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Tellus Border: Geochemical analysis of stream water samples

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Tellus Border: Geochemical analysis of stream water samples

C J Milne, T S Barlow, S R N Chenery, C J B Gowing, H M Harrison, E R Raycraft, C L Richardson, L J Sklenars, J O Warham and M J Watts

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Front cover picture

Preparing stream water samples for analysis on the ion chromatograph.

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British Geological Survey offices

BGS Central Enquiries Desk

Tel 0115 936 3143 Fax 0115 936 3276
email enquiries@bgs.ac.uk

Environmental Science Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3241 Fax 0115 936 3488
email sales@bgs.ac.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

Tel 0131 667 1000 Fax 0131 668 2683
email scotsales@bgs.ac.uk

Natural History Museum, Cromwell Road, London SW7 5BD

Tel 020 7589 4090 Fax 020 7584 8270
Tel 020 7942 5344/45 email bgs london@bgs.ac.uk

Columbus House, Greenmeadow Springs, Tongwynlais, Cardiff CF15 7NE

Tel 029 2052 1962 Fax 029 2052 1963

Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB

Tel 01491 838800 Fax 01491 692345

Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF

Tel 028 9038 8462 Fax 028 9038 8461
www.bgs.ac.uk/gsni/

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500 Fax 01793 411501
www.nerc.ac.uk

Website www.bgs.ac.uk

Shop online at www.geologyshop.com

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Summary

From April 2012 – January 2013 BGS Analytical Geochemistry Facility undertook a substantial programme of geochemical sample preparation and analysis on behalf of the Geological Survey of Ireland (GSI). The work formed part of the Tellus Border project to collect scientific data on soils, water and rocks across the six border counties of the Republic of Ireland (Donegal, Sligo, Leitrim, Cavan, Monaghan and Louth). The project is a collaboration between the Geological Survey of Ireland, the Geological Survey of Northern Ireland, the Dundalk Institute of Technology and Queen's University, Belfast, funded by the INTERREG IVA programme of the European Regional Development Fund and the Departments of Environment from Northern Ireland and the Republic of Ireland.

The work described in this report involved analysis of approximately 4400 stream water samples for determination of:

- An extensive suite of metals and trace elements by inductively-coupled plasma mass spectrometry (ICP-MS);
- Major and minor anions by ion chromatography (IC);
- Dissolved organic carbon (measured as non-purgeable organic carbon (NPOC)).

The results of the analyses have been compiled and reported separately in a series of laboratory reports over the course of the project. This report provides a summary record of the methods, progress and analytical quality control which were used during the analytical programme.

1 Introduction

Tellus Border is a €4.5 million (£4 million) mapping project, funded by the INTERREG IVA programme of the European Regional Development Fund and the Departments of Environment from Northern Ireland and the Republic of Ireland to collect scientific data on soils, water and rocks across the six border counties of the Republic of Ireland (Donegal, Sligo, Leitrim, Cavan, Monaghan and Louth). Information from the project will help manage the environment and support sustainable development of natural resources in the region.

The project is designed to build on the successful Tellus project, already completed in Northern Ireland, by compiling a comparable body of data which is capable of seamless integration with the data for the six counties of Northern Ireland. The Tellus Border project is a multi-partner initiative involving cross-border collaboration between the Geological Survey of Ireland, the Geological Survey of Northern Ireland, the Dundalk Institute of Technology and Queen's University, Belfast. Further information can be found on the project website at <http://www.tellusborder.eu>.

There are two major survey components to the Tellus Border project: an airborne geophysical survey conducted during September 2011 to July 2012 and a geochemical sampling survey of soils and streams carried out between August 2011 and May 2012. The activities of the geochemical survey were divided into a number of major work packages for field sampling activities, and for subsequent preparation and laboratory geochemical analysis of the samples collected.

Following a tender exercise published through the Official Journal of the European Union (OJEU), the British Geological Survey (BGS) was contracted by GSI to undertake several of the work packages (Lots) for provision of services for sample preparation and geochemical analysis. This report summarises work carried out under:

- Lot 5 –Multi-element analyses of filtered stream water samples

The requirements of Lot 5 included analysis by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) or equivalent alternative, non-purgeable organic carbon (NPOC); major anions by ion chromatography (IC).

The analytical work programme was tendered during January–February 2012, with contractual negotiations completed during March to enable work to begin in early April 2012. Due to the time constraints of the overall Tellus Border project, there was significant pressure to ensure that the analytical programme was completed as quickly as practicable, to allow for subsequent data interpretation activities. Analytical throughput and turnaround time was therefore an explicit consideration during tender evaluation and a major priority throughout the execution.

BGS has long experience of undertaking stream water analysis for major geochemical survey programmes both in the UK and overseas. The BGS geochemistry laboratories are equipped with a range of modern state-of-the-art analytical instrumentation for the techniques concerned and operate a laboratory quality management system accredited by UKAS to the standards of ISO 17025.

Details of the procedures used for the different analyses are provided in the following sections.

2 Sample handling and preparation

2.1 SAMPLE TRANSPORT AND RECEIPT

Samples were collected from the field areas over a period of several months during two field seasons, in autumn 2011 and spring 2012. The field programmes were contracted separately by GSI, outside the scope of the current analytical work programme and so are not discussed further here, except in so far as the scheduling of the sample collection necessarily influenced the scheduling of the corresponding analysis.

