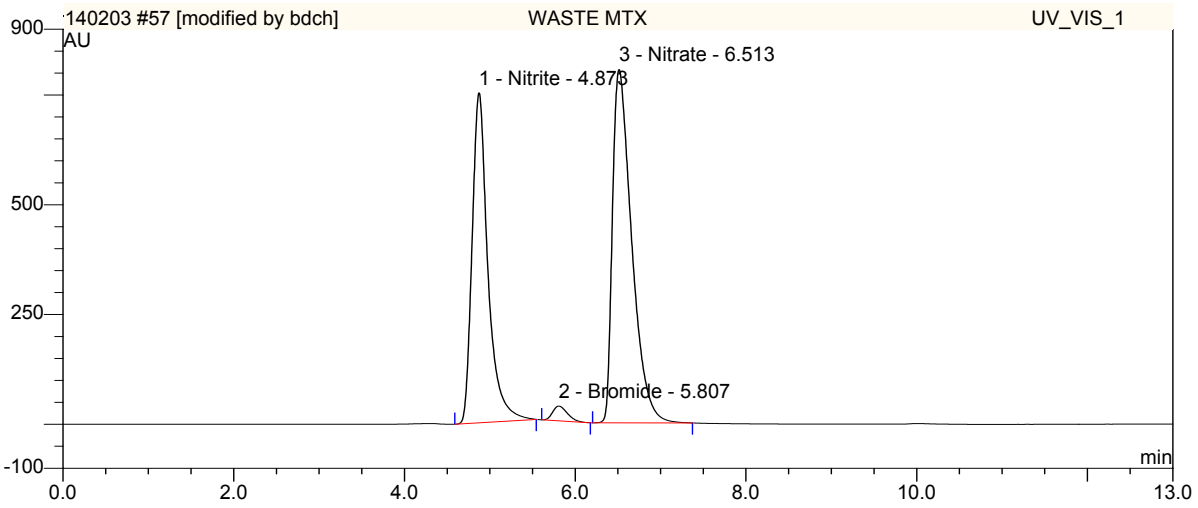

Figure 25 Example Waste Matrix Neat Sample AD Chromatogram

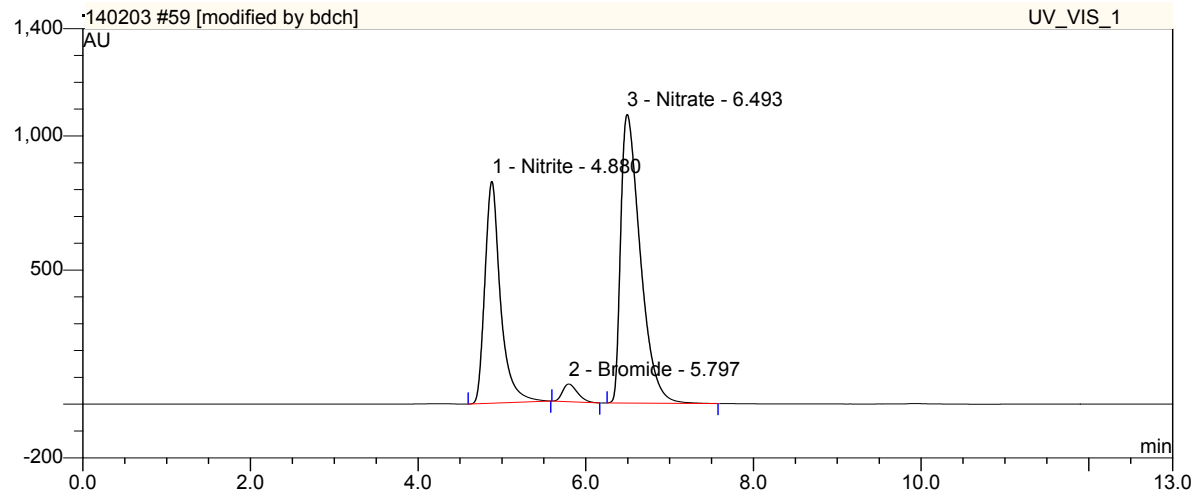

Figure 26 Example Waste Matrix Plus Spike AD Chromatogram

8. Limits of Quantification

Limits of detection are calculated automatically as part of the validation exercise based on data gathered for the pseudo blank (see Table 2).

For all species, the Cheeseman and Wilson limits of detection are below the target values (see Table 5). A coverage factor of approximately 2 has been applied to these data in order to obtain the overall estimated method limits of quantification. Summary LoQ data are given in Table 22.

Table 22 Summary of Cheeseman and Wilson Calculated Limits of Detection (LoD) and Estimated Method Limits of Quantification (LoQ)

	Electrochemical Detector							Absorbance Detector		
	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}	NO_2^-	Br^-	NO_3^-
	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}
CW LoD	0.004	0.017	0.008	0.011	0.014	0.042	0.022	0.005	0.009	0.011
LOQ	**0.010**	**0.050**	**0.020**	**0.030**	**0.030**	**0.100**	**0.050**	**0.010**	**0.020**	**0.020**

Other data gathered for the pseudo blank as part of the validation study, indicate that the overall bias (see Section 5.1.1, Table 9) and precision (see Section 6, Table 21) appears acceptably close to (and even below) the estimated limit of quantification.

The estimated method limits of quantification given in Table 22, met the target values established as part of the acceptance criteria (see Section 3) for all determinands except nitrate. Although the Cheeseman and Wilson calculated limit of detection for nitrate by AD more or less met the original target limit of quantification (0.01 mg l^{-1}), it was decided to increase the actual limit of quantification to 0.02 mg l^{-1}.

9. Measurement of Uncertainty

For each of the solutions analysed as part of the validation tests, the Cheeseman and Wilson spreadsheet calculates the estimated bias and precision. These data are given in Appendix 1 and summarised in Tables 9 and 21 respectively. These data have been used to estimate the measurement of uncertainty for each determinand according to the requirements of Operating Procedure AGN 1.6.

For each solution, the precision and bias have been expressed as percentage deviations from the nominal value. At each concentration, the combined uncertainty of the % bias and the % standard deviation (calculated as the square root of the sum of the squares of bias and standard deviation) have been used to represent the standard uncertainty at the concentration being measured. This value has then been multiplied by a coverage factor of 2 to give an expanded uncertainty.

The expanded uncertainties for all validation solutions have been plotted against concentration to provide an estimate of expanded uncertainty over the validated concentration range. These data are summarised in Figures 27 to 36. The key below gives the source of the data presented in each chart:

Colour	Description
	20% and 80% standard data
	Low salinity matrix data
	High salinity matrix data
	Waste matrix data
	High salinity matrix data using ‘within-batch’ standard deviation
	Waste matrix data using ‘within-batch’ standard deviation

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
0.0288	0.0288	0.0344	119.2912	0.0000	119.2912	2.0	238.6
0.0897	0.0897	0.0040	4.4615	0.0000	4.4615	2.0	8.9
0.3512	0.3512	0.0142	4.0385	0.0000	4.0385	2.0	8.1
1.0000	1.0038	0.0132	1.3162	0.3765	1.3690	2.0	2.7
2.5285	2.4350	0.0775	3.1826	-3.6996	4.8802	2.0	9.8
2.5888	2.5372	0.1024	4.0375	-1.9956	4.5037	2.0	9.0
2.8477	2.8544	0.0905	3.1699	0.2367	3.1787	2.0	6.4
4.0000	4.0172	0.0514	1.2784	0.4289	1.3484	2.0	2.7

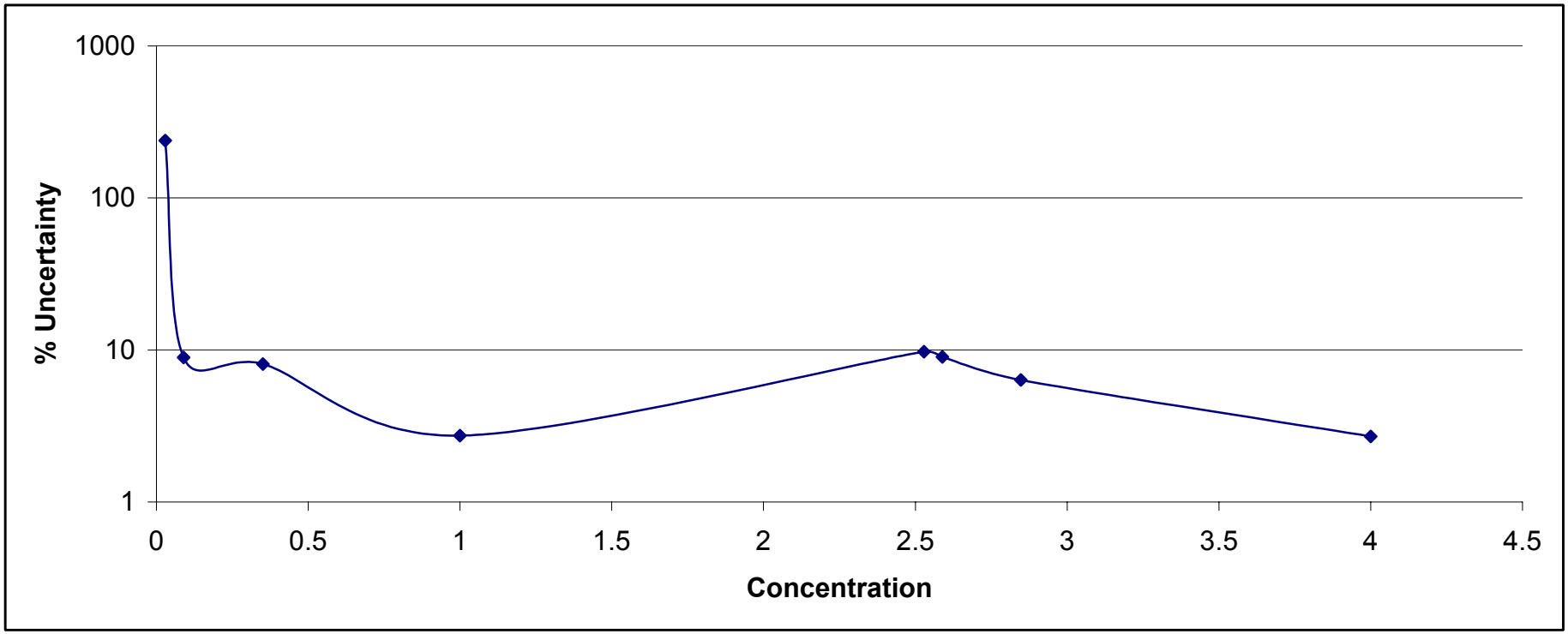

Figure 27 Summary Chart of Estimated Expanded Uncertainty Data for Fluoride

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
20.0000	20.6234	0.2400	1.1639	3.1170	3.3272	2.0	6.7
34.0654	34.0654	0.2444	0.7175	0.0000	0.7175	2.0	1.4
43.7247	43.9825	0.3120	0.7095	0.5895	0.9224	2.0	1.8
77.6564	77.6564	0.4489	0.5780	0.0000	0.5780	2.0	1.2
80.0000	81.2359	0.5190	0.6389	1.5449	1.6718	2.0	3.3

