British Geological Survey
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Validation Report for the Determination of Non-Purgeable Organic Carbon by TOC-V Analyser

Science Facilities Programme

Internal Report IR/11/043

BRITISH GEOLOGICAL SURVEY

SCIENCE FACILITIES PROGRAMME

INTERNAL REPORT IR/11/043

Validation Report for the Determination of Non-Purgeable Organic Carbon by TOC-V Analyser

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Keywords

TOC, NPOC, UKAS, validation.

Front cover

The Shimadzu TOC-V

Bibliographical reference

RICHARDSON C L, SHAW R A AND GOWING C J B. 2011. Validation Report for the Determination of Non-Purgeable Organic Carbon by TOC-V Analyser. *British Geological Survey Internal Report*, IR/11/043. 21pp.

Keyworth, Nottingham British Geological Survey 2011

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Summary

This report describes the validation of Technical Procedure AGN 2.3.8, Determination of Non-Purgeable Organic Carbon (NPOC), in preparation for accreditation of the analytical method by the United Kingdom Accreditation Service (UKAS).

1 Method Overview

1.1 INSTRUMENTATION

The determination of the NPOC content of water samples is carried out using a Shimadzu TOC-V CPH analyser (Serial No. 41546360) with associated Shimadzu ASI-V auto-sampler (Serial No. 41D78299). The system is controlled by a PC installed with TOC Control V Software. The carrier gas is high purity air supplied by a Parker Balston 78-40-220 TOC gas generator (Serial No. 78402200242B) connected to a compressed air line.

1.2 THEORY

A volume of hydrochloric acid is added to the sample which is then purged with a stream of high purity air. Inorganic carbon within the sample is converted to CO_2 which is released from the sample together with volatile organic compounds. The acid treated and purged sample is then injected into a combustion tube where the sample is heated to release CO_2. A non-dispersive infrared (NDIR) detector is used to determine the amount of CO_2 released by energy absorption. The output analogue signal of the NDIR detector is displayed as a response peak, the area of which is proportional to the NPOC concentration. The NPOC concentration can be determined from a calibration curve prepared using standard solutions containing known amounts of organic carbon.

1.3 OUTLINE

Determination of NPOC involves the removal of inorganic carbon content by acidification and sparging prior to analysis. The oxidation of organic carbon to carbon dioxide is achieved by high temperature combustion; the evolved carbon dioxide is then measured using a NDIR detector.

1.4 ANALYTICAL METHOD

The performance of the instrument is checked before each analytical run using a 100 mg l^{-1} standard and a blank. To calibrate, two working standards (10 mg l^{-1} and 100 mg l^{-1}) are freshly prepared manually from a 1000 mg l^{-1} organic carbon (OC) stock standard. The standards are then automatically diluted by the instrument to derive standards in the low (0-10 mg l^{-1}) and high (10-100 mg l^{-1}) calibration ranges.

The sample or standard is poured into the sample vials and covered with laboratory film to prevent absorption of CO_2 from the atmosphere. Normally a minimum of approximately 6 ml of sample is used to ensure there is sufficient volume for analysis. During analysis, an aliquot is drawn from the sample vial by the auto-sampler into a syringe where it is acidified with 10% hydrochloric acid reagent. Carrier gas is bubbled through the sample for 5 minutes to remove any inorganic carbon by liberating it as CO_2 prior to measurement. Working QC standards are prepared from a stock QC standard on the day of analysis at concentrations applicable to the levels in the samples (normally 50 mg l^{-1}, 10 mg l^{-1} and 5 mg l^{-1}). The QC samples are run after no more than 20 samples and also at the beginning and end of every run, where a blank is also analysed.