During the first field sampling campaign in autumn 2011 approximately 600 sites were sampled. Two sets of water samples for analysis were taken at each field site; one to be used for analysis of metals and trace elements by ICP-MS, the other for analysis of anions and NPOC. Both were filtered in the field (to 0.45 μm) and collected in HDPE Nalgene™ bottles (60 mL for ICP-MS and 30 mL for IC/NPOC). The 60 mL sample was acidified at the field base and on the day of collection with 60 μL (approximately 1% v/v) Aristar grade concentrated nitric acid (HNO_3) to stabilize elements in solution during storage. Samples were then assembled at GSI in Dublin as they were collected. All samples were kept refrigerated during transport after collection and at GSI pending transfer to the laboratory as soon as the contract commenced.

There were six field batches or 'hundreds' (*i.e.* approximately 600 samples) available at the time the contract was negotiated in March 2012. A further ca. 3800 samples were collected in the field during April and May 2012. The need for timely completion of the analytical programme coupled with the significant instrument time required for IC in particular meant it was necessary to begin analysis promptly before all the sampling was complete. The available samples were therefore delivered immediately at the outset of the project with the remaining samples delivered later.

Three major sample transfer trips were used for water samples by arranging rendezvous at Holyhead Port in North Wales; a member of staff from GSI took samples in crates containing insulated cool-bags in a transit-size van on the ferry from Dublin to meet a member of BGS staff with a second van at the port. The first trip supplied all the samples collected during the winter season plus the first 1000 collected during April 2012, so 1600 samples in all. The two subsequent trips were then arranged at roughly monthly intervals as the remaining samples were accumulated at GSI.

The transport arrangements provided the dual advantages of ensuring direct staff oversight of the samples from door-to-door and of ensuring that samples were kept cool enough without the use of specialised refrigerated container transport.

Each shipment was accompanied by a sample checklist supplied in summary on paper and in detail digitally. On receipt at BGS sample bags were checked off against the list and immediately transferred to a secure, walk-in refrigerated sample store pending processing in the laboratory. Samples for ICP-MS were further acidified with 300 μL (approximately 0.5% v/v) high-purity (Romil SpA grade) concentrated hydrochloric acid (HNO_3) prior to analysis.

2.2 INSERTION OF REFERENCE MATERIALS

The project analytical protocol specified the inclusion of a number of control samples including duplicates, Certified Reference Materials (CRMs) and Secondary Reference Materials (SRMs) within the analytical schedule. The collection, transport, storage and analysis of all samples was organised in nominal 'hundreds'. When submitted to the lab each hundred contained two duplicates and up to six reference materials. CRMs (which are supplied already stabilised with acid) were introduced to the sequences after sample acidification in order to prevent inadvertent double acidification. This was carried out by a designated member of BGS staff who received independent instruction directly from GSI and prepared the samples into standard laboratory racks with the samples in the required numerical sequence order. The identities and positions of all the reference materials were therefore kept blind to any staff carrying out the analysis, who received the reference samples as unknowns numbered in

sequence with the true samples. The pattern of references and duplicates was varied by GSI from hundred to hundred to reduce the likelihood of the identities becoming apparent to the analysts. The results of these analyses can then be used by the project to provide independent assessment and verification of the laboratory analytical results.

3 Analysis of stream water samples

Analysis of stream water samples was carried out using analytical methods which were already established and operational at BGS's laboratories at Keyworth, Nottingham. The full analytical suite contracted required the use of three separate analytical techniques:

- major, trace and ultra-trace elements determined by ICP-MS;
- major and minor inorganic anions determined by ion chromatography (IC);
- NPOC determined using a TIC/TOC combustion analyser.

The BGS methods have been developed and optimised to obtain highest-quality data with lowest practicable detection limits, specifically for the purposes of research-grade investigation and baseline geochemical survey. Analytical performance is therefore often better than can be achieved during threshold or compliance monitoring.

The performance parameters provided met or exceeded the specifications required by GSI in almost every respect except for recommendations for some variations in the element suite, particularly for ICP-MS, based on BGS' previous experience of undertaking similar large-scale regional survey programmes. The proposed variations, to omit some ultra-trace elements but include others, reflect experience of the value and usefulness of the data so obtained. Full details are contained in the technical explanations below.

3.1 ANALYSIS OF METALS AND TRACE ELEMENTS BY ICP-MS

3.1.1 Instrumentation

The determination of major, trace and ultra-trace elements in stream waters was carried out using an Agilent 7500cx series quadrupole inductively-coupled plasma mass spectrometer (ICP-MS) fitted with an Octopole Reaction System (ORS), in combination with a CETAC autosampler. The system is controlled by a PC through dedicated software (Agilent MassHunter), which also controls the autosampler.

3.1.2 Theory

A quadrupole ICP-MS instrument consists of an inductively coupled plasma, which provides a source of positively charged ions, a quadrupole mass filter, and a detector which detects these ions, linked by an interface. Liquid samples are pumped through a nebuliser, and the resulting sample aerosol and argon mixture passes through a water-cooled spray chamber. Larger droplets collide with the spray chamber wall and a pumped drain channel removes the excess solution, before the smaller aerosol droplets are injected into the central channel of the ICP torch. Energy transfer processes in the plasma result in rapid desolvation, atomisation and ionisation of the sample aerosol.

The positively charged ions formed in the aerosol are extracted into the first vacuum chamber through a sampling cone with an orifice of 1.0 mm diameter. This is an expansion region evacuated by a rotary pump. The ions then pass through a skimmer cone with an orifice of 0.4 mm diameter, which acts as a differential aperture between the interface and intermediate vacuum stage. Ions are then collimated by two conical extraction lenses before being focussed by the ion optics. The ion lenses focus the ion beam and prevents photons and neutral species produced in the plasma from reaching the detector by deflecting the beam approximately 5 mm off-axis into the front plate of the quadrupole mass filter. Photons and neutral species are not deflected and thus do not enter the quadrupole.