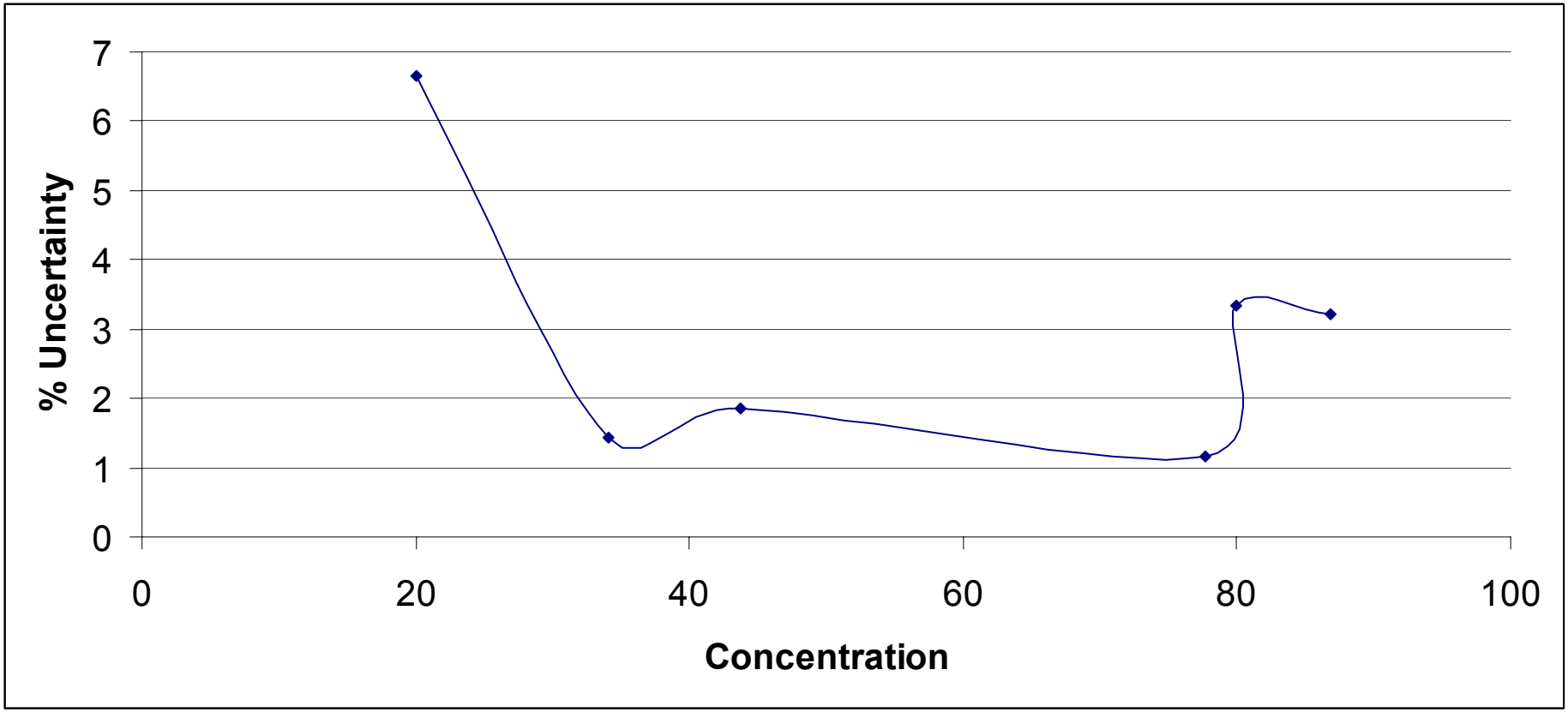

Figure 28 Summary Chart of Estimated Expanded Uncertainty Data for Chloride

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
1.0000	1.0124	0.0146	1.4446	1.2415	1.9048	2.0	3.8
2.5000	2.4765	0.0574	2.3161	-0.9386	2.4991	2.0	5.0
2.6210	2.6210	0.0573	2.1871	0.0000	2.1871	2.0	4.4
2.6210	2.6210	0.1762	6.7230	0.0000	6.7230	2.0	13.4
4.0000	4.0226	0.0460	1.1432	0.5644	1.2749	2.0	2.5
5.0947	4.9801	0.1014	2.0364	-2.2497	3.0345	2.0	6.1

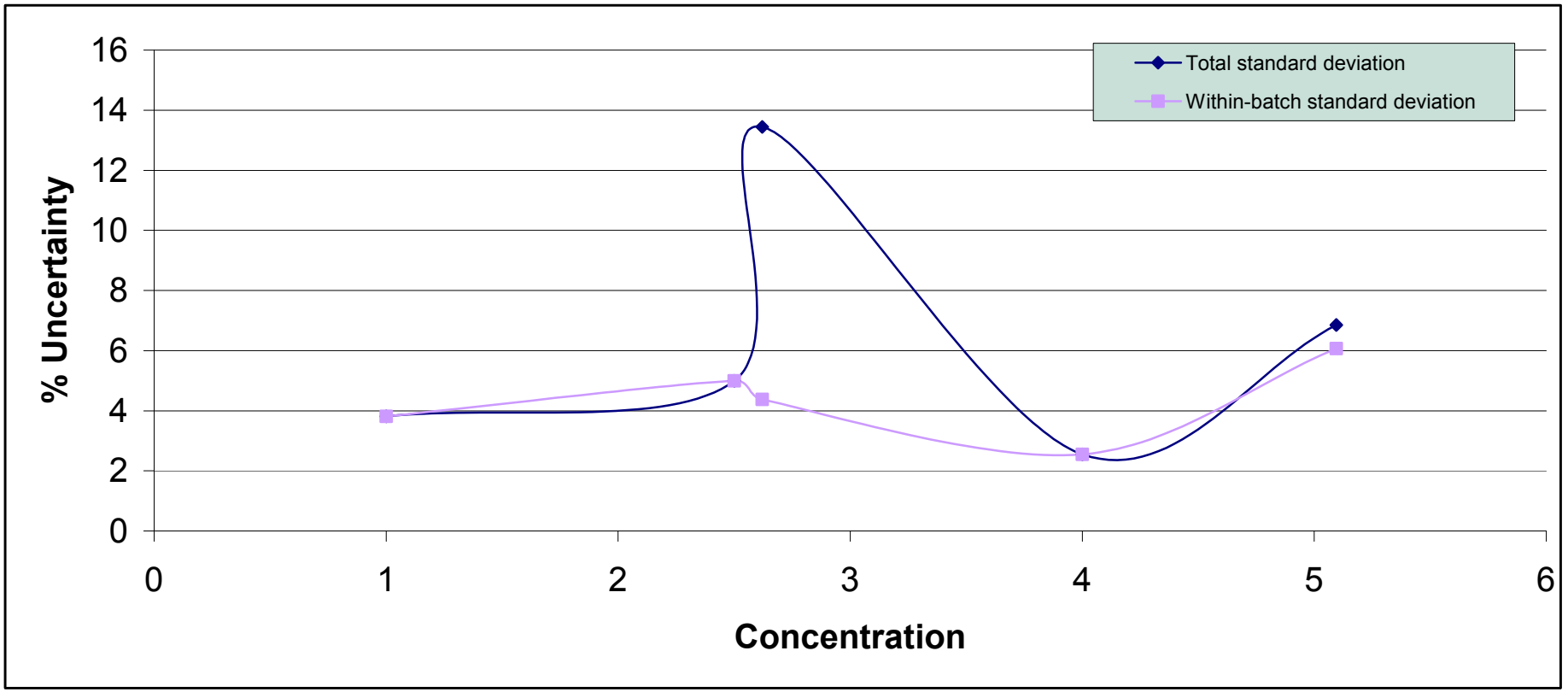

Figure 29 Summary Chart of Estimated Expanded Uncertainty Data for Nitrite by ECD

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
0.0304	0.0304	0.0052	17.1865	0.0000	17.1865	2.0	34.4
1.0000	1.0109	0.0096	0.9523	1.0920	1.4489	2.0	2.9
1.3252	1.3252	0.0292	2.1999	0.0000	2.1999	2.0	4.4
2.5301	2.5485	0.0455	1.7860	0.7276	1.9285	2.0	3.9
2.5968	2.5968	0.1050	4.0422	0.0000	4.0422	2.0	8.1
3.8120	3.8511	0.0904	2.3467	1.0254	2.5609	2.0	5.1
4.0000	4.0111	0.0303	0.7554	0.2769	0.8045	2.0	1.6

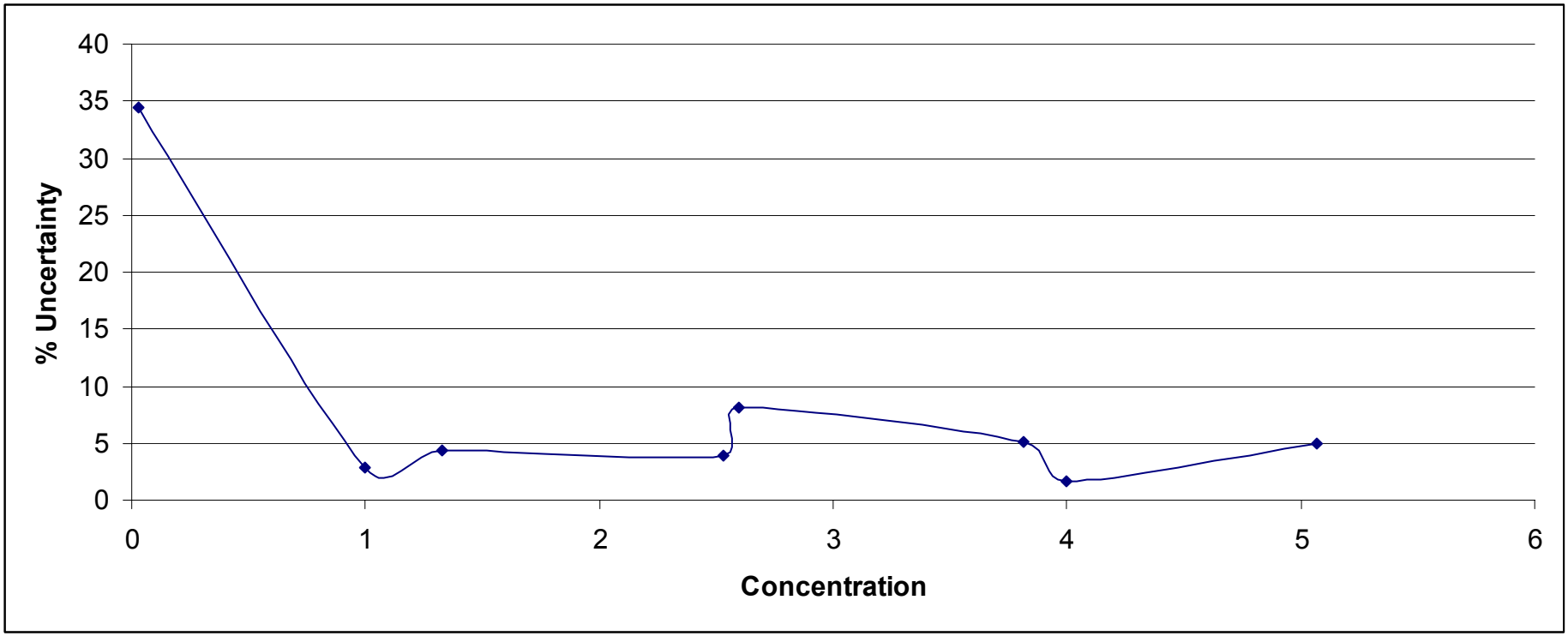

Figure 30 Summary Chart of Estimated Expanded Uncertainty Data for Bromide by ECD

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
0.0212	0.0212	0.0648	306.1701	0.0000	306.1701	2.0	612.3
10.0000	10.0943	0.1702	1.6864	0.9435	1.9323	2.0	3.9
10.0209	9.9968	0.1716	1.7164	-0.2414	1.7333	2.0	3.5
17.3228	17.3228	0.2120	1.2240	0.0000	1.2240	2.0	2.4
25.4633	25.4633	0.7290	2.8631	0.0000	2.8631	2.0	5.7
27.1496	27.4528	0.6210	2.2621	1.1169	2.5228	2.0	5.0
35.2087	34.7734	0.2859	0.8221	-1.2363	1.4847	2.0	3.0
40.0000	40.3884	0.4933	1.2214	0.9709	1.5603	2.0	3.1

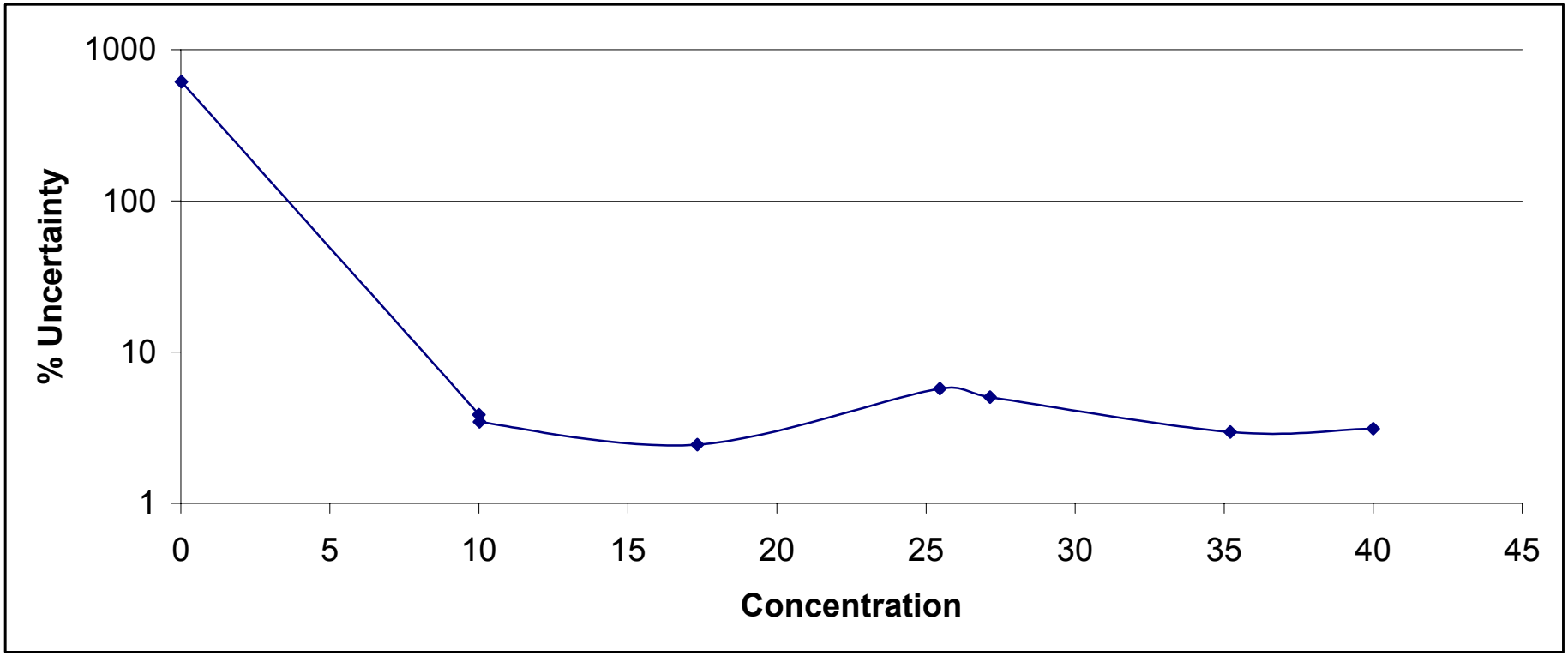

Figure 31 Summary Chart of Estimated Expanded Uncertainty Data for Nitrate by ECD