2 Method Scope

The scope of Technical Procedure AGN 2.3.8 is the determination of Total Organic Carbon (TOC) or Dissolved Organic Carbon (DOC) according to whether the sample has been filtered or not. For analytical purposes TOC and DOC are often expressed as Non-Purgeable Organic Carbon (NPOC). The term NPOC is usually preferred because the sparging process will remove volatile organic compounds that are purgeable from the sample. The method can be used for a range of natural waters, including pore-waters, and synthetic or experimental fluids, including hydrothermal fluids and aqueous leachates, received by the Laboratory

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 protocol of Cheeseman and Wilson (1989). The Cheeseman and Wilson model used was based on duplicate analysis of each test solution on eleven separate analytical runs.

3.1 PREPARATION AND MEASUREMENT OF VALIDATION SOLUTIONS

3.1.1 Test Solutions for Cheeseman and Wilson Validation Exercise

All solutions were taken through the normal analytical procedure and analysed in duplicate, in random order, on eleven analytical runs. Normal instrument shutdown was performed between each run. In addition, recent saline potable Aquacheck samples and the QC sample identified in AGN 2.3.8 were included within the validation runs to provide supporting data on the method's accuracy and precision, where appropriate. Deionised water blanks and serial dilutions of low calibration standards, at 0.2 and 0.5 mg l^{-1}, were also included to provide supporting evidence for the limits of quantification. The solutions analysed are summarised in Table 1.

Table 1 Validation Solutions Analysed

Validation Solution	Description of Solution
Blank	Fresh deionised water
LOQ Standards	Described in 3.1.1.1
Low Matrix	Described in 3.1.1.3 (i)
Low Matrix Spiked	Low Matrix + 100 mg l^{-1} spike (1+1)
High Matrix	Described in 3.1.1.3 (ii)
High Matrix Spiked	High Matrix + 100 mg l^{-1} spike (1+1)
Contaminated Matrix	Described in 3.1.1.3 (iii)
Contaminated Matrix Spiked	Contaminated matrix + 100 mg l^{-1} spike (1+1)
Low Standard	20% of upper calibration limit (20 mg l^{-1})
High Standard	80% of upper calibration limit (80 mg l^{-1})

3.1.1.1 BLANK AND LOQ STANDARDS

Freshly prepared deionised water was used for the blank. Serial dilutions of low calibration standards to give concentrations at 0.2 and 0.5 mg l^{-1} were used in order to provide supporting evidence for the limits of quantification.

3.1.1.2 HIGH AND LOW STANDARDS

The Cheeseman and Wilson (1989) protocol specifies the use of low and high standards of approximately 20% (20 mg l^{-1} NPOC) and 80% (80 mg l^{-1} NPOC) of the highest calibration standard.

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) - a typical, low salinity, uncontaminated water representative of a typical potable, ground or surface water.

(ii) Atlantic Ocean seawater (high salinity matrix) - a commercially available natural ocean water purchased from Ocean Scientific International.

(iii) Contaminated groundwater - a typical contaminated landfill leachate filtered to 0.45 µm.

Each of the three test matrices above was also spiked (1:1), on the day of analysis, with a 100 mg l^{-1} potassium hydrogen phthalate solution prepared from the same reagent used to make the QC. This gives a spike concentration of 50 mg l^{-1} organic carbon when mixed with each test matrix.

3.1.1.4 AQUACHECK PROFICIENCY TESTING SAMPLES

Aquacheck saline water samples, including distributions 314, 318 and 322 were analysed as part of the validation exercise; TOC is not determined on either waste or clean water distributions.

3.2 VALIDATION CALCULATIONS

Results for each of the validation runs were compiled into an Excel spreadsheet. NPOC data for each matrix were subsequently transferred into separate spreadsheets to allow calculation of parameters following the model outlined in Cheeseman and Wilson (1989). Calculations performed automatically within the Cheeseman and Wilson spreadsheets provide:

Limits of detection (LoD);

Standard deviation;

Percent bias;

Percent recovery of spiked samples;

Degrees of freedom;

Uncertainty (derived from estimated bias and precision).