The octopole reaction system (ORS) is situated between the ion lens assembly and the quadrupole mass filter. This is an octopole ion guide contained within a stainless steel vessel that is pressurised with helium or hydrogen or evacuated depending on the operating gas mode. The interaction between the plasma ions and the collision gas in the ORS is used to eliminate interferences caused by the sample matrix, plasma or atmosphere. An octopole is used as the 8 rods in the octopole produces better transmission efficiency than a 6-rod hexapole or a 4-rod quadrupole. During routine operation of the BGS waters method data are collected during three separate acquisitions with the ORS automatically

switching between three distinct operating modes (i.e. hydrogen collision gas, helium collision gas, no gas) for each sample. In this way every element can be determined using the most suitable mode to minimize the size and impact of interferences.

The quadrupole mass filter has DC and RF voltages applied to opposite pairs of the four rods. When the voltages are varied only ions of a given mass: charge ratio (m/z) will have a stable path through the rods and emerge the other end. These voltages change rapidly and the mass spectrometer is able to scan across the mass range from 0 to 260 mass units in 100 milliseconds resulting spectra of mass versus intensity can be obtained for all elements virtually simultaneously. Although the quadrupole mass filter has a relatively low resolving power (<400), it is sufficient to separate ion m/z from ion $(m/z) + 1$ but not from a polyatomic ion with a similar m/z .

Ions leaving the quadrupole analyser are detected using an electron multiplier detector. Depending on the concentration of the analytes being measured, the detector operates in one of two modes; pulse counting for low sample concentrations and analogue for high sample concentrations. Counts for a particular mass are proportional to the concentration of the element in the aspirated solution. The response at any mass is calibrated against standards of known concentrations for the elements of interest.

3.1.3 Analytical method

The instrument was calibrated every analytical run using a minimum four-point calibration (i.e. three standards and a blank) for all elements determined. The Upper Calibration Limits (UCL) of the elements determined are indicated in Table 1, Table 2 and Table 3, together with the primary isotopes used for analysis of each element.

In addition, multi-element internal standardisation was used in order to correct for any sample-to-sample variations in signal intensity arising from matrix or plasma effects. A mixed internal standard solution containing Sc, Ge, Rh, In, Te, Re and Ir was added to the samples in at a fixed ratio of approximately 1:10 via a T-piece. Any suppression of the instrument signal caused by the matrix was corrected by the software using the response of the internal standard. The response of each of the elements determined is related to one of the internal standard elements. The choice of these elements as internal standards is a combination not only of their distribution across the mass-range but also the fact that they tend to occur in negligible or undetectable concentrations in most natural waters. Their use in this way necessarily precludes the possibility of determining these elements in samples. Of the elements affected:

- only Rh formed part of the 'required' suite proposed by GSI in the request for tender;
- In, Re, Sc and Te were listed as desirable but not required;
- Ge and Ir were not requested.

In exceptional circumstances, where it is considered that the use of internal standards would degrade the quality of the analysis, e.g. by causing contamination or preventing the analysis of a specifically-required element, then it is possible to omit a particular internal standard. However, this approach was not adopted for the Tellus Border project as to do so would have risked compromising the quality of data for other more significant elements normally corrected using the internal standard(s) in question and may also have resulted in data falling outside the scope of the method accreditation.

3.1.4 Data Quality

BGS operates a method (detailed as BGS Technical Procedure AG 2.3.18) for determination of 57 major and trace elements in natural waters and other aqueous samples which is fully accredited by UKAS to the requirements of BS EN ISO/IEC 17025:2005. Of the 57 elements, 54 are within scope of the accreditation; Ag, S and P are excluded from the scope as they exhibit larger analytical uncertainty.

Samples were received from GSI already filtered to 0.45 μm and preserved with 1% v/v concentrated nitric acid to stabilise elements in solution. Prior to analysis the samples were further preserved with 0.5% v/v concentrated hydrochloric acid. The addition of chloride enhances the stability of several

elements in the analytical suite (notably Sb and Sn) and therefore improves overall analytical precision for these elements. Although there was a significant delay between the collection of the samples and their analysis, their preservation with acid and subsequent refrigerated storage mean that they are unlikely to have suffered any marked deterioration or change in composition.

There are numerous documented potential interference effects when using ICP-MS. Rigorous steps were taken to minimize and correct for these. First, the ORS was used to enable physical reduction or elimination of interferences before detection. Then numerical corrections for isobaric and polyatomic interferences were applied automatically by the instrument software during data processing.

3.1.5 Performance parameters

The performance of the analytical methods used for water analysis at BGS has been verified using rigorous method validation tests data carried out following the protocol based on that recommended as standard across the UK Water Industry (Cheeseman and Wilson, 1989). This requires replicate analyses on multiple occasions of a range of test solutions covering the full scope of the method, in order to assess intra- and inter-run variation, combined method uncertainty and upper and lower range limits. Comprehensive details of these validation tests and results are recorded in a laboratory technical report (Breward *et al.*, 2009).

Table 1 shows the Method Lower Limits of Detection (LLD) achieved with the ICP-MS method for the list of elements identified as required by GSI in the tender specification, alongside the Guide LLD originally proposed by GSI as a target. The Method LLDs quoted here are robust estimates derived from calculations of 3σ uncertainty observed on a minimum of 20 between-run blank determinations. There are some variations to the element suite described. The use of Rh as an internal standard has been described earlier. Br cannot be measured effectively by ICP-MS but was included in the suite of anions determined by ion chromatography. In addition, of the elements listed as required, we did not recommend inclusion of Au, Pt and Pd. In our experience these elements do not occur in natural waters at levels which can be measured by ICP-MS without the use of preconcentration techniques. Determination as part of this suite was likely to yield below detection limit values for all samples and would have required additional calibration and attention to QC compliance which would not have been justified or cost-effective.