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
0.2890	0.2890	0.0152	5.2766	0.0000	5.2766	2.0	10.6
2.0000	2.0144	0.0203	1.0099	0.7213	1.2410	2.0	2.5
2.5594	2.5594	0.0508	1.9861	0.0000	1.9861	2.0	4.0
5.0000	4.8840	0.1054	2.1571	-2.3207	3.1684	2.0	6.3
5.2861	5.2094	0.2134	4.0968	-1.4507	4.3460	2.0	8.7
7.5338	7.4073	0.1637	2.2099	-1.6790	2.7753	2.0	5.6
8.0000	8.0097	0.0521	0.6508	0.1206	0.6619	2.0	1.3

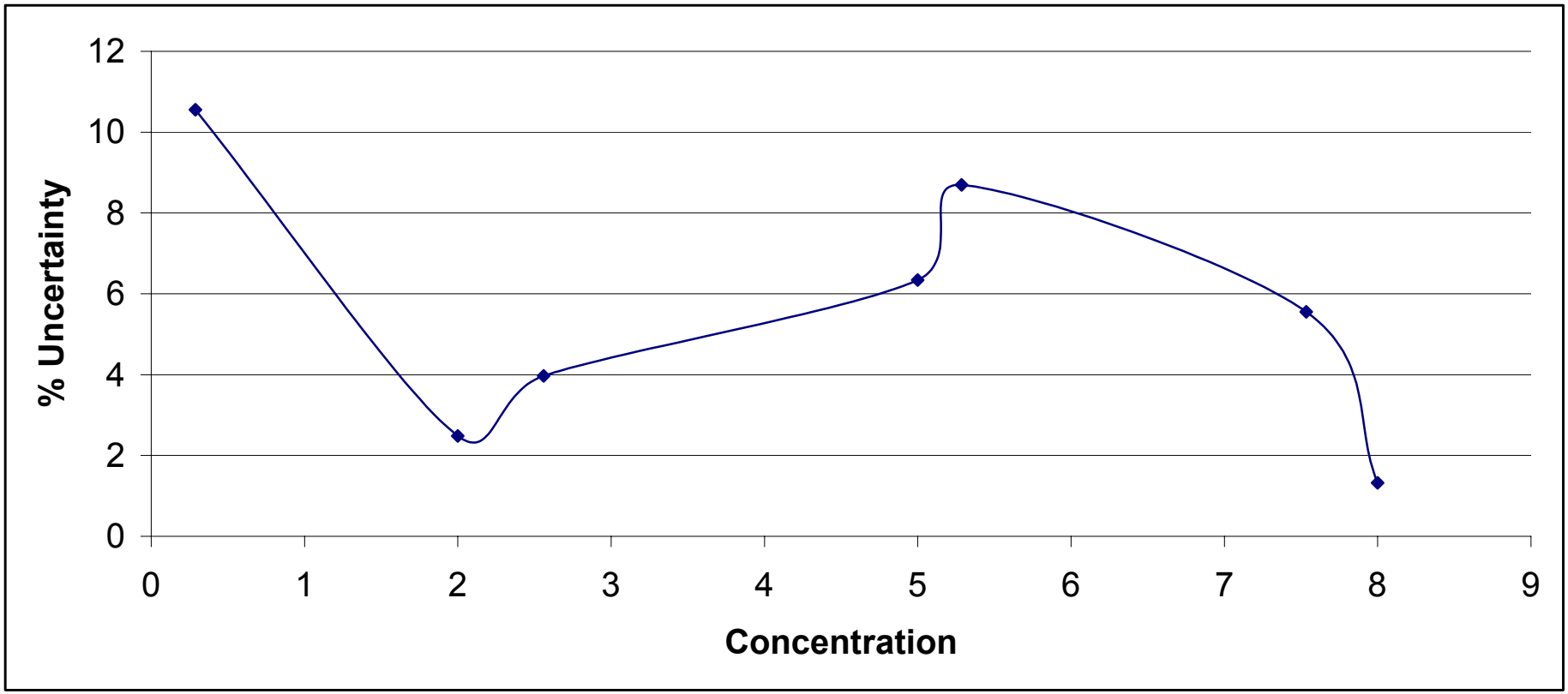

Figure 32 Summary Chart of Estimated Expanded Uncertainty Data for Phosphate

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
40.0000	40.9955	0.3773	0.9205	2.4887	2.6535	2.0	5.3
58.0074	58.0074	0.5447	0.9390	0.0000	0.9390	2.0	1.9
71.4534	71.4534	0.5151	0.7209	0.0000	0.7209	2.0	1.4
105.4113	105.4113	0.8852	0.8398	0.0000	0.8398	2.0	1.7
107.4273	109.8497	1.1716	1.0666	2.2549	2.4945	2.0	5.0
120.7388	121.4188	0.9302	0.7661	0.5632	0.9509	2.0	1.9
154.3572	151.8921	1.1245	0.7403	-1.5970	1.7603	2.0	3.5
160.0000	161.8161	0.9654	0.5966	1.1350	1.2823	2.0	2.6

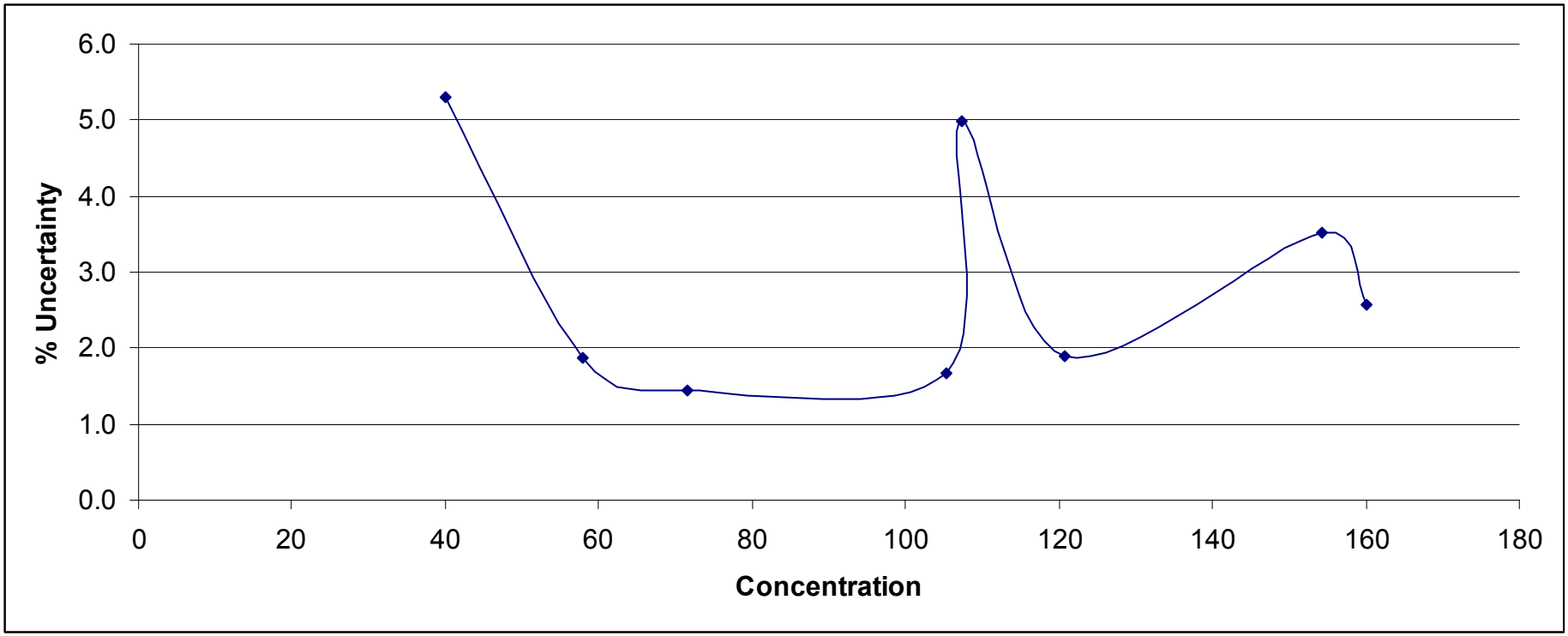

Figure 33 Summary Chart of Estimated Expanded Uncertainty Data for Sulphate

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
0.0005	0.0005	0.0010	188.2007	0.0000	188.2007	2.0	376.4
0.0005	0.0005	0.0010	181.1222	0.0000	181.1222	2.0	362.2
0.0005	0.0005	0.0003	50.8738	0.0000	50.8738	2.0	101.7
1.0000	1.0032	0.0140	1.3978	0.3160	1.4330	2.0	2.9
2.5005	2.4988	0.0637	2.5502	-0.0696	2.5511	2.0	5.1
2.5005	2.3825	0.0498	2.0884	-4.7216	5.1628	2.0	10.3
2.5005	2.3825	0.0796	3.3414	-4.7216	5.7843	2.0	11.6
2.5569	2.5569	0.0400	1.5631	0.0000	1.5631	2.0	3.1
4.0000	4.0028	0.0300	0.7496	0.0698	0.7529	2.0	1.5

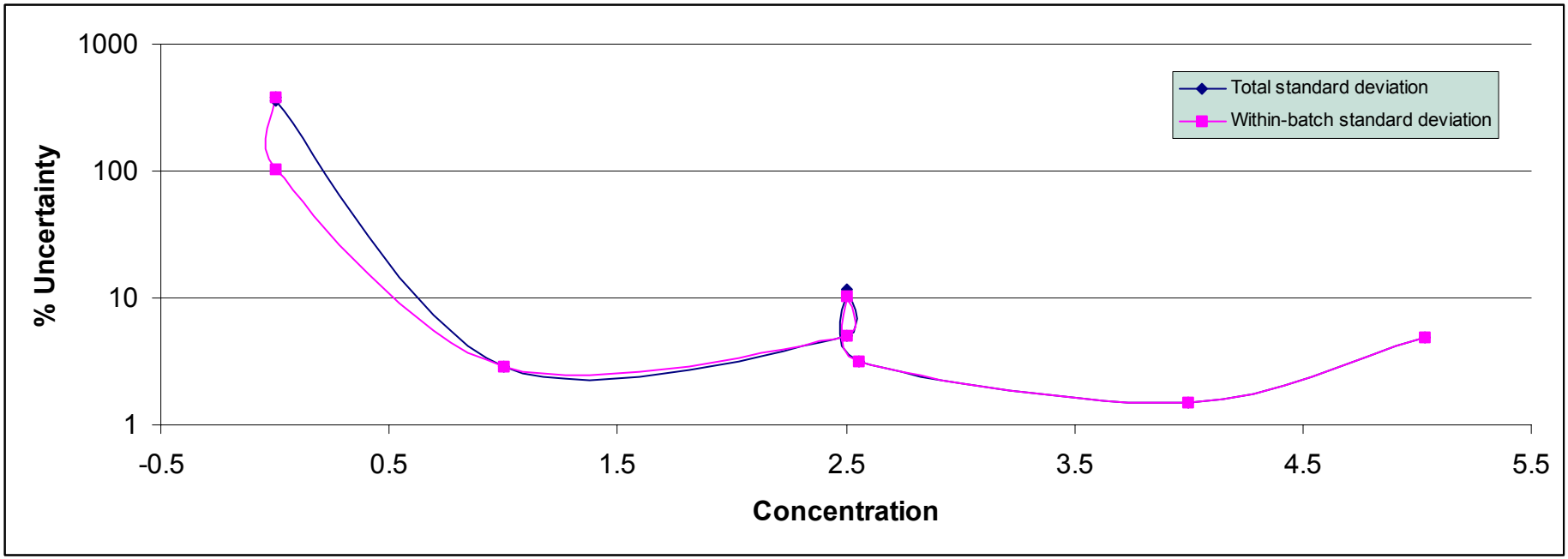

Figure 34 Summary Chart of Estimated Expanded Uncertainty Data for Nitrite by AD

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
0.0340	0.0340	0.0030	8.8697	0.0000	8.8697	2.0	17.7
1.0000	1.0078	0.0221	2.1966	0.7820	2.3316	2.0	4.7
1.4725	1.4725	0.0190	1.2873	0.0000	1.2873	2.0	2.6
2.5337	2.5220	0.0650	2.5772	-0.4592	2.6178	2.0	5.2
2.5748	2.5748	0.0521	2.0246	0.0000	2.0246	2.0	4.0
3.9578	3.9590	0.0624	1.5761	0.0303	1.5763	2.0	3.2
4.0000	4.0088	0.0323	0.8050	0.2202	0.8346	2.0	1.7