3.3 ACCEPTANCE CRITERIA

3.3.1 Accuracy and Bias

The absolute value of percentage bias for the high and low standard solutions should be <5% and the percentage spike recovery should be between 95 and 105% for all matrices. Supporting data from the analysis of Aquacheck samples should be within ±10% of accepted reference values.

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 5%. Supporting data from analysis of the QC solution and Aquacheck samples 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 the target limit of quantification, 0.5 mg l^{-1}. The limit of detection should be less than four times the limit of quantification.

3.3.4 Measurement of Uncertainty

The expanded uncertainty for all determinands should be better than 10% at concentrations an order of magnitude or more above the limit of quantification.

4 Calibration Range

Calibration was performed as described in Technical Procedure AGN 2.3.8. The final concentrations of the calibration standards in each range are shown in Table 2.

Table 2 Final Calibration Concentrations

Dilution	Low Range Standards mg l^{-1}	High Range Standards mg l^{-1}
10	1.00	10.0
4	2.50	25.0
2	5.00	50.0
1	10.0	100

Example calibration data from one of the 11 runs are shown in Table 3. The R^2 value calculated by the software after the completion of each calibration is also included, demonstrating linearity over each of the calibration ranges.

Table 3 Example of Calibration Data

Run Date	Calibration Range	R^2 Value	Standard Concentration mg l^{-1}	Mean Area
08/08/2007	Low	1.0000	1.00	4.006
			2.50	9.679
			5.00	19.12
			10.0	37.99
	High	0.9999	10.0	37.62
			25.0	95.99
			50.0	195.1
			100	397.3

The maximum concentration that can be determined is 100 mg l^{-1} (the top calibration standard concentration). Samples above this concentration should be diluted to bring the measured concentration into the calibrated range.

4.1 PERFORMANCE CHECK

The performance check is run prior to the calibration as described in Technical Procedure AGN 2.3.8. Data from each of the 11 runs, for both the 100 mg l^{-1} TOC standard and the blank, are shown in Table 4.

Table 4 Performance Data

Run Date	Performance Check (Mean Area)	Blank Check (Mean Area)
20/06/07	385.4	0.028
21/06/07	386.6	0.247
03/07/07	388.4	0.276
04/07/07	389.5	0.000
09/07/07	396.0	0.378
10/07/07	387.8	0.282
20/07/07	389.4	0.325
02/08/07	396.3	0.246
08/08/07	399.4	0.361
21/08/07	384.1	0.168
23/08/07	392.1	0.162

The data show that all the performance checks during the validation period met the set peak area criteria. The mean areas for the TOC standard were above 300 and for the blanks were below 1.

5 Accuracy and Precision

Accuracy and precision were estimated from the QC standards and saline Aquacheck samples analysed during the 11 Cheeseman and Wilson validation runs (see Appendix 1). A summary of the data is given in Table 5, Table 6 and Table 8. Despite the minor bias observed in the 20% standard, the accuracy data meet acceptance criteria. The precision of analyses meets the acceptance criteria.

5.1 QC STANDARDS

Table 5 shows the average data collected from each of the 11 validation runs from the QC standards.

Table 5 QC Data

Run Date	5 mg l^{-1}	10 mg l^{-1}	50 mg l^{-1}
20/06/07	5.05	10.16	48.90
21/06/07	5.03	10.19	49.01
03/07/07	5.09	10.06	48.95
04/07/07	5.16	10.29	48.95
09/07/07	5.02	10.07	48.87
10/07/07	5.06	10.10	48.27
20/07/07	4.99	9.93	49.09
02/08/07	5.02	10.01	49.01
08/08/07	4.99	9.90	49.09
21/08/07	5.03	10.15	49.37
23/08/07	5.07	10.07	49.88
Average	5.05	10.08	49.03
% RSD	1.19	1.19	0.95
% Bias	0.91	0.83	-1.93

The bias and RSD are both well within the target value of ±5%; they are all within 2%**.**

5.2 AQUACHECK

Table 6 shows the data collected from the saline Aquacheck distributions. Only 10 runs were achieved for distribution 314 due to there being limited sample and one value was excluded as an outlier. Data from only 10 runs were used for distribution 322 due to one outlier pair.