Further elements, not required, were identified as desirable. Of the desirable elements (Table 2), it was possible to include determination of Ce, Ga, Hf, Nd, Sm and Ta as standard in the suite analysed. The elements In, Re, Sc and Te were used as internal standards in the method, as discussed above. Also analysis of I in the standard suite was not included as direct analysis of I in natural waters by ICP-MS is not usually effective. A separate method for low-level analysis of I by ICP-MS following additional chemical stabilisation is available, but this needs to be carried out as a separate analytical procedure and would therefore have increased the costs significantly. It was not considered for use in the Tellus Border project.

On the other hand, it was possible to include several additional elements in the standard suite without penalty, namely Dy, Er, Eu, Gd, Lu, Nb, Pr, Tb, Tm and Yb (Table 3). These rare-earth elements give stable signals and are relatively easy to determine. They were already included as standard in BGS' UKAS accredited method. Given the increasing demand for rare-earth elements in high-technology applications, the current scarcity and political pressures on existing global rare-earth mineral deposits, and the interest in identifying potential new sources, the inclusion of these elements as part of the suite at no additional cost seemed appropriate.

Table 1. Stream waters geochemical analysis by ICP: Guide lower limits of detection and upper calibration limits for 46 required analytes.

Analyte	Isotope	Units	Guide LLD	Method LLD	UCL	Notes
Ag	107	µg L ⁻¹	0.01	0.05	100	
Al	27	µg L ⁻¹	0.50	1	1000	
As	75	µg L ⁻¹	0.05	0.02	100	
Au		µg L ⁻¹	0.10			Not analysed. See text.
B	11	µg L ⁻¹	1.00	10	4000	
Ba	137	µg L ⁻¹	0.05	0.1	1000	
Be	9	µg L ⁻¹	0.05	0.01	100	
Bi	209	µg L ⁻¹	0.02	0.01	100	
Br		µg L ⁻¹	10.00			Not analysed by ICP. See IC.
Ca	43	mg L ⁻¹	0.10	0.3	200	
Cd	111	µg L ⁻¹	0.02	0.01	100	
Co	59	µg L ⁻¹	0.02	0.01	100	
Cr	52	µg L ⁻¹	0.20	0.05	100	
Cs	133	µg L ⁻¹	0.01	0.005	100	
Cu	63	µg L ⁻¹	0.10	0.4	100	
Fe	56	µg L ⁻¹	10	1	4000	
Ho	165	µg L ⁻¹	0.001	0.002	100	
K	39	mg L ⁻¹	0.01	0.02	40	
La	139	µg L ⁻¹	0.001	0.002	100	
Li	7	µg L ⁻¹	0.02	1	4000	
Mg	24	mg L ⁻¹	0.10	0.01	40	
Mn	55	µg L ⁻¹	0.02	0.2	1000	
Mo	95	µg L ⁻¹	0.02	0.03	100	
Na	23	mg L ⁻¹	0.20	0.2	400	
Ni	60	µg L ⁻¹	0.05	0.1	100	
P	31	mg L ⁻¹	0.01	0.01	20	
Pb	208	µg L ⁻¹	0.05	0.02	100	
Pd		µg L ⁻¹	0.10			Not analysed. See text.
Pt		µg L ⁻¹	0.02			Not analysed. See text.
Rb	85	µg L ⁻¹	0.01	0.01	100	
Rh		µg L ⁻¹	0.01			Not analysed. Used as internal standard
Sb	121	µg L ⁻¹	0.02	0.005	100	
Se	78	µg L ⁻¹	0.50	0.1	100	
S (total)	34	mg L ⁻¹	0.30	1	400	
Si	28	µg L ⁻¹	60	50	20000	
Sn	118	µg L ⁻¹	0.05	0.02	100	
Sr	88	µg L ⁻¹	0.10	0.1	4000	
Th	232	µg L ⁻¹	0.01	0.005	100	
Ti	47	µg L ⁻¹	0.50	0.05	100	
Tl	205	µg L ⁻¹	0.01	0.01	100	
U	238	µg L ⁻¹	0.01	0.002	100	
V	51	µg L ⁻¹	0.05	0.1	100	
W	184	µg L ⁻¹	0.01	0.05	100	
Y	89	µg L ⁻¹	0.001	0.005	100	
Zn	66	µg L ⁻¹	0.20	0.5	1000	
Zr	90	µg L ⁻¹	0.03	0.05	100	

Table 2. Stream waters geochemical analysis by ICP: Guide lower limits of detection and upper calibration limits for 11 desirable analytes.

Desirable Analyte	Isotope	Units	Guide LLD	Proposed LLD	UCL	Notes
Ce	140	$\mu\text{g L}^{-1}$	0.002	0.002	100	
Ga	71	$\mu\text{g L}^{-1}$	0.05	0.03	100	
Hf	178	$\mu\text{g L}^{-1}$	0.002	0.01	100	
I		$\mu\text{g L}^{-1}$	0.05			Not included. See text.
In		$\mu\text{g L}^{-1}$	0.002			Used as internal standard.
Nd	146	$\mu\text{g L}^{-1}$	0.005	0.01	100	
Re		$\mu\text{g L}^{-1}$	0.001			Used as internal standard.
Sc		$\mu\text{g L}^{-1}$	0.001			Used as internal standard.
Sm	147	$\mu\text{g L}^{-1}$	0.002	0.002	100	
Ta	181	$\mu\text{g L}^{-1}$	0.05	0.02	100	
Te		$\mu\text{g L}^{-1}$	0.05			Used as internal standard.

Table 3. Stream waters geochemical analysis by ICP: lower limits of detection and upper calibration limits for 10 additional analytes.