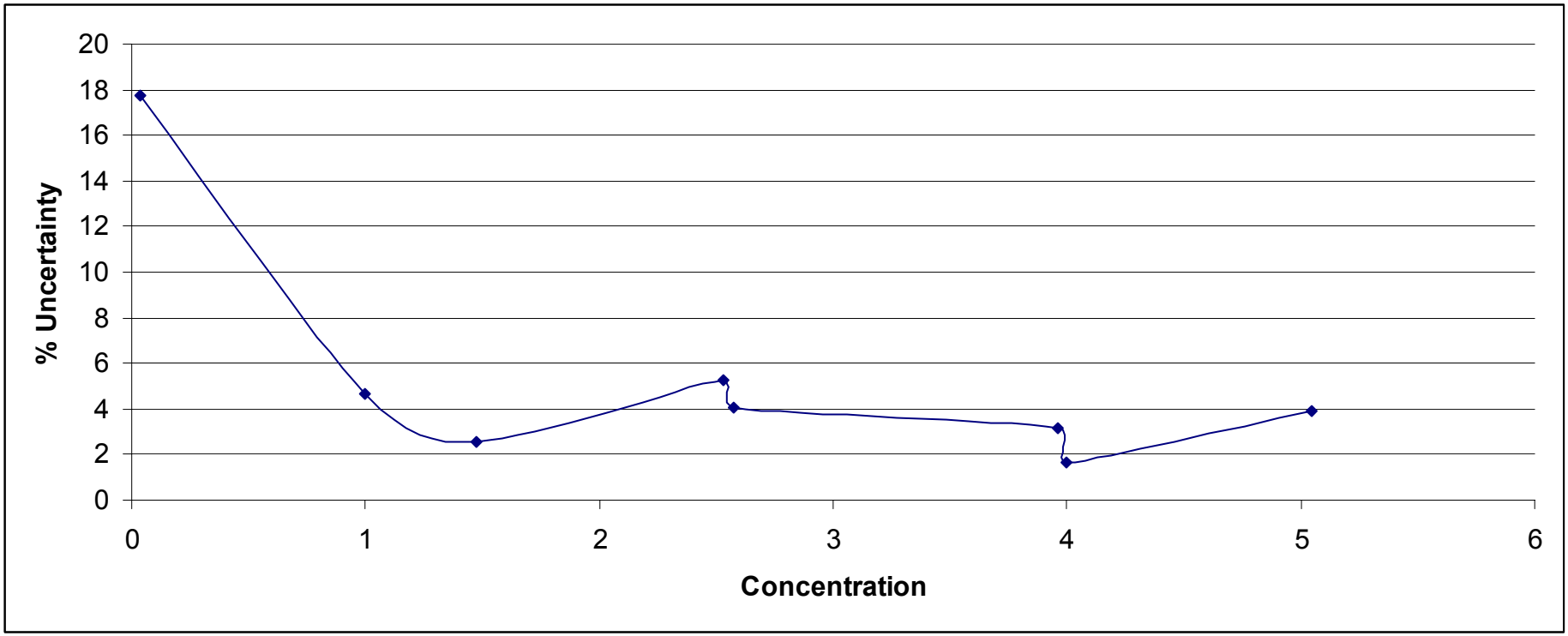

Figure 36 Summary Chart of Estimated Expanded Uncertainty Data for Bromide by AD

Nominal conc	Found	Standard deviation	RSD	Bias	%Error	Coverage factor	Uncertainty %
0.0116	0.0116	0.0171	146.9317	0.0000	146.9317	2.0	293.9
0.0116	0.0116	0.0041	35.3480	0.0000	35.3480	2.0	70.7
10.0000	10.0539	0.1665	1.6561	0.5385	1.7415	2.0	3.5
10.0115	10.2180	0.3275	3.2053	2.0630	3.8119	2.0	7.6
10.0115	10.2180	0.2099	2.0546	2.0630	2.9116	2.0	5.8
17.2150	17.2150	0.0975	0.5666	0.0000	0.5666	2.0	1.1
24.8034	24.8034	0.2769	1.1166	0.0000	1.1166	2.0	2.2
27.0429	27.2397	0.4330	1.5897	0.7280	1.7485	2.0	3.5
34.5553	34.2797	0.3855	1.1246	-0.7976	1.3787	2.0	2.8
40.0000	40.2399	0.2695	0.6697	0.5998	0.8990	2.0	1.8

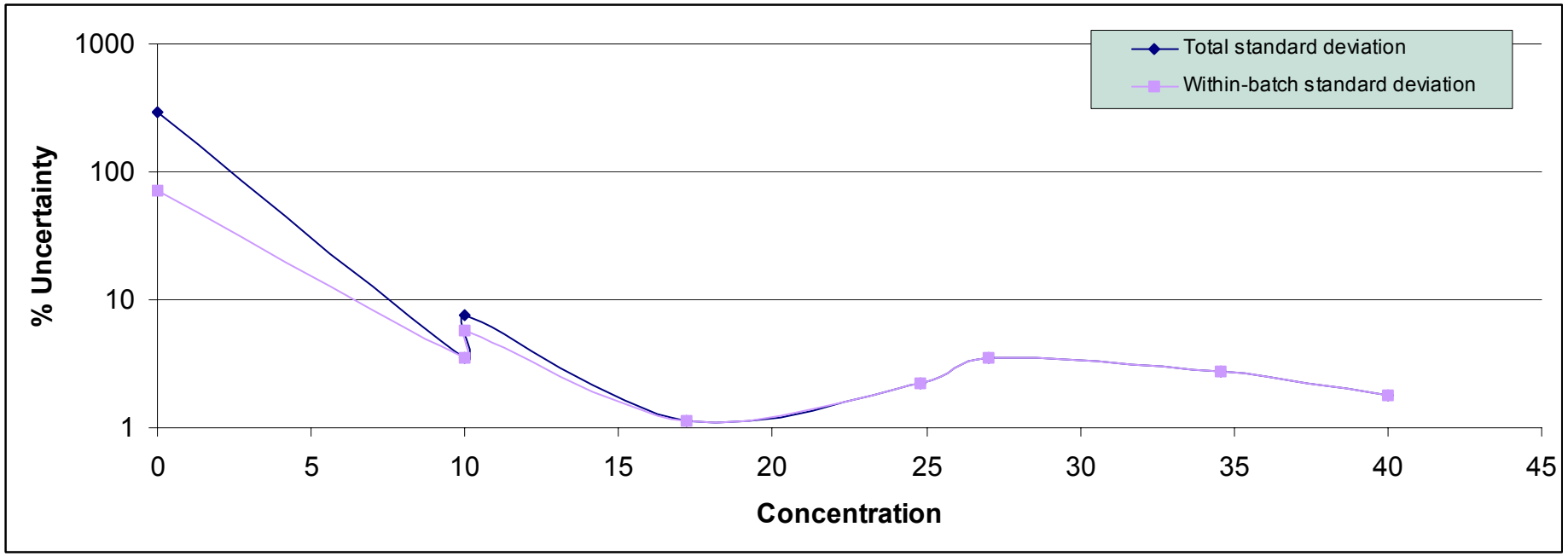

Figure 34 Summary Chart of Estimated Expanded Uncertainty Data for Nitrate by AD

For most determinands, the uncertainly-concentration profiles give typical responses, with uncertainty increasing approximately exponentially as concentration approaches the limit of quantification. For some species, e.g. chloride and sulphate, no data are available close to the limit of quantification.

The overall expanded uncertainties have been estimated from these charts and are summarised in Table 23.

These uncertainties are based on the highest uncertainty obtained for all the validation samples included as part of the study having a concentration at least an order of magnitude above the limit of quantification. Although this probably gives an over-estimate of the uncertainty compared to taking an average value, all of the expanded uncertainties are nevertheless within the target value of 10%. For nitrite, the anomalous data for the waste and high salinity matrices using total standard deviation data have been excluded. The maximum uncertainties in these cases have been based on 'within-batch' standard deviation data.

Table 23 Overall Estimated Expanded Uncertainty Data

	Electrochemical Detector							Absorbance Detector		
	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}	NO_2^-	Br^-	NO_3^-
	%	%	%	%	%	%	%	%	%	%
Uncertainty	**10**	**7**	**7**	**8**	**6**	**9**	**6**	**10**	**6**	**8**

These uncertainty data have been used to set the method specification limits for the QC charts. In all cases (see Figures 3 to 12), the uncertainty data give limits that are commensurate with the 3s precision data obtained for QC samples to date.

10. Conclusions

As described in considerable detail in the main body of this report, a comprehensive validation of the determination of anions on the DX-600 ion chromatography has been successfully undertaken. With only a few insignificant exceptions, all of the acceptance criteria proposed prior to validation (Section 3) have been met and, in many cases, exceeded. As a result, the method has been demonstrated to be fit for its intended use.

11. References

Cheeseman RV and Wilson AL. 1989. NS30 – A manual on analytical quality control for the water industry. Water Research Centre.

Vanatta LE and Coleman DE. 1997. Calculation of detection limits for a single laboratory ion chromatographic method to determine parts per trillion ions in ultra pure water. *Journal of Chromatography A*, **770**, 105.