Table 6 Average Distribution Data

Distribution	Reference Value	Mean	Bias	RSD	Z-Score
	mg l^{-1}	mg l^{-1}	%	%	%
314	10.50	10.20	-2.89	1.21	-0.15
318	8.72	7.44	-14.73	2.01	-1.47
322	15.20	13.41	-11.75	1.30	-1.18

The RSD for all distributions fall within the set criteria. The bias for distribution 314 falls within the acceptable limit of no more than ±10% of the reference value, distributions 318 and 322 are both <15%. However, the data in this exercise compare well with data submitted to Aquacheck at the time of reporting (Distribution 318: z-score = -1.54; Distribution 322: z-score = -1.13). Although the data from the validation exercise exceed the specified acceptance criteria, the z-scores are acceptable.

Data from recent submissions from the Aquacheck PT scheme are summarised in Table 7 and have shown a bias better than 10% for 8 out of the last 9 distributions covering a concentration range of 4-12 mg l^{-1}. The z-scores for these distributions were consistently acceptable (max 1.1).

Table 7 Data from Recent Aquacheck Distributions

Distribution	Reference value mg l^{-1}	Measured value mg l^{-1}	Z-score	Bias %
346	4.22	3.84	-0.90	-9.0
350	5.72	5.28	-0.78	-7.8
362	7.54	6.80	-0.98	-9.8
366	4.60	4.20	-0.90	-9.0
370	6.57	6.50	-0.11	-1.1
382	12.1	12.05	0.00	0.0
386	10.5	9.84	-0.66	-6.6
390	9.09	8.22	-0.95	-9.5
402	4.55	5.05	1.09	10.9
Average			-0.47	-4.7

5.3 HIGH AND LOW STANDARDS

Table 8 Accuracy and bias data for NPOC

Standard	Mean mg l^{-1}	RSD %	Bias %
20% Standard	18.57	1.89	-7.15
80% Standard	78.50	0.77	-1.88

The absolute percentage bias for the high and low standard solutions should be <5%. The high standard falls within this value and is actually <2%. The low standard bias is just over 7%.

6 Spike Recovery

Spike tests were carried out using spikes as described in Section 3.1.1.3. Summary data from the Cheeseman and Wilson calculations (Appendix 1) are given in Table 9. The spike recoveries for all matrices are within the target specification of ±5%; indeed they are better than 2%.

Table 9 Spike Recovery Data

	Tap Water Matrix mg l^{-1}	**Saline Matrix** mg l^{-1}	**Waste Matrix** mg l^{-1}
% Spike Recovery	99.58	101.97	101.35

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 two months.

Data reported in the previous sections have been acquired throughout this period and show no signs of deterioration, thus demonstrating the ruggedness of the method.

8 Limits of Quantification

The limit of quantification is calculated from the standard deviation determined from analyses of a blank water samples. The blank data indicate that the limit of detection should be <0.4 mg l^{-1}. The practical limit of quantification used for reporting is 0.5 mg l^{-1}.

To provide evidence on the suitability of the detection limit, separate tests were conducted on low concentration standards. Data from these tests are summarised in Table 10.

Table 10 Summary of Analysis of Low Concentration Standards

Target concentration mg l^{-1}	**Mean** mg l^{-1}	**Std Dev** mg l^{-1}	**RSD** %
Blank	0.116	0.108	93.5
0.2	0.348	0.091	26.2
0.5	0.636	0.079	12.4

9 Measurement of Uncertainty

The bias and precision have been estimated for each of the solutions analysed as part of the validation exercise. These data are given in Appendix 1 and are summarised in tables above. These data have been used to estimate the measurement of uncertainty according to the requirements of Operating Procedure AGN 1.6.