Additional Analyte	Isotope	Units	Guide LLD	Proposed LLD	UCL	Notes
Dy	163	$\mu\text{g L}^{-1}$	–	0.002	100	
Er	166	$\mu\text{g L}^{-1}$	–	0.002	100	
Eu	151	$\mu\text{g L}^{-1}$	–	0.002	100	
Gd	160	$\mu\text{g L}^{-1}$	–	0.002	100	
Lu	175	$\mu\text{g L}^{-1}$	–	0.002	100	
Nb	93	$\mu\text{g L}^{-1}$	–	0.02	100	
Pr	141	$\mu\text{g L}^{-1}$	–	0.002	100	
Tb	159	$\mu\text{g L}^{-1}$	–	0.002	100	
Tm	169	$\mu\text{g L}^{-1}$	–	0.002	100	
Yb	172	$\mu\text{g L}^{-1}$	–	0.002	100	

In the analytical data reports batch-specific detection limits have been reported at the top of the sample data together with the overall typical Method LLDs obtained from the method validation. These serve to illustrate the extent of variability in instrument performance and sensitivity between different batches of samples. Some variation in instrument performance is expected under normal use. The standard method performance parameters have been derived from statistical analysis of multiple runs to try to provide a certain level of confidence that the actual observed performance on any given occasion will fall within the parameters. For a very large dataset, such as the ICP-MS data for the Tellus Border samples (57 parameters on ca. 4500 samples, so approximately 250,000 analytical determinations), it is almost inevitable that sometimes the instrument performance will happen to fall at the margins of the specified performance limits.

The batch-specific LLDs used have been calculated as five times the actual standard deviation for the run of the mixed acid blanks inserted at regular intervals during the analysis. These should be compared with the method limits shown which are based on 3σ levels obtained from the original method validation tests. Considering the two reported limits on the same basis indicates that the vast majority of the individual batch LLDs fall within the overall method limits (i.e. equal or better). Of those that don't many are close to the published limits and can be considered as statistical variation; they do not show variations in sensitivity of orders of magnitude in concentration, and as the ICP-MS is highly sensitive for many elements, the sensitivity is likely to have little impact on the observed sample concentrations which are significantly above detection limits.

There are two areas where the observed variation in sensitivity demonstrated by the batch LLDs is potentially more significant. First, for sample batch 20004 (sample IDs 585501–586000) the batch

detection limits were outside the normal method limits for approximately two-thirds of all elements. The implications of this were discussed with GSI staff at the time of reporting. It was concluded that for many elements, particularly the ultra-trace elements such as rare-earths, the concentrations observed in the samples were predominantly low. Consequently, where significant variations in concentrations were observed, the analyte concentrations were clearly distinguishable from the detection limits and the change in instrument sensitivity had no material impact on the resolution of the data. To assess the impact on other elements (notably Mn, where the batch LLD of $3 \mu\text{g L}^{-1}$ compared poorly with the usual method LLD of $0.2 \mu\text{g L}^{-1}$) some reanalysis was carried out. The repeat run exhibited improved instrument sensitivity that was well within the normal method limits and yielded very similar data to the original analyses, even at levels below the apparently poor batch LLD. This demonstrates that the issue was associated more with the stability of the blank analyses for the run, rather than fundamental loss of analytical sensitivity during analysis of the samples. On this basis the data for the batch were accepted as fit-for-purpose.

The other significant issue with variation in sensitivity concerns batch LLDs consistently poorer than the stated overall method LLDs for three elements; Nd, Ga and V. The underlying cause(s) for these variations are under investigation as part of the laboratories programme of continuous method development. None of the three elements are usually observed at significant concentrations in natural waters so in practice the instrument sensitivity is not considered to have adversely impacted the data. Almost without exception, the actual raw measured concentrations of Ga in the Tellus Border samples fell below the method sensitivity. For Nd and V, much of the observed data was within a range of a few multiples of the detection limit. It is considered that the poorer sensitivity may have contributed to an increased analytical uncertainty (poorer precision) associated with results for these elements at low concentrations, but should not have caused any gross distortion in the variation or pattern of the observed concentrations.

Maximum overall method uncertainties associated with any individual measurement by ICP-MS at concentrations greater than an order of magnitude above the detection limits are estimated to be typically in the range $\pm 15\text{--}20\%$, although for Al, P and S uncertainty may be of the order of $\pm 30\%$.

3.2 ANALYSIS OF ANIONS BY ION CHROMATOGRAPHY

3.2.1 Instrumentation

Anions were determined by ion chromatography (IC) using a method documented as BGS Technical Procedure AG 2.3.19. This method has been developed, in conjunction with the instrument manufacturer (Dionex UK), to provide a reliable method capable of determining a full suite of anions which occur at highly variable range of concentrations which occur in natural waters. It determines both the major ions (i.e. Cl^- , NO_3^- and SO_4^{2-}) at levels of tens of mg L^{-1} , but also resolves the common trace anions (F^- , Br^- and NO_2^- and HPO_4^{2-}) with great sensitivity at sub- mg L^{-1} levels.

Analysis was performed using a latest-generation high performance Dionex ICS5000 ion chromatograph using reagent-free eluent generation (EG) and a conductivity detector. This technique uses KOH eluent generated and regulated at highly accurate concentrations by the instrument control software. Separation is performed with AG19 guard and AS19 high-capacity analytical microbore (2 mm diameter) columns using a typical injection volume of $10 \mu\text{L}$. After separation, the K is removed electrochemically leaving only water as carrier at the electrochemical detector (ECD). The resulting analytical background signal is at least an order of magnitude lower than for a conventional carbonate eluent, yielding much better sensitivity for trace ions. System control and data capture is achieved by a dedicated computer running Dionex Chromeleon Software (currently version 7.1).