Appendix 1 Summary Cheeseman and Wilson Validation Sheets

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	0.3512	
Determinand =	F	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.3512	mg/l	
Nominal value	0.005	1	4	Calc Spike Value=	2.8477	mg/l
Mean	0.0041	1.0038	4.0172	0.3477	2.8544	mg/l
Percentage Bias =	-18.40	0.38	0.43	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0003	0.0059	0.0002	0.0162	
Mo	0.0000	0.0001		0.0002	0.0055	
F value (M1/Mo)	1.4378	2.8803	3.7437	1.2925	2.9230	
Sw	0.0008	0.0109	0.0396	0.0137	0.0744	
Sb	0.0003	0.0075	0.0328	0.0037	0.0516	
St	0.0009	0.0132	0.0514	0.0142	0.0905	
Target maximum St	0.0002	0.0502	0.2009	0.0176	0.1427	
St (as percent of mean)	21.5892	1.3162	1.2784	4.0793	3.1699	
Tabulated F, 0.05	1.61	1.72	1.79	1.61	1.72	
Calculated f	18.6437	0.0693	0.0654	0.6524	0.4019	
Degrees of freedom	18	13	11	18	13	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0039	0.0507	-	0.0637	-	mg/l
(based on each solution)						
Percent Spike Recovery =	100.27	Percent Sample Recovery=		101.94		
+/- (95 percentile)	2.51					
Std.dev.of mean recoveries	0.078664473					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.003888616 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.000880838	0.0132	0.0514	0.0142	0.0905
St (as percent of mean)	21.5892	1.3162	1.2784	4.0793	3.1699
% Bias =	-	0.38	0.43	-	-
% Spike Recovery =	100.27				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	0.0000	
Determinand =	HPO_4	High Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		500	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		5.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0000	mg/l	
Nominal value	0.05	2	8	Calc Spike Value=	5.0000	mg/l
Mean	0.0408	2.0144	8.0097	0.0000	4.8840	mg/l
Percentage Bias =	-18.43	0.72	0.12	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.0006	0.0050	0.0000	0.0078	
Mo	0.0001	0.0004		0.0000	0.0122	
F value (M1/Mo)	1.3506	1.6777	2.5107	#DIV/0!	0.6427	
Sw	0.0091	0.0188	0.0444	0.0000	0.1104	
Sb	0.0027	0.0077	0.0273	0.0000	0.0000	
St	0.0094	0.0203	0.0521	0.0000	0.1054	
Target maximum St	0.0020	0.1007	0.4005	no target	0.2442	
St (as percent of mean)	23.1449	1.0099	0.6508	#DIV/0!	2.1571	
Tabulated F, 0.05	1.61	1.63	1.69	#DIV/0!	1.59	
Calculated f	21.4274	0.0408	0.0169	#DIV/0!	0.1861	
Degrees of freedom	18	17	14	#DIV/0!	19	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0421	0.0875	-	0.0000	-	mg/l
(based on each solution)						
Percent Spike Recovery =	97.68	Percent Sample Recovery=		#DIV/0!		
+/- (95 percentile)	0.74					
Std.dev.of mean recoveries	0.0481706					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.042088665 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.009439631	0.0203	0.0521	0.0000	0.1054
St (as percent of mean)	23.1449	1.0099	0.6508	#DIV/0!	2.1571
% Bias =	-	0.72	0.12	-	-
% Spike Recovery =	97.68				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	0.0897	
Determinand =	F	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0897	mg/l	
Nominal value	0.005	1	4	Calc Spike Value=	2.5888	mg/l
Mean	0.0041	1.0038	4.0172	0.0888	2.5372	mg/l
Percentage Bias =	-18.40	0.38	0.43	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0003	0.0059	0.0000	0.0233	
Mo	0.0000	0.0001		0.0000	0.0062	
F value (M1/Mo)	1.4378	2.8803	3.7437	1.0452	3.7299	
Sw	0.0008	0.0109	0.0396	0.0040	0.0790	
Sb	0.0003	0.0075	0.0328	0.0004	0.0652	
St	0.0009	0.0132	0.0514	0.0040	0.1024	
Target maximum St	0.0002	0.0502	0.2009	0.0045	0.1269	
St (as percent of mean)	21.5892	1.3162	1.2784	4.5066	4.0375	
Tabulated F, 0.05	1.61	1.72	1.79	1.79	2.1	
Calculated f	18.6437	0.0693	0.0654	0.7962	0.6521	
Degrees of freedom	18	13	11	11	6	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0039	0.0507	-	0.0185	-	mg/l
(based on each solution)						
Percent Spike Recovery =	97.93	Percent Sample Recovery=		41.830		
+/- (95 percentile)	2.57					
Std.dev.of mean recoveries	0.060812711					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.003888616 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.000880838	0.0132	0.0514	0.0040	0.1024
St (as percent of mean)	21.5892	1.3162	1.2784	4.5066	4.0375
% Bias =	-	0.38	0.43	-	-
% Spike Recovery =	97.93				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	34.0654	
Determinand =	Cl	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				34.0654	mg/l	
Nominal value	0.025	20	80	Calc Spike Value=	43.7247	mg/l
Mean	0.0351	20.6234	81.2359	33.7247	43.9825	mg/l
Percentage Bias =	40.44	3.12	1.54	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0002	0.1605	0.9751	0.1929	0.2194	
Mo	0.0000	0.0233		0.0153	0.0567	
F value (M1/Mo)	15.3472	6.8854	28.5244	12.5803	3.8718	
Sw	0.0036	0.1527	0.1849	0.1238	0.2381	
Sb	0.0067	0.1852	0.4850	0.2107	0.2017	
St	0.0076	0.2400	0.5190	0.2444	0.3120	
Target maximum St	0.0018	1.0312	4.0618	1.7033	2.1991	
St (as percent of mean)	21.6714	1.1639	0.6389	0.7247	0.7095	
Tabulated F, 0.05	2.1	1.94	2.21	2.1	1.79	
Calculated f	18.7861	0.0542	0.0163	0.0206	0.0201	
Degrees of freedom	6	8	5	6	11	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0165	0.7100	-	0.5759	-	mg/l
(based on each solution)						
Percent Spike Recovery =	102.58	Percent Sample Recovery=		100.76		
+/- (95 percentile)	1.56					
Std.dev.of mean recoveries	0.198005096					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.016520266 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.007608844	0.2400	0.5190	0.2444	0.3120
St (as percent of mean)	21.6714	1.1639	0.6389	0.7247	0.7095
% Bias =	-	3.12	1.54	-	-
% Spike Recovery =	102.58				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	77.6564	
Determinand =	Cl	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				77.6564	mg/l	
Nominal value	0.025	20	80	Calc Spike Value=	86.8798	mg/l
Mean	0.0351	20.6234	81.2359	76.8798	85.5371	mg/l
Percentage Bias =	40.44	3.12	1.54	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0002	0.1605	0.9751	0.3783	0.2253	
Mo	0.0000	0.0233		0.1425	0.1250	
F value (M1/Mo)	15.3472	6.8854	28.5244	2.6542	1.8018	
Sw	0.0036	0.1527	0.1849	0.3775	0.3536	
Sb	0.0067	0.1852	0.4850	0.2428	0.1583	
St	0.0076	0.2400	0.5190	0.4489	0.3874	
Target maximum St	0.0018	1.0312	4.0618	3.8828	4.2769	
St (as percent of mean)	21.6714	1.1639	0.6389	0.5839	0.4529	
Tabulated F, 0.05	2.1	1.94	2.21	2.01	1.88	
Calculated f	18.7861	0.0542	0.0163	0.0134	0.0082	
Degrees of freedom	6	8	5	7	9	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0165	0.7100	-	1.7555	-	mg/l
(based on each solution)						
Percent Spike Recovery =	86.57	Percent Sample Recovery=		98.25		
+/- (95 percentile)	6.38					
Std.dev.of mean recoveries	0.548254485					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.016520266 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.007608844	0.2400	0.5190	0.4489	0.3874
St (as percent of mean)	21.6714	1.1639	0.6389	0.5839	0.4529
% Bias =	-	3.12	1.54	-	-
% Spike Recovery =	86.57				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	0.0000	
Determinand =	NO_2 Cond.	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0000	mg/l	
Nominal value	0.01	1	4	Calc Spike Value=	2.5000	mg/l
Mean	0.0092	1.0124	4.0226	0.0000	2.4765	mg/l
Percentage Bias =	-8.10	1.24	0.56	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0002	0.0040	0.0000	0.0049	
Mo	0.0000	0.0002		0.0000	0.0028	
F value (M1/Mo)	1.8060	0.7534	2.6967	#DIV/0!	1.7769	
Sw	0.0017	0.0151	0.0385	0.0000	0.0525	
Sb	0.0008	0.0000	0.0251	0.0000	0.0231	
St	0.0019	0.0146	0.0460	0.0000	0.0574	
Target maximum St	0.0005	0.0506	0.2011	no target	0.1238	
St (as percent of mean)	20.3570	1.4446	1.1432	#DIV/0!	2.3161	
Tabulated F, 0.05	1.65	1.59	1.72	#DIV/0!	1.65	
Calculated f	16.5764	0.0835	0.0523	#DIV/0!	0.2146	
Degrees of freedom	16	19	13	#DIV/0!	16	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0079	0.0702	-	0.0000	-	mg/l
(based on each solution)						
Percent Spike Recovery =	99.06	Percent Sample Recovery=		#DIV/0!		
+/- (95 percentile)	1.58					
Std.dev.of mean recoveries	0.049079125					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.007936394 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.001870812	0.0146	0.0460	0.0000	0.0574
St (as percent of mean)	20.3570	1.4446	1.1432	#DIV/0!	2.3161
% Bias =	-	1.24	0.56	-	-
% Spike Recovery =	99.06				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	2.6210	
Determinand =	NO_2 Cond.	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				2.6210	mg/l	
Nominal value	0.01	1	4	Calc Spike Value=	5.0947	mg/l
Mean	0.0092	1.0124	4.0226	2.5947	4.9801	mg/l
Percentage Bias =	-8.10	1.24	0.56	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0002	0.0040	0.1143	0.0382	
Mo	0.0000	0.0002		0.0033	0.0093	
F value (M1/Mo)	1.8060	0.7534	2.6967	34.7966	4.1016	
Sw	0.0017	0.0151	0.0385	0.0573	0.0965	
Sb	0.0008	0.0000	0.0251	0.1666	0.0850	
St	0.0019	0.0146	0.0460	0.1762	0.1286	
Target maximum St	0.0005	0.0506	0.2011	0.1310	0.2490	
St (as percent of mean)	20.3570	1.4446	1.1432	6.7909	2.5829	
Tabulated F, 0.05	1.65	1.59	1.72	3.84	2.6	
Calculated f	16.5764	0.0835	0.0523	1.8080	0.2669	
Degrees of freedom	16	19	13	1	3	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0079	0.0702	-	0.2666	-	mg/l
(based on each solution)						
Percent Spike Recovery =	95.42	Percent Sample Recovery=		95.58		
+/- (95 percentile)	64.66					
Std.dev.of mean recoveries	0.362038672					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.007936394 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.001870812	0.0146	0.0460	0.1762	0.1286
St (as percent of mean)	20.3570	1.4446	1.1432	6.7909	2.5829
% Bias =	-	1.24	0.56	-	-
% Spike Recovery =	95.42				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	2.6210	
Determinand =	NO_2 Cond.	Waste Matrix	Use Sb from standards (Y/N) =		y	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				2.6210	mg/l	
Nominal value	0.01	1	4	Calc Spike Value=	5.0947	mg/l
Mean	0.0092	1.0124	4.0226	2.5947	4.9801	mg/l
Percentage Bias =	-8.10	1.24	0.56	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0002	0.0040	0.0002	0.0040	
Mo	0.0000	0.0002		0.0033	0.0093	
F value (M1/Mo)	1.8060	0.7534	2.6967	0.0523	0.4297	
Sw	0.0017	0.0151	0.0385	0.0573	0.0965	
Sb	0.0008	0.0000	0.0251	Sb from low std	Sb from high std	
St	0.0019	0.0146	0.0460	0.0573	0.1014	
Target maximum St	0.0005	0.0506	0.2011	0.1310	0.2490	
St (as percent of mean)	20.3570	1.4446	1.1432	2.2092	2.0364	
Tabulated F, 0.05	1.65	1.59	1.72	2.1	2.01	
Calculated f	16.5764	0.0835	0.0523	0.1913	0.1659	
Degrees of freedom	16	19	13	6	7	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0079	0.0702	-	0.2666	-	mg/l
(based on each solution)						
Percent Spike Recovery =	95.42	Percent Sample Recovery=		95.58		
+/- (95 percentile)	64.66					
Std.dev.of mean recoveries	0.362038672					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.007936394 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.001870812	0.0146	0.0460	0.0573	0.1014
St (as percent of mean)	20.3570	1.4446	1.1432	2.2092	2.0364
% Bias =	-	1.24	0.56	-	-
% Spike Recovery =	95.42				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	0.0304	
Determinand =	Br Cond.	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0304	mg/l	
Nominal value	0.02	1	4	Calc Spike Value=	2.5301	mg/l
Mean	0.0206	1.0109	4.0111	0.0301	2.5485	mg/l
Percentage Bias =	3.20	1.09	0.28	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0002	0.0008	0.0001	0.0031	
Mo	0.0000	0.0000		0.0000	0.0017	
F value (M1/Mo)	0.3565	5.6557	0.8343	11.0468	1.7990	
Sw	0.0024	0.0065	0.0309	0.0028	0.0416	
Sb	0.0000	0.0071	0.0000	0.0044	0.0186	
St	0.0022	0.0096	0.0303	0.0052	0.0455	
Target maximum St	0.0010	0.0505	0.2006	0.0015	0.1274	
St (as percent of mean)	10.5563	0.9523	0.7554	17.3601	1.7860	
Tabulated F, 0.05	1.61	1.88	1.59	2.1	1.65	
Calculated f	4.4574	0.0363	0.0228	11.8150	0.1276	
Degrees of freedom	18	9	19	6	16	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	FAIL	PASS	
Limit of Detection	0.0111	0.0304	-	0.0130	-	mg/l
(based on each solution)						
Percent Spike Recovery =	100.74	Percent Sample Recovery=		161.16		
+/- (95 percentile)	1.18					
Std.dev.of mean recoveries	0.037640992					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.011060094 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.002178818	0.0096	0.0303	0.0052	0.0455
St (as percent of mean)	10.5563	0.9523	0.7554	17.3601	1.7860
% Bias =	-	1.09	0.28	-	-
% Spike Recovery =	100.74				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	1.3252	
Determinand =	Br Cond.	High Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				1.3252	mg/l	
Nominal value	0.02	1	4	Calc Spike Value=	3.8120	mg/l
Mean	0.0206	1.0109	4.0111	1.3120	3.8511	mg/l
Percentage Bias =	3.20	1.09	0.28	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0002	0.0008	0.0031	0.0185	
Mo	0.0000	0.0000		0.0001	0.0047	
F value (M1/Mo)	0.3565	5.6557	0.8343	27.0960	3.9185	
Sw	0.0024	0.0065	0.0309	0.0106	0.0687	
Sb	0.0000	0.0071	0.0000	0.0271	0.0587	
St	0.0022	0.0096	0.0303	0.0292	0.0904	
Target maximum St	0.0010	0.0505	0.2006	0.0663	0.1926	
St (as percent of mean)	10.5563	0.9523	0.7554	2.2221	2.3467	
Tabulated F, 0.05	1.61	1.88	1.59	2.21	1.79	
Calculated f	4.4574	0.0363	0.0228	0.1936	0.2203	
Degrees of freedom	18	9	19	5	11	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0111	0.0304	-	0.0494	-	mg/l
(based on each solution)						
Percent Spike Recovery =	101.56	Percent Sample Recovery=		102.98		
+/- (95 percentile)	2.64					
Std.dev.of mean recoveries	0.083451029					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.011060094 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.002178818	0.0096	0.0303	0.0292	0.0904
St (as percent of mean)	10.5563	0.9523	0.7554	2.2221	2.3467
% Bias =	-	1.09	0.28	-	-
% Spike Recovery =	101.56				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	2.5968	
Determinand =	Br Cond.	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				2.5968	mg/l	
Nominal value	0.02	1	4	Calc Spike Value=	5.0708	mg/l
Mean	0.0206	1.0109	4.0111	2.5708	4.9862	mg/l
Percentage Bias =	3.20	1.09	0.28	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0002	0.0008	0.0147	0.0046	
Mo	0.0000	0.0000		0.0098	0.0092	
F value (M1/Mo)	0.3565	5.6557	0.8343	1.5028	0.5054	
Sw	0.0024	0.0065	0.0309	0.0989	0.0957	
Sb	0.0000	0.0071	0.0000	0.0351	0.0000	
St	0.0022	0.0096	0.0303	0.1050	0.0896	
Target maximum St	0.0010	0.0505	0.2006	0.1298	0.2493	
St (as percent of mean)	10.5563	0.9523	0.7554	4.0830	1.7961	