The bias has been expressed as percentage deviation from the nominal value. At each concentration, the combined uncertainty of the relative bias and the relative standard deviation (calculated as the square root of the sum of the squares of bias and standard deviation) has 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 (Table 11 and Figure 1).

Table 11 Data for calculation of expanded uncertainty

Matrix type	Nominal conc mg l^{-1}	Measured conc mg l^{-1}	Std dev mg l^{-1}	RSD %	Bias %	Combined Uncertainty %	Coverage factor	Expanded Uncertainty %
High salinity	1.04	1.04	0.04	4.24	0.00	4.24	2	8.5
Low salinity	1.33	1.33	0.05	3.42	0.00	3.42	2	6.8
Low standard	20.0	18.6	0.36	1.93	-7.15	7.41	2	14.8
High salinity	50.5	51.5	3.95	7.68	1.95	7.92	2	15.8
Low salinity	50.7	50.5	2.11	4.18	-0.41	4.20	2	8.4
High standard	80.0	78.5	0.62	0.79	-1.88	2.04	2	4.1
Waste water	147.9	148.6	1.26	0.85	0.46	0.97	2	1.9
Waste water	195.9	195.9	1.03	0.53	0.00	0.53	2	1.1

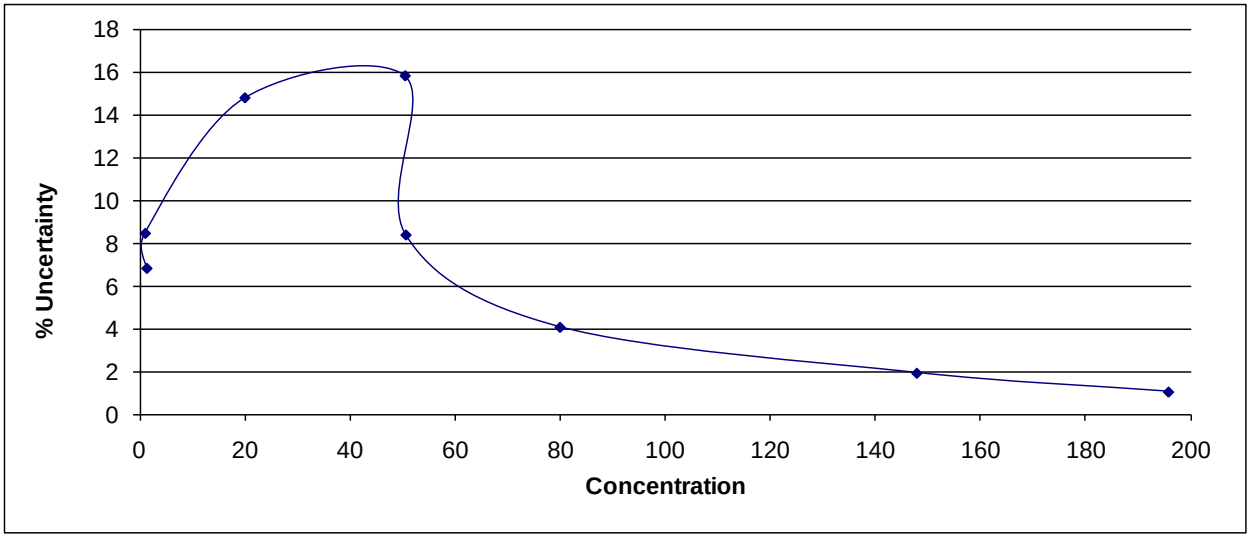

Figure 1 Estimated percentage uncertainty data for NPOC

Most of the expanded uncertainties are within the target value of 10%, the exceptions being the low standard and the spiked high salinity matrix that are both around 15%. The acceptable precision for the low standard has been compounded by an unusually poor bias, there being no systematic bias across the validation standard set, and acceptable bias for the spiked high salinity sample has been compounded by an unusually poor precision. From Figure 1, the overall expanded uncertainty is estimated to be 8%; being based on an average value across all validation samples.