3.2.2 Theory

A known volume ($10 \mu\text{L}$) of unpreserved (i.e. unacidified) sample is injected into a flow of eluent maintained by the instrument's pump. The flow passes through the columns containing a stationary phase of ion-exchange material. The different ions are then partitioned between the stationary adsorbent and the mobile eluent phase. As the eluent continues to flow the fraction of species in the mobile phase moves on and the sorption equilibrium progressively shifts towards desorption from the

adsorbent. Different species are desorbed from the resin sequentially according to their respective binding strengths and the analytes therefore move down the column at different speeds and become separated from each other. As the flow emerges from the column it passes into a detector where the conductivity of the flow is monitored. Any ionic analyte species contained in the eluent flow causes a change in conductivity which is recorded as a signal, the strength of which is proportional to the concentration of species.

Using the ICS5000 with AS19 column in reagent free mode, the eluent is a potassium hydroxide (KOH) solution generated on-line using pure water and a cartridge of concentrated KOH. The concentration of the eluent is variable and is software controlled by the instrument. By increasing the concentration of eluent over the course of an analysis it is possible to mimic the behaviour of gradient chromatography where the flow of eluent is varied, and to accelerate the elution of analytes in the later stages of the analysis. This both increases analytical sensitivity and reduces overall run-time. Before the detector is reached, a suppressor is used to neutralise the KOH eluent, thus significantly reducing the background conductance of the eluent and providing greatly enhanced signal-to-noise ratios. A carbonate removal device is also used to remove carbonate alkalinity species which can otherwise cause interferences and overlap on the signals of the desired analytes. Quantification is subsequently achieved using the dedicated instrument software by comparing the measured peak areas to those of standards with known concentrations.

3.2.3 Analytical method

The instrument was calibrated at the beginning of every analytical run using six manually prepared standards. Calibration uses a linear algorithm on all six standards for the major ions (Cl^- , SO_4^{2-} , NO_3^-), but quadratic fits to five standards for F^- , and four for NO_2^- , Br^- , HPO_4^{2-} . In occasional cases the concentration of these minor ions can exceed the usual calibration ranges; the ranges can then be extended by using a linear algorithm with inclusion of the fifth and sixth calibration standards. Samples which still exceed this extended range require dilution. This combination has been demonstrated during method validation to provide the best performance in terms of analytical sensitivity and bias over typical sample concentration ranges. A blank sample was analysed at the start of each run with QC samples analysed at the start and end of each run and after no more than every 20 samples. A calibration drift check standard was run at the end of each run and after no more than every 50 samples. The analysis followed a pre-programmed schedule and the software collected the data with peaks identified by retention time.

For higher total concentration loads the analytical column can become overloaded, causing poor peak shapes, variable retention times and thus unreliable results. To overcome this problem, more concentrated solutions were diluted with deionized water. In addition, where necessary, sample dilution was also used to bring one or more analyte concentrations within the concentration range covered by the standards. Results for sample affected were reported 'as received', i.e. with corrections for any dilution factors already applied before reporting. Such data are therefore not necessarily apparent from the analytical reports. However, the laboratory maintains full records of all dilutions and repeat analyses enabling a full audit trail to be obtained for any individual result if required.

Great care was taken during the method development to eliminate any potential for significant interferences. The chromatographic separation of the analytes is excellent, so that even high concentrations of a given element are unlikely to compromise the determination of another. Using the KOH eluent generation technique, rather than the classical mixed carbonate eluent, it is possible to observe a signal for carbonate or bicarbonate in the sample. In natural waters with high alkalinity this could in principle be significant but is effectively eliminated using a carbonate-removal device (CRD) in the chromatography line. As a further precaution, the method was specifically optimised to ensure that even in the event of a carbonate peak occurring, it lies away from any of the elements being determined. In practice, experience has shown the most likely source of interference for these analyses is that the instrument is sufficiently sensitive to detect cellulose breakdown products derived from the cellulose ester filters commonly used during field sampling. Such interferences are invariably at trace level; they are most likely to affect the determination of F, but they are easily identified during data

processing. No significant problems with cellulose degradations products were encountered during analysis of the Tellus Border samples.

The Dionex ICS5000 equipment used is fitted with two independent column and detection systems allowing two methods to be operated simultaneously on the same instrument. The elution time required for a single sample injection using IC can be significant, and in this case was approximately 25 minutes per sample. Given the large number of samples in the Tellus Border project the overall analytical run time was therefore very substantial. In order to maximise the throughput of the samples and meet the required completion dates, both channels on the instrument were configured identically to provide two parallel analytical systems running the same method and doubling the capacity of the instrument. The two systems are simply identified as Channels 1 & 2, but under the quality and data management systems measurements on any given sample can be traced back to the individual analytical run with the instrument channel identified. Both channels were subject to full quality control procedures during the run; to demonstrate consistency between the channels the QC data are presented separately in the discussion and tables below.

3.2.4 Data Quality

The method has been validated, audited and prepared for accreditation following the introduction of new equipment shortly before the Tellus Border project. The updated method has been fully documented and submitted to UKAS for consideration and a decision is pending. It is expected that the method will be added to the formal scope of BGS UKAS accreditation shortly. In fact, the validation data used to support the current analyses form the basis of the submission to UKAS (Harrison *et al.*, 2012).

Most anions are stable in solution for an appreciable length of time, and certainly within the period between sampling and analysis. Nitrite, orthophosphate and, to a lesser extent, nitrate, may, however, be modified by microbial activity. To minimize this sample are filtered to 0.45 µm stored in a refrigerator between 1°C and 8°C. The laboratory also makes every effort to carry out analyses as soon as possible after receipt.