Tabulated F, 0.05	1.61	1.88	1.59	1.83	1.79	
Calculated f	4.4574	0.0363	0.0228	0.6536	0.1290	
Degrees of freedom	18	9	19	10	11	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0111	0.0304	-	0.4600	-	mg/l
(based on each solution)						
Percent Spike Recovery =	96.61	Percent Sample Recovery=		96.71		
+/- (95 percentile)	1.72					
Std.dev.of mean recoveries	0.041569861					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.011060094 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.002178818	0.0096	0.0303	0.1050	0.0896
St (as percent of mean)	10.5563	0.9523	0.7554	4.0830	1.7961
% Bias =	-	1.09	0.28	-	-
% Spike Recovery =	96.61				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	17.3228	
Determinand =	NO_3 Cond.	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				17.3228	mg/l	
Nominal value	0.01	10	40	Calc Spike Value=	27.1496	mg/l
Mean	0.0142	10.0943	40.3884	17.1496	27.4528	mg/l
Percentage Bias =	41.85	0.94	0.97	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.0408	0.8851	0.1540	1.0569	
Mo	0.0000	0.0250		0.0086	0.1619	
F value (M1/Mo)	5.8883	1.6282	30.0703	17.8725	6.5274	
Sw	0.0029	0.1583	0.1716	0.0928	0.4024	
Sb	0.0032	0.0627	0.4625	0.1906	0.4730	
St	0.0044	0.1702	0.4933	0.2120	0.6210	
Target maximum St	0.0007	0.5047	2.0194	0.8661	1.3726	
St (as percent of mean)	30.7240	1.6864	1.2214	1.2364	2.2621	
Tabulated F, 0.05	1.88	1.63	2.21	2.21	1.94	
Calculated f	37.7585	0.1138	0.0597	0.0599	0.2047	
Degrees of freedom	9	17	5	5	8	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0136	0.7359	-	0.4316	-	mg/l
(based on each solution)						
Percent Spike Recovery =	103.03	Percent Sample Recovery=		101.77		
+/- (95 percentile)	2.65					
Std.dev.of mean recoveries	0.319088713					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.013595055 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.004358196	0.1702	0.4933	0.2120	0.6210
St (as percent of mean)	30.7240	1.6864	1.2214	1.2364	2.2621
% Bias =	-	0.94	0.97	-	-
% Spike Recovery =	103.03				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	0.0212	
Determinand =	NO_3 Cond.	High Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0212	mg/l	
Nominal value	0.01	10	40	Calc Spike Value=	10.0209	mg/l
Mean	0.0142	10.0943	40.3884	0.0209	9.9968	mg/l
Percentage Bias =	41.85	0.94	0.97	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.0408	0.8851	0.0072	0.0750	
Mo	0.0000	0.0250		0.0032	0.0143	
F value (M1/Mo)	5.8883	1.6282	30.0703	2.2403	5.2628	
Sw	0.0029	0.1583	0.1716	0.0566	0.1194	
Sb	0.0032	0.0627	0.4625	0.0315	0.1232	
St	0.0044	0.1702	0.4933	0.0648	0.1716	
Target maximum St	0.0007	0.5047	2.0194	0.0011	0.4998	
St (as percent of mean)	30.7240	1.6864	1.2214	309.2628	1.7164	
Tabulated F, 0.05	1.88	1.63	2.21	1.67	1.88	
Calculated f	37.7585	0.1138	0.0597	3749.6060	0.1178	
Degrees of freedom	9	17	5	15	9	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	FAIL	PASS	
Limit of Detection	0.0136	0.7359	-	0.2632	-	mg/l
(based on each solution)						
Percent Spike Recovery =	99.76	Percent Sample Recovery=		-15.49		
+/- (95 percentile)	0.66					
Std.dev.of mean recoveries	0.083529332					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.013595055 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.004358196	0.1702	0.4933	0.0648	0.1716
St (as percent of mean)	30.7240	1.6864	1.2214	309.2628	1.7164
% Bias =	-	0.94	0.97	-	-
% Spike Recovery =	99.76				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	25.4633	
Determinand =	NO_3 Cond.	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				25.4633	mg/l	
Nominal value	0.01	10	40	Calc Spike Value=	35.2087	mg/l
Mean	0.0142	10.0943	40.3884	25.2087	34.7734	mg/l
Percentage Bias =	41.85	0.94	0.97	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.0408	0.8851	0.5090	0.0152	
Mo	0.0000	0.0250		0.5390	0.1039	
F value (M1/Mo)	5.8883	1.6282	30.0703	0.9443	0.1466	
Sw	0.0029	0.1583	0.1716	0.7342	0.3223	
Sb	0.0032	0.0627	0.4625	0.0000	0.0000	
St	0.0044	0.1702	0.4933	0.7290	0.2859	
Target maximum St	0.0007	0.5047	2.0194	1.2732	1.7387	
St (as percent of mean)	30.7240	1.6864	1.2214	2.8920	0.8221	
Tabulated F, 0.05	1.88	1.63	2.21	1.79	1.83	
Calculated f	37.7585	0.1138	0.0597	0.3279	0.0270	
Degrees of freedom	9	17	5	11	10	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0136	0.7359	-	3.4139	-	mg/l
(based on each solution)						
Percent Spike Recovery =	95.65	Percent Sample Recovery=		98.27		
+/- (95 percentile)	7.43					
Std.dev.of mean recoveries	0.691749442					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.013595055 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.004358196	0.1702	0.4933	0.7290	0.2859
St (as percent of mean)	30.7240	1.6864	1.2214	2.8920	0.8221
% Bias =	-	0.94	0.97	-	-
% Spike Recovery =	95.65				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	2.5594	
Determinand =	HPO_4	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		500	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		5.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				2.5594	mg/l	
Nominal value	0.05	2	8	Calc Spike Value=	7.5338	mg/l
Mean	0.0408	2.0144	8.0097	2.5338	7.4073	mg/l
Percentage Bias =	-18.43	0.72	0.12	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.0006	0.0050	0.0051	0.0256	
Mo	0.0001	0.0004		0.0018	0.0272	
F value (M1/Mo)	1.3506	1.6777	2.5107	2.8674	0.9390	
Sw	0.0091	0.0188	0.0444	0.0420	0.1650	
Sb	0.0027	0.0077	0.0273	0.0287	0.0000	
St	0.0094	0.0203	0.0521	0.0508	0.1637	
Target maximum St	0.0020	0.1007	0.4005	0.1280	0.3704	
St (as percent of mean)	23.1449	1.0099	0.6508	2.0061	2.2099	
Tabulated F, 0.05	1.61	1.63	1.69	1.72	1.59	
Calculated f	21.4274	0.0408	0.0169	0.1578	0.1953	
Degrees of freedom	18	17	14	13	19	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0421	0.0875	-	0.1952	-	mg/l
(based on each solution)						
Percent Spike Recovery =	97.47	Percent Sample Recovery=		95.01		
+/- (95 percentile)	1.06					
Std.dev.of mean recoveries	0.068614394					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.042088665 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.009439631	0.0203	0.0521	0.0508	0.1637
St (as percent of mean)	23.1449	1.0099	0.6508	2.0061	2.2099
% Bias =	-	0.72	0.12	-	-
% Spike Recovery =	97.47				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	0.0000	
Determinand =	HPO_4	High Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		500	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		5.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0000	mg/l	
Nominal value	0.05	2	8	Calc Spike Value=	5.0000	mg/l
Mean	0.0408	2.0144	8.0097	0.0000	4.8840	mg/l
Percentage Bias =	-18.43	0.72	0.12	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.0006	0.0050	0.0000	0.0078	
Mo	0.0001	0.0004		0.0000	0.0122	
F value (M1/Mo)	1.3506	1.6777	2.5107	#DIV/0!	0.6427	
Sw	0.0091	0.0188	0.0444	0.0000	0.1104	
Sb	0.0027	0.0077	0.0273	0.0000	0.0000	
St	0.0094	0.0203	0.0521	0.0000	0.1054	
Target maximum St	0.0020	0.1007	0.4005	no target	0.2442	
St (as percent of mean)	23.1449	1.0099	0.6508	#DIV/0!	2.1571	
Tabulated F, 0.05	1.61	1.63	1.69	#DIV/0!	1.59	
Calculated f	21.4274	0.0408	0.0169	#DIV/0!	0.1861	
Degrees of freedom	18	17	14	#DIV/0!	19	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0421	0.0875	-	0.0000	-	mg/l
(based on each solution)						
Percent Spike Recovery =	97.68	Percent Sample Recovery=		#DIV/0!		
+/- (95 percentile)	0.74					
Std.dev.of mean recoveries	0.0481706					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.042088665 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.009439631	0.0203	0.0521	0.0000	0.1054
St (as percent of mean)	23.1449	1.0099	0.6508	#DIV/0!	2.1571
% Bias =	-	0.72	0.12	-	-
% Spike Recovery =	97.68				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	0.2890	
Determinand =	HPO_4	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		500	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		5.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.2890	mg/l	
Nominal value	0.05	2	8	Calc Spike Value=	5.2861	mg/l
Mean	0.0408	2.0144	8.0097	0.2861	5.2094	mg/l
Percentage Bias =	-18.43	0.72	0.12	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.0006	0.0050	0.0002	0.0123	
Mo	0.0001	0.0004		0.0002	0.0566	
F value (M1/Mo)	1.3506	1.6777	2.5107	0.8791	0.2180	
Sw	0.0091	0.0188	0.0444	0.0155	0.2379	
Sb	0.0027	0.0077	0.0273	0.0000	0.0000	
St	0.0094	0.0203	0.0521	0.0152	0.2134	
Target maximum St	0.0020	0.1007	0.4005	0.0144	0.2605	
St (as percent of mean)	23.1449	1.0099	0.6508	5.3299	4.0968	
Tabulated F, 0.05	1.61	1.63	1.69	1.79	1.83	
Calculated f	21.4274	0.0408	0.0169	1.1137	0.6713	
Degrees of freedom	18	17	14	11	10	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0421	0.0875	-	0.0720	-	mg/l
(based on each solution)						
Percent Spike Recovery =	98.47	Percent Sample Recovery=		73.19		
+/- (95 percentile)	2.11					
Std.dev.of mean recoveries	0.101564282					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.042088665 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.009439631	0.0203	0.0521	0.0152	0.2134
St (as percent of mean)	23.1449	1.0099	0.6508	5.3299	4.0968
% Bias =	-	0.72	0.12	-	-
% Spike Recovery =	98.47				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	71.4534	
Determinand =	SO_4	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		5000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		50.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				71.4534	mg/l	
Nominal value	0.05	40	160	Calc Spike Value=	120.7388	mg/l
Mean	0.0441	40.9955	161.8161	70.7388	121.4188	mg/l
Percentage Bias =	-11.76	2.49	1.14	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.3763	2.5535	1.0133	1.7746	
Mo	0.0000	0.0644		0.0160	0.5623	
F value (M1/Mo)	5.5047	5.8432	6.5243	63.1596	3.1560	
Sw	0.0048	0.2538	0.6256	0.1267	0.7499	
Sb	0.0050	0.2793	0.7352	0.4993	0.5505	
St	0.0069	0.3773	0.9654	0.5151	0.9302	
Target maximum St	0.0022	2.0498	8.0908	3.5727	6.0709	
St (as percent of mean)	15.7026	0.9205	0.5966	0.7282	0.7661	
Tabulated F, 0.05	1.88	1.88	1.94	2.37	1.75	
Calculated f	9.8628	0.0339	0.0142	0.0208	0.0235	
Degrees of freedom	9	9	8	4	12	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0221	1.1801	-	0.5890	-	mg/l
(based on each solution)						
Percent Spike Recovery =	101.36	Percent Sample Recovery=		100.96		
+/- (95 percentile)	0.57					
Std.dev.of mean recoveries	0.366734818					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.022093291 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.006927973	0.3773	0.9654	0.5151	0.9302
St (as percent of mean)	15.7026	0.9205	0.5966	0.7282	0.7661
% Bias =	-	2.49	1.14	-	-
% Spike Recovery =	101.36				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	58.0074	
Determinand =	SO_4	High Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		5000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		50.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				58.0074	mg/l	
Nominal value	0.05	40	160	Calc Spike Value=	107.4273	mg/l
Mean	0.0441	40.9955	161.8161	57.4273	109.8497	mg/l
Percentage Bias =	-11.76	2.49	1.14	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.3763	2.5535	1.0704	3.7870	
Mo	0.0000	0.0644		0.0388	0.5679	
F value (M1/Mo)	5.5047	5.8432	6.5243	27.5816	6.6687	
Sw	0.0048	0.2538	0.6256	0.1970	0.7536	
Sb	0.0050	0.2793	0.7352	0.5078	0.8971	
St	0.0069	0.3773	0.9654	0.5447	1.1716	
Target maximum St	0.0022	2.0498	8.0908	2.9004	5.4925	
St (as percent of mean)	15.7026	0.9205	0.5966	0.9485	1.0666	
Tabulated F, 0.05	1.88	1.88	1.94	2.21	1.94	
Calculated f	9.8628	0.0339	0.0142	0.0353	0.0455	
Degrees of freedom	9	9	8	5	8	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0221	1.1801	-	0.9161	-	mg/l
(based on each solution)						
Percent Spike Recovery =	104.84	Percent Sample Recovery=		104.22		
+/- (95 percentile)	1.23					
Std.dev.of mean recoveries	0.706927851					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.022093291 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.006927973	0.3773	0.9654	0.5447	1.1716
St (as percent of mean)	15.7026	0.9205	0.5966	0.9485	1.0666
% Bias =	-	2.49	1.14	-	-
% Spike Recovery =	104.84				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	105.4113	
Determinand =	SO_4	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		5000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		50.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				105.4113	mg/l	
Nominal value	0.05	40	160	Calc Spike Value=	154.3572	mg/l
Mean	0.0441	40.9955	161.8161	104.3572	151.8921	mg/l
Percentage Bias =	-11.76	2.49	1.14	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0001	0.3763	2.5535	3.0257	0.0646	
Mo	0.0000	0.0644		0.0362	1.6643	
F value (M1/Mo)	5.5047	5.8432	6.5243	83.5954	0.0388	
Sw	0.0048	0.2538	0.6256	0.1903	1.2901	
Sb	0.0050	0.2793	0.7352	0.8645	0.0000	
St	0.0069	0.3773	0.9654	0.8852	1.1245	
Target maximum St	0.0022	2.0498	8.0908	5.2706	7.5946	
St (as percent of mean)	15.7026	0.9205	0.5966	0.8482	0.7403	
Tabulated F, 0.05	1.88	1.88	1.94	3	1.88	
Calculated f	9.8628	0.0339	0.0142	0.0282	0.0219	
Degrees of freedom	9	9	8	2	9	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0221	1.1801	-	0.8847	-	mg/l
(based on each solution)						
Percent Spike Recovery =	95.07	Percent Sample Recovery=		97.64		
+/- (95 percentile)	2.52					
Std.dev.of mean recoveries	1.123060129					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.022093291 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.006927973	0.3773	0.9654	0.8852	1.1245
St (as percent of mean)	15.7026	0.9205	0.5966	0.8482	0.7403
% Bias =	-	2.49	1.14	-	-
% Spike Recovery =	95.07				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	0.0005	
Determinand =	NO_2 ABS	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0005	mg/l	
Nominal value	0.01	1	4	Calc Spike Value=	2.5005	mg/l
Mean	0.0081	1.0032	4.0028	0.0005	2.4988	mg/l
Percentage Bias =	-18.80	0.32	0.07	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0006	0.0015	0.0000	0.0040	
Mo	0.0000	0.0001		0.0000	0.0041	
F value (M1/Mo)	2.7702	7.7226	2.2241	0.9083	0.9769	
Sw	0.0010	0.0086	0.0263	0.0010	0.0639	
Sb	0.0007	0.0111	0.0145	0.0000	0.0000	
St	0.0012	0.0140	0.0300	0.0010	0.0637	
Target maximum St	0.0004	0.0502	0.2001	0.0000	0.1249	
St (as percent of mean)	14.7889	1.3978	0.7496	190.1017	2.5502	
Tabulated F, 0.05	1.72	2.01	1.67	1.59	1.59	
Calculated f	8.7485	0.0781	0.0225	1416.7800	0.2601	
Degrees of freedom	13	7	15	19	19	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	FAIL	PASS	