The Method Specification Limits (MSL) have been set at 10% of the target value. These SLs are commensurate with the 3s precision data obtained for the QC samples to date; indeed the 3s uncertainty is about 4-6%.

10 Conclusions

A comprehensive validation of the determination of NPOC on the TOC-V has been successfully undertaken. Except for a few minor exceptions, all of the acceptance criteria proposed prior to validation have been met and, in many cases, exceeded. The overall expanded uncertainty for NPOC has met original criteria and the validation data obtained are considered to be fit for purpose given constraints discussed above. As a result, the method has been demonstrated to be appropriate for its intended use.

11 References

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

Appendix 1 Summary Cheeseman and Wilson Validation Sheets

Results of Method Validation Test				Date report produced=	13/04/2011	
Laboratory :	Aqueous Analytical					
Operator name :	Claire Williams			Reference		
UKAS Method Reference =	AGN 2.3.7		Test solution	Tap Water	1.33	
Determinand =	NPOC		Use Sb from standards (Y/N) =		n	
Units =	ppm		Concentration of spiking soln. =		100	ppm
Date analysis started	20/06/2007		Volume of spiking solution (mls) =		3	
Date analysis completed	08/08/2007		Volume of sample used (mls) =		3	
Target conc Std. Dev. =		0.125	Total volume produced (mls) =		6	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		50.0000	ppm
	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				1.33	ppm	
Nominal value	-	20	80	Calc Spike Value=	50.6672	ppm
Mean	0.1155	18.5698	78.4962	0.6672	50.4570	ppm
Percentage Bias =	-	-7.15	-1.88	-	-	
Pass/Fail		Pass	Pass			
M1	0.0175	0.2525	0.7127	0.0035	7.5910	
Mo	0.0063	0.0048	0.0581	0.0007	1.2962	
F value (M1/Mo)	2.7643	52.9267	12.2726	5.0911	5.8563	
Sw	0.0797	0.0691	0.2410	0.0261	1.1385	
Sb	-	0.3519	0.5721	0.0374	1.7741	
St	-	0.3586	0.6208	0.0456	2.1080	
Target maximum St	-	0.9285	3.9248	0.1250	2.5228	
St (as percent of mean)		1.9312	0.7908	6.8364	4.1778	
Tabulated F, 0.05	1.63	1.83	1.75	1.69	1.72	
Calculated f	0.7646	0.1492	0.0250	0.1332	0.6982	
Degrees of freedom	17	10	12	14	13	
Pass/Fail (LoD & S.D.s)	PASS	PASS	PASS	PASS	PASS	
Limit of Detection	0.3705	0.3211	1.1205	0.1215	5.2941	ppm
(based on each solution)						
Percent Spike Recovery =	99.58					
+/- (95 percentile)	2.09					
Std.dev.of mean recoveries	1.956566271					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.370470286 Units = ppm

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.109301605	0.3586	0.6208	0.0456	2.1080
% Bias =	-	-7.15	-1.88	-	-
% Spike Recovery =	99.58				