3.2.5 Performance parameters

Of the suite elements requested by GSI for ion chromatography analysis, all the required elements were provided, as shown in Table 4, with method Lower limits of Detection better or comparable to those requested. Also shown are the reported method Limits of Quantification (LOQ), the Upper Calibration Limit (UCL) and the extended UCL applicable if the additional calibration points were included, as described above.

Table 4. Lower limits of detection and other performance parameters for Required Analytes in stream water analysis by IC.

Required Analyte	Units	Guide LLD	Method LLD	Reported LLD	Method LOQ	UCL	Extended UCL
Fluoride F ⁻	mg L ⁻¹	0.01	0.005	0.01	0.01	2.5	5.0
Chloride Cl ⁻	mg L ⁻¹	0.05	0.05	0.05	0.05	100	–
Nitrite NO ₂ ⁻	mg L ⁻¹	0.01	0.005	0.01	0.01	1.25	5.0
Bromide Br ⁻	mg L ⁻¹	0.02	0.01	0.02	0.02	1.25	5.0
Nitrate NO ₃ ⁻	mg L ⁻¹	0.02	0.03	0.05	0.05	60	–
Sulphate SO ₄ ²⁻	mg L ⁻¹	0.05	0.05	0.1	0.1	50	–
Orthophosphate HPO ₄ ²⁻	mg L ⁻¹	0.01	0.01	0.1	0.1	2.5	10

Only one anion, I⁻, was listed as desirable. However, at the concentrations observed in natural waters determination of I⁻ by IC is not sufficiently sensitive to provide useful data and therefore was not undertaken.

It should be noted that for some IC anions there are differences between the Method LLD defined in this summary report and the LLDs presented in the individual analytical data reports (reproduced in Table 4).

These arise because the formal method validation was ongoing at the outset of the Tellus Border work. The first batches of data were reported against LLDs which the laboratory could be confident would be met on the basis of only partial validation (i.e. they were conservative). The completion of the validation and documentation for submission to UKAS has demonstrated that in fact the method can consistently achieve better than those provisional LLDs, and better (lower) limits are now published in the UKAS method. The data obtained during the course of the Tellus Border work provided an important contribution to the overall validation. The new formal method figures are therefore presented here in the summary report, although the original higher LLDs have been retained in all the analytical data reports for the purposes of internal consistency and should be considered as the operational LLDs for these data.

3.3 ANALYSIS OF NON-PURGEABLE ORGANIC CARBON

3.3.1 Instrumentation

The determination of NPOC was carried out using a Shimadzu TOC-V CPH total organic carbon analyser fitted with an ASI-V autosampler, utilizing a Parker Balston gas generator as a carbon-free air supply.

The BGS method (BGS Technical Procedure AG 2.3.8) covers the analysis of natural waters including pore-waters, and synthetic or experimental fluids, including hydrothermal fluids and aqueous leachates for 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 expressed as Non-Purgeable Organic Carbon (NPOC) to reflect the sparging inherent in the method.

3.3.2 Theory

The procedure first involves the removal of inorganic carbon content by acidification and sparging. Before analysis commences, 0.1 mL of 10% hydrochloric acid is added to each sample (5 mL) and the carrier gas is bubbled through the sample for approximately five minutes in order to liberate any inorganic carbon (IC) to the atmosphere as CO₂.

For NPOC measurement, sample is carried through the instrument into the total carbon (TC) combustion tube by a purified air carrier gas (i.e. containing no CO₂) flowing at 150 mL min⁻¹. The combustion tube is packed with Pt-coated alumina catalyst maintained at 680°C by an electrically heated furnace. When the sample enters the TC combustion tube, all of the remaining carbon is oxidised to carbon dioxide and swept out of the tube by the carrier gas into a non-dispersive infrared (NDIR) detector which measures the evolved carbon dioxide concentration by energy absorption.

The output analogue signal of the NDIR detector is displayed as a response peak. The area of the peak is proportional to the NPOC concentration, as all IC in the sample was purged before analysis. The NPOC concentration in a sample is determined from the calibration curve prepared using standard solutions containing known amounts of organic carbon (OC).

3.3.3 Analytical method

The instrument was calibrated across two concentration ranges: 0–10 mg L⁻¹ and 0–100 mg L⁻¹ using automatic dilution of the two primary working standards (10 mg L⁻¹ and 100 mg L⁻¹) to give a total of four calibration standards in each of the ranges (1, 2.5, 5 & 10 mg L⁻¹ and 10, 25, 50 & 100 mg L⁻¹, respectively). The calibrations are calculated using linear regression with zero shift to obtain R² value equal to or better than 0.99.

Usually the instrument can be recalibrated for each analytical run, but the calibration typically remains stable for several days if the instrument is maintained under constant and stable operating conditions. The autosampler capacity allows for analysis of approximately 60–65 samples every 24 hours (allowing for inclusion of suitable blanks and controls) enabling an overall throughput of some 250–300 samples per week during the intensive throughput used for the Tellus Border project. The instrument was therefore recalibrated weekly, with the continuing validity of the calibration monitored by use of check standards, quality control solutions and certified reference material interspersed throughout each run.

Quality control standards containing 5, 10 and 50 mg L⁻¹ OC were analysed at the beginning and end of each run and after not more than 10 unknown samples. Samples exceeding the top calibration standard were diluted with deionized water to bring them into the calibration range. Results were calculated automatically and stored in data files by the instrument software.

3.3.4 Data quality

The method is fully accredited under the scope of BGS UKAS accreditation. The method is validated for a concentration range up to 100 mg L⁻¹, with a Method Detection Limit (MDL) of 0.5 mg L⁻¹. A minimum 6 mL aliquot size is usually required for analysis, although smaller volumes may be analysed following dilution. In such cases the method performance characteristics will change accordingly. Samples with known high salinity will also usually be diluted before analysis.