Limit of Detection	0.0046	0.0398	-	0.0046	-	mg/l
(based on each solution)						
Percent Spike Recovery =	99.93	Percent Sample Recovery=		-234.73		
+/- (95 percentile)	1.96					
Std.dev.of mean recoveries	0.061512686					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.004649225 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.001200859	0.0140	0.0300	0.0010	0.0637
St (as percent of mean)	14.7889	1.3978	0.7496	190.1017	2.5502
% Bias =	-	0.32	0.07	-	-
% Spike Recovery =	99.93				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	0.0005	
Determinand =	NO_2 ABS	High Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0005	mg/l	
Nominal value	0.01	1	4	Calc Spike Value=	2.5005	mg/l
Mean	0.0081	1.0032	4.0028	0.0005	2.3825	mg/l
Percentage Bias =	-18.80	0.32	0.07	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0006	0.0015	0.0000	0.0181	
Mo	0.0000	0.0001		0.0000	0.0024	
F value (M1/Mo)	2.7702	7.7226	2.2241	47.7248	7.5590	
Sw	0.0010	0.0086	0.0263	0.0003	0.0490	
Sb	0.0007	0.0111	0.0145	0.0009	0.0627	
St	0.0012	0.0140	0.0300	0.0010	0.0796	
Target maximum St	0.0004	0.0502	0.2001	0.0000	0.1191	
St (as percent of mean)	14.7889	1.3978	0.7496	182.9518	3.3414	
Tabulated F, 0.05	1.72	2.01	1.67	2.21	2.01	
Calculated f	8.7485	0.0781	0.0225	1312.2108	0.4466	
Degrees of freedom	13	7	15	5	7	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	FAIL	PASS	
Limit of Detection	0.0046	0.0398	-	0.0013	-	mg/l
(based on each solution)						
Percent Spike Recovery =	95.28	Percent Sample Recovery=		-22401.37		
+/- (95 percentile)	2.74					
Std.dev.of mean recoveries	0.076005942					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.004649225 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.001200859	0.0140	0.0300	0.0010	0.0796
St (as percent of mean)	14.7889	1.3978	0.7496	182.9518	3.3414
% Bias =	-	0.32	0.07	-	-
% Spike Recovery =	95.28				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	0.0005	
Determinand =	NO_2 ABS	High Matrix	Use Sb from standards (Y/N) =		y	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0005	mg/l	
Nominal value	0.01	1	4	Calc Spike Value=	2.5005	mg/l
Mean	0.0081	1.0032	4.0028	0.0005	2.3825	mg/l
Percentage Bias =	-18.80	0.32	0.07	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0006	0.0015	0.0006	0.0015	
Mo	0.0000	0.0001		0.0000	0.0024	
F value (M1/Mo)	2.7702	7.7226	2.2241	7794.6433	0.6387	
Sw	0.0010	0.0086	0.0263	0.0003	0.0490	
Sb	0.0007	0.0111	0.0145	Sb from low std	Sb from high std	
St	0.0012	0.0140	0.0300	0.0003	0.0498	
Target maximum St	0.0004	0.0502	0.2001	0.0000	0.1191	
St (as percent of mean)	14.7889	1.3978	0.7496	51.3877	2.0884	
Tabulated F, 0.05	1.72	2.01	1.67	2.37	1.59	
Calculated f	8.7485	0.0781	0.0225	103.5259	0.1744	
Degrees of freedom	13	7	15	4	19	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	FAIL	PASS	
Limit of Detection	0.0046	0.0398	-	0.0013	-	mg/l
(based on each solution)						
Percent Spike Recovery =	95.28	Percent Sample Recovery=		-22401.37		
+/- (95 percentile)	2.74					
Std.dev.of mean recoveries	0.076005942					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.004649225 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.001200859	0.0140	0.0300	0.0003	0.0498
St (as percent of mean)	14.7889	1.3978	0.7496	51.3877	2.0884
% Bias =	-	0.32	0.07	-	-
% Spike Recovery =	95.28				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	2.5569	
Determinand =	NO_2 ABS	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				2.5569	mg/l	
Nominal value	0.01	1	4	Calc Spike Value=	5.0313	mg/l
Mean	0.0081	1.0032	4.0028	2.5313	4.9590	mg/l
Percentage Bias =	-18.80	0.32	0.07	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0006	0.0015	0.0009	0.0262	
Mo	0.0000	0.0001		0.0018	0.0036	
F value (M1/Mo)	2.7702	7.7226	2.2241	0.5214	7.3380	
Sw	0.0010	0.0086	0.0263	0.0426	0.0598	
Sb	0.0007	0.0111	0.0145	0.0000	0.0752	
St	0.0012	0.0140	0.0300	0.0400	0.0961	
Target maximum St	0.0004	0.0502	0.2001	0.1278	0.2480	
St (as percent of mean)	14.7889	1.3978	0.7496	1.5789	1.9379	
Tabulated F, 0.05	1.72	2.01	1.67	2.01	3	
Calculated f	8.7485	0.0781	0.0225	0.0977	0.1502	
Degrees of freedom	13	7	15	7	2	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0046	0.0398	-	0.1981	-	mg/l
(based on each solution)						
Percent Spike Recovery =	97.11	Percent Sample Recovery=		97.14		
+/- (95 percentile)	6.83					
Std.dev.of mean recoveries	0.082731493					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.004649225 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.001200859	0.0140	0.0300	0.0400	0.0961
St (as percent of mean)	14.7889	1.3978	0.7496	1.5789	1.9379
% Bias =	-	0.32	0.07	-	-
% Spike Recovery =	97.11				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	2.5569	
Determinand =	NO_2 ABS	Waste Matrix	Use Sb from standards (Y/N) =		y	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				2.5569	mg/l	
Nominal value	0.01	1	4	Calc Spike Value=	5.0313	mg/l
Mean	0.0081	1.0032	4.0028	2.5313	4.9590	mg/l
Percentage Bias =	-18.80	0.32	0.07	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0006	0.0015	0.0006	0.0015	
Mo	0.0000	0.0001		0.0018	0.0036	
F value (M1/Mo)	2.7702	7.7226	2.2241	0.3122	0.4291	
Sw	0.0010	0.0086	0.0263	0.0426	0.0598	
Sb	0.0007	0.0111	0.0145	Sb from low std	Sb from high std	
St	0.0012	0.0140	0.0300	0.0511	0.0624	
Target maximum St	0.0004	0.0502	0.2001	0.1278	0.2480	
St (as percent of mean)	14.7889	1.3978	0.7496	2.0203	1.2589	
Tabulated F, 0.05	1.72	2.01	1.67	2.01	2.01	
Calculated f	8.7485	0.0781	0.0225	0.1600	0.0634	
Degrees of freedom	13	7	15	7	7	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0046	0.0398	-	0.1981	-	mg/l
(based on each solution)						
Percent Spike Recovery =	97.11	Percent Sample Recovery=		97.14		
+/- (95 percentile)	6.83					
Std.dev.of mean recoveries	0.082731493					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.004649225 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.001200859	0.0140	0.0300	0.0511	0.0624
St (as percent of mean)	14.7889	1.3978	0.7496	2.0203	1.2589
% Bias =	-	0.32	0.07	-	-
% Spike Recovery =	97.11				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	0.0340	
Determinand =	Br ABS	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0340	mg/l	
Nominal value	0.02	1	4	Calc Spike Value=	2.5337	mg/l
Mean	0.0200	1.0078	4.0088	0.0337	2.5220	mg/l
Percentage Bias =	-0.17	0.78	0.22	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0013	0.0019	0.0000	0.0008	
Mo	0.0000	0.0002		0.0000	0.0054	
F value (M1/Mo)	0.5372	5.4498	2.6089	0.8070	0.1575	
Sw	0.0018	0.0152	0.0273	0.0031	0.0732	
Sb	0.0000	0.0161	0.0173	0.0000	0.0000	
St	0.0017	0.0221	0.0323	0.0030	0.0650	
Target maximum St	0.0010	0.0504	0.2004	0.0017	0.1261	
St (as percent of mean)	8.6177	2.1966	0.8050	8.9592	2.5772	
Tabulated F, 0.05	1.59	1.88	1.69	1.59	1.65	
Calculated f	2.9706	0.1930	0.0259	3.1468	0.2657	
Degrees of freedom	19	9	14	19	16	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	FAIL	PASS	
Limit of Detection	0.0085	0.0708	-	0.0144	-	mg/l
(based on each solution)						
Percent Spike Recovery =	99.53	Percent Sample Recovery=		65.44		
+/- (95 percentile)	1.65					
Std.dev.of mean recoveries	0.052858663					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.008507721 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.00172052	0.0221	0.0323	0.0030	0.0650
St (as percent of mean)	8.6177	2.1966	0.8050	8.9592	2.5772
% Bias =	-	0.78	0.22	-	-
% Spike Recovery =	99.53				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	1.4725	
Determinand =	Br ABS	High Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				1.4725	mg/l	
Nominal value	0.02	1	4	Calc Spike Value=	3.9578	mg/l
Mean	0.0200	1.0078	4.0088	1.4578	3.9590	mg/l
Percentage Bias =	-0.17	0.78	0.22	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0013	0.0019	0.0007	0.0081	
Mo	0.0000	0.0002		0.0003	0.0025	
F value (M1/Mo)	0.5372	5.4498	2.6089	2.7155	3.2382	
Sw	0.0018	0.0152	0.0273	0.0159	0.0500	
Sb	0.0000	0.0161	0.0173	0.0104	0.0374	
St	0.0017	0.0221	0.0323	0.0190	0.0624	
Target maximum St	0.0010	0.0504	0.2004	0.0736	0.1979	
St (as percent of mean)	8.6177	2.1966	0.8050	1.3003	1.5761	
Tabulated F, 0.05	1.59	1.88	1.69	1.72	1.75	
Calculated f	2.9706	0.1930	0.0259	0.0663	0.0994	
Degrees of freedom	19	9	14	13	12	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0085	0.0708	-	0.0737	-	mg/l
(based on each solution)						
Percent Spike Recovery =	100.05	Percent Sample Recovery=		100.08		
+/- (95 percentile)	1.54					
Std.dev.of mean recoveries	0.047862707					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.008507721 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.00172052	0.0221	0.0323	0.0190	0.0624
St (as percent of mean)	8.6177	2.1966	0.8050	1.3003	1.5761
% Bias =	-	0.78	0.22	-	-
% Spike Recovery =	100.05				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	2.5748	
Determinand =	Br ABS	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		250	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		2.5000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				2.5748	mg/l	
Nominal value	0.02	1	4	Calc Spike Value=	5.0490	mg/l
Mean	0.0200	1.0078	4.0088	2.5490	4.9966	mg/l
Percentage Bias =	-0.17	0.78	0.22	-	-	
Pass/Fail	Pass	Pass	Pass			
M1	0.0000	0.0013	0.0019	0.0063	0.0093	
Mo	0.0000	0.0002		0.0015	0.0061	
F value (M1/Mo)	0.5372	5.4498	2.6089	4.1647	1.5330	
Sw	0.0018	0.0152	0.0273	0.0390	0.0779	
Sb	0.0000	0.0161	0.0173	0.0346	0.0285	
St	0.0017	0.0221	0.0323	0.0521	0.0830	
Target maximum St	0.0010	0.0504	0.2004	0.1287	0.2498	
St (as percent of mean)	8.6177	2.1966	0.8050	2.0451	1.6605	
Tabulated F, 0.05	1.59	1.88	1.69	2.21	1.88	
Calculated f	2.9706	0.1930	0.0259	0.1640	0.1103	
Degrees of freedom	19	9	14	5	9	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0085	0.0708	-	0.1811	-	mg/l
(based on each solution)						
Percent Spike Recovery =	97.90	Percent Sample Recovery=		97.94		
+/- (95 percentile)	1.32					
Std.dev.of mean recoveries	0.031934503					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.008507721 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.00172052	0.0221	0.0323	0.0521	0.0830
St (as percent of mean)	8.6177	2.1966	0.8050	2.0451	1.6605
% Bias =	-	0.78	0.22	-	-
% Spike Recovery =	97.90				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Low Matrix	17.2150	
Determinand =	NO_3 ABS	Low Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				17.2150	mg/l	
Nominal value	0.01	10	40	Calc Spike Value=	27.0429	mg/l
Mean	0.0126	10.0539	40.2399	17.0429	27.2397	mg/l
Percentage Bias =	26.40	0.54	0.60	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0907	0.1701	0.0090	0.0465	
Mo	0.0000	0.0067		0.0097	0.2345	
F value (M1/Mo)	3.1629	13.4521	4.2390	0.9303	0.1984	
Sw	0.0023	0.0821	0.2003	0.0984	0.4843	
Sb	0.0017	0.1449	0.1803	0.0000	0.0000	
St	0.0028	0.1665	0.2695	0.0975	0.4330	
Target maximum St	0.0006	0.5027	2.0120	0.8608	1.3620	
St (as percent of mean)	22.2840	1.6561	0.6697	0.5724	1.5897	
Tabulated F, 0.05	1.75	2.1	1.83	1.59	1.63	
Calculated f	19.8630	0.1097	0.0179	0.0128	0.1011	
Degrees of freedom	12	6	10	19	17	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0106	0.3818	-	0.4576	-	mg/l
(based on each solution)						
Percent Spike Recovery =	101.97	Percent Sample Recovery=		101.16		
+/- (95 percentile)	2.62					
Std.dev.of mean recoveries	0.325881661					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.010551846 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.002816691	0.1665	0.2695	0.0975	0.4330
St (as percent of mean)	22.2840	1.6561	0.6697	0.5724	1.5897
% Bias =	-	0.54	0.60	-	-
% Spike Recovery =	101.97				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	0.0116	
Determinand =	NO_3 ABS	High Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0116	mg/l	
Nominal value	0.01	10	40	Calc Spike Value=	10.0115	mg/l
Mean	0.0126	10.0539	40.2399	0.0115	10.2180	mg/l
Percentage Bias =	26.40	0.54	0.60	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0907	0.1701	0.0011	0.3031	
Mo	0.0000	0.0067		0.0000	0.0420	
F value (M1/Mo)	3.1629	13.4521	4.2390	66.2284	7.2217	
Sw	0.0023	0.0821	0.2003	0.0041	0.2049	
Sb	0.0017	0.1449	0.1803	0.0166	0.2555	
St	0.0028	0.1665	0.2695	0.0171	0.3275	
Target maximum St	0.0006	0.5027	2.0120	0.0006	0.5109	
St (as percent of mean)	22.2840	1.6561	0.6697	148.4159	3.2053	
Tabulated F, 0.05	1.75	2.1	1.83	2.37	1.94	
Calculated f	19.8630	0.1097	0.0179	863.5574	0.4110	
Degrees of freedom	12	6	10	4	8	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	FAIL	PASS	
Limit of Detection	0.0106	0.3818	-	0.0191	-	mg/l
(based on each solution)						
Percent Spike Recovery =	102.07	Percent Sample Recovery=		1896.19		
+/- (95 percentile)	3.70					
Std.dev.of mean recoveries	0.410776018					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.010551846 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.002816691	0.1665	0.2695	0.0171	0.3275
St (as percent of mean)	22.2840	1.6561	0.6697	148.4159	3.2053
% Bias =	-	0.54	0.60	-	-
% Spike Recovery =	102.07				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	High Matrix	0.0116	
Determinand =	NO_3 ABS	High Matrix	Use Sb from standards (Y/N) =		y	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				0.0116	mg/l	
Nominal value	0.01	10	40	Calc Spike Value=	10.0115	mg/l
Mean	0.0126	10.0539	40.2399	0.0115	10.2180	mg/l
Percentage Bias =	26.40	0.54	0.60	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0907	0.1701	0.0907	0.1701	
Mo	0.0000	0.0067		0.0000	0.0420	
F value (M1/Mo)	3.1629	13.4521	4.2390	5388.0313	4.0524	
Sw	0.0023	0.0821	0.2003	0.0041	0.2049	
Sb	0.0017	0.1449	0.1803	Sb from low std	Sb from high std	
St	0.0028	0.1665	0.2695	0.0041	0.2099	
Target maximum St	0.0006	0.5027	2.0120	0.0006	0.5109	
St (as percent of mean)	22.2840	1.6561	0.6697	35.7050	2.0546	
Tabulated F, 0.05	1.75	2.1	1.83	2.37	1.79	
Calculated f	19.8630	0.1097	0.0179	49.9792	0.1688	
Degrees of freedom	12	6	10	4	11	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	FAIL	PASS	
Limit of Detection	0.0106	0.3818	-	0.0191	-	mg/l
(based on each solution)						
Percent Spike Recovery =	102.07	Percent Sample Recovery=		1896.19		
+/- (95 percentile)	3.70					
Std.dev.of mean recoveries	0.410776018					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.010551846 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.002816691	0.1665	0.2695	0.0041	0.2099
St (as percent of mean)	22.2840	1.6561	0.6697	35.7050	2.0546
% Bias =	-	0.54	0.60	-	-
% Spike Recovery =	102.07				