Results of Method Validation Test				Date report produced=	13/04/2011	
Laboratory :	Aqueous Analytical					
Operator name :	Claire Williams			Reference		
UKAS Method Reference =	AGN 2.3.7		Test solution	Saline Water	1.04	
Determinand =	NPOC		Use Sb from standards (Y/N) =		n	
Units =	ppm		Concentration of spiking soln. =		100	ppm
Date analysis started	20/06/2007		Volume of spiking solution (mls) =		3	
Date analysis completed	08/08/2007		Volume of sample used (mls) =		3	
Target conc Std. Dev. =		0.125	Total volume produced (mls) =		6	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		50.0000	ppm
	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				1.04	ppm	
Nominal value		20	80	Calc Spike Value=	50.5184	ppm
Mean	0.1155	18.5698	78.4962	0.5184	51.5029	ppm
Percentage Bias =	-	-7.15	-1.88	-	-	
Pass/Fail		Pass	Pass			
M1	0.0175	0.2525	0.7127	0.0028	18.6588	
Mo	0.0063	0.0048	0.0581	0.0011	12.6125	
F value (M1/Mo)	2.7643	52.9267	12.2726	2.5630	1.4794	
Sw	0.0797	0.0691	0.2410	0.0329	3.5514	
Sb	-	0.3519	0.5721	0.0291	1.7387	
St	-	0.3586	0.6208	0.0439	3.9542	
Target maximum St	-	0.9285	3.9248	0.1250	2.5751	
St (as percent of mean)		1.9312	0.7908	8.4728	7.6776	
Tabulated F, 0.05	1.63	1.83	1.75	1.63	1.57	
Calculated f	0.7646	0.1492	0.0250	0.1235	2.3578	
Degrees of freedom	17	10	12	17	20	
Pass/Fail (LoD & S.D.s)	PASS	PASS	PASS	PASS	FAIL	
Limit of Detection	0.3705	0.3211	1.1205	0.1530	16.5141	ppm
(based on each solution)						
Percent Spike Recovery =	101.97					
+/- (95 percentile)	3.19					
Std.dev.of mean recoveries	3.070055501					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.370470286 Units = ppm

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.109301605	0.3586	0.6208	0.0439	3.9542
% Bias =	-	-7.15	-1.88	-	-
% Spike Recovery =	101.97				

Results of Method Validation Test				Date report produced=	13/04/2011	
Laboratory :	Aqueous Analytical					
Operator name :	Claire Williams			Reference		
UKAS Method Reference =	AGN 2.3.7		Test solution	Waste Water	195.8727	
Determinand =	NPOC		Use Sb from standards (Y/N) =		n	
Units =	ppm		Concentration of spiking soln. =		100	ppm
Date analysis started	20/06/2007		Volume of spiking solution (mls) =		3	
Date analysis completed	08/08/2007		Volume of sample used (mls) =		3	
Target conc Std. Dev. =		0.125	Total volume produced (mls) =		6	
Target Maximum percentage Std. Dev. =		5	Effect of added spike (plus,calcd)=		50.0000	ppm
	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				195.8727	ppm	
Nominal value	0	20	80	Calc Spike Value=	147.9364	ppm
Mean	0.1155	18.5698	78.4962	97.9364	148.6136	ppm
Percentage Bias =	-	-7.15	-1.88	-	-	
Pass/Fail		Pass	Pass			
M1	0.0175	0.2525	0.7127	1.7044	2.3411	
Mo	0.0063	0.0048	0.0581	0.4127	0.8486	
F value (M1/Mo)	2.7643	52.9267	12.2726	4.1295	2.7587	
Sw	0.0797	0.0691	0.2410	0.6424	0.9212	
Sb	-	0.3519	0.5721	0.8036	0.8638	
St	-	0.3586	0.6208	1.0289	1.2629	
Target maximum St	-	0.9285	3.9248	9.7936	7.4307	
St (as percent of mean)		1.9312	0.7908	1.0505	0.8498	
Tabulated F, 0.05	1.63	1.83	1.75	1.67	1.63	
Calculated f	0.7646	0.1492	0.0250	0.0110	0.0289	
Degrees of freedom	17	10	12	15	17	
Pass/Fail (LoD & S.D.s)	PASS	PASS	PASS	PASS	PASS	
Limit of Detection	0.3705	0.3211	1.1205	2.9873	4.2836	ppm
(based on each solution)						
Percent Spike Recovery =	101.35					
+/- (95 percentile)	0.87					
Std.dev.of mean recoveries	0.830908594					

SUMMARY OF PERFORMANCE DATA

Limit of Detection = 0.370470286 Units = ppm

	BLANK	LOW STD.	HIGH STD.	SAMPLE	SPIKE
Total Standard Deviation =	0.109301605	0.3586	0.6208	1.0289	1.2629
% Bias =	-	-7.15	-1.88	-	-
% Spike Recovery =	101.35				