The laboratory makes every effort to analyse sample promptly after receipt in order to minimize the possibility of sample degradation, although evidence suggests that samples are stable for an extended time if the sample is filtered to 0.45 µm stored between 1 and 8°C. Stability checks using repeat analysis of stored samples over a several months period showed that NPOC concentrations in samples which had been correctly filtered and stored were stable within analytical error during this time. The method is essentially interference free as any IC in the sample is removed prior to analysis by the instrument and any OC is fully converted to CO₂ during the oxidation procedure. This has been thoroughly investigated by the instrument manufacturer and is also verified by the external check standards that are run. To all intents and purposes, NPOC data are equivalent to dissolved organic carbon (DOC).

The Limit of Quantification (LoQ) reported for NPOC is 0.5 mg L⁻¹ (Table 5). The overall expanded uncertainty is estimated to be 8%; based on an average value across all validation samples (Richardson *et al.*, 2011).

3.3.5 Performance parameters

The analytical method used fully met the performance requirements specified by GSI. The method performance parameters were determined using the same validation procedures as described for ICP-MS (see Section 3.1.5).

Table 5. Method performance parameters for stream water analysis of NPOC.

Required Analyte	Units	Guide LLD	Method LLD	Method LOQ	UCL
Non-purgeable organic carbon (by TIC/TOC)	mg L ⁻¹	0.50	–	0.5	100

3.4 ANALYTICAL QUALITY CONTROL

The Analytical Quality Control (AQC) regime operated by the BGS laboratory has three key aspects: QC standards, Certified Reference Materials (CRMs) and Proficiency-Testing (PT). For all three of the methods used here (ICP-MS, IC and NPOC) QC standards were analysed throughout each analytical run. In-house QC standards prepared on the day of analysis were analysed after at most every 20 samples and additionally at the beginning and end of each run. The QC data were verified against defined limits using Shewhart charts and any part of the analysis run in which bracketing QC samples did not meet the specified criteria was repeated for the non-compliant elements.

Deionized water or acid reagent blanks were run at similar intervals throughout each analytical run. The results were assessed against the validated method performance to identify any evidence of contamination, carry-over or deterioration in sensitivity. In the event of unsatisfactory blanks the cause was investigated and, if necessary, analysis of affected samples was repeated.

In addition to the in-house materials, an internationally-traceable CRM was analysed in every analytical run. For the purposes of the Tellus Border project the following CRMs were considered suitable and were used throughout the project:

- For ICP-MS, NIST standard SRM1643e, Trace-elements in water;
- For IC, a NIST-traceable commercial multi-anion standard, Spex ICMIX6, used at three different dilutions (x10, x25 and x100) to accommodate the different analytical ranges of the method;
- For NPOC, a NIST-traceable potassium hydrogen phthalate (KHP) 100 mg L⁻¹ solution (ERA), diluted to 10 mg L⁻¹ and prepared from stock daily.

Results were tested against the certified reference values on a pass/fail basis using fixed limits calculated for each element from the combination of the published certificate uncertainty and the validated method uncertainty. Full details are provided in the method validation report (Breward et al, 2009).

Proficiency Testing (PT) for the methods is provided by participation in the Aquacheck inter-laboratory proficiency testing scheme for waters, operated by LGC, in which approximately 350 laboratories participate worldwide. Both hard and soft clean water, waste water and saline potable water samples are analysed blind approximately every two months (for a selection of Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Ni, Mg, Mn, Mo, Na, P, Pb, S, Sb, Se, Si, Sn, Sr, V, Zn, Cl⁻, SO₄²⁻, NO₃⁻, Br⁻, NO₂⁻, HPO₄²⁻, F⁻, and NPOC). Results are reported to the organisers for comparison against other laboratories. The BGS laboratory consistently obtains good z-scores in these comparisons. Full details of PT performance is not tabulated here but can be provided on request.

Data for all the CRMs used during the analysis are presented in the Appendix. Each CRM was analysed many hundreds of times so summary statistics are used for each determinand and method. The lower rows in each case show the mean relative bias observed compared to the certified value of the CRM, and the relative standard deviation of the observed results, both expressed as a percentage. These provide the simplest, at-a-glance, interpretation of the overall datasets.

3.4.1 AQC performance for ICP-MS

Prepared multi-element quality control (QC) check standards were analysed at the start and end of each run and after no more than every 30 samples. Two of these QC solutions contained the trace elements of interest at 5 µg L⁻¹ (except for Ag at 1.25 µg L⁻¹):

- QCA3 – Li, Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Tl, Pb, U
- QCBC – Ti, Rb, Y, Nb, Sn, Cs, La, Ce, Pr, Nd, Sm, Eu, Tb, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Th

A separate QC solution was used for major elements at varying element concentration:

- QCMaj – Li, B, Na, Mg, Al, Si, P, S, K, Ca, Fe, Zn, Sr, Ba

The trace element CRM, NIST 1643e (Trace elements in water), was run between each block of quality control standards, so typically after every 30 samples.

Data for analysis of the QC solutions were assessed after each run by using Shewhart Charts. In addition, data are viewed after plotting in sequence order to check for any step changes between runs, changes in blank values or other anomalous results. Each analytical run was independently verified by a different analyst, including checking the post processing of the data for drift, dilution and collation.

Data for the NIST 1643e natural water reference material was very encouraging over the full dataset of some 180 determinations of all elements. There is little evidence of any significant bias from the internationally accepted certified values for any elements with the possible exceptions of slightly poorer performance for Ag and, to a lesser extent, Ti. Even then, in both cases the observed bias was not alarming, and was within stated method uncertainties. Furthermore, both elements are difficult to stabilise in solution and correspondingly