Results of Method Validation Test				Date report produced=	27/01/2004	
Laboratory :	BGS E block					
Operator name :	Ben Charlton/Mike Watts			Reference		
UKAS Method Reference =	AGN 2.3.6		Test solution	Waste Matrix	24.8034	
Determinand =	NO_3 ABS	Waste Matrix	Use Sb from standards (Y/N) =		n	
Units =	mg/l		Concentration of spiking soln. =		1000	mg/l
Date analysis started		30/01/2003	Volume of spiking solution (mls) =		0.5	
Date analysis completed			Volume of sample used (mls) =		49.5	
Target conc Std. Dev. =			Total volume produced (mls) =		50	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		10.0000	mg/l
	Soln/Sample A	Soln/Sample B	Soln/Sample C	Soln/Sample D	Soln/Sample E	
Identity	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE	
Measured Sample soln D				24.8034	mg/l	
Nominal value	0.01	10	40	Calc Spike Value=	34.5553	mg/l
Mean	0.0126	10.0539	40.2399	24.5553	34.2797	mg/l
Percentage Bias =	26.40	0.54	0.60	-	-	
Pass/Fail	Fail	Pass	Pass			
M1	0.0000	0.0907	0.1701	0.0322	0.2423	
Mo	0.0000	0.0067		0.0915	0.1174	
F value (M1/Mo)	3.1629	13.4521	4.2390	0.3519	2.0641	
Sw	0.0023	0.0821	0.2003	0.3025	0.3426	
Sb	0.0017	0.1449	0.1803	0.0000	0.1767	
St	0.0028	0.1665	0.2695	0.2769	0.3855	
Target maximum St	0.0006	0.5027	2.0120	1.2402	1.7140	
St (as percent of mean)	22.2840	1.6561	0.6697	1.1279	1.1246	
Tabulated F, 0.05	1.75	2.1	1.83	1.79	1.94	
Calculated f	19.8630	0.1097	0.0179	0.0499	0.0506	
Degrees of freedom	12	6	10	11	8	
Pass/Fail (LoD & S.D.s)	FAIL	PASS	PASS	PASS	PASS	
Limit of Detection	0.0106	0.3818	-	1.4068	-	mg/l
(based on each solution)						
Percent Spike Recovery =	97.24	Percent Sample Recovery=		98.88		
+/- (95 percentile)	0.92					
Std.dev.of mean recoveries	0.08893336					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.010551846 Units = mg/l

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.002816691	0.1665	0.2695	0.2769	0.3855
St (as percent of mean)	22.2840	1.6561	0.6697	1.1279	1.1246
% Bias =	-	0.54	0.60	-	-
% Spike Recovery =	97.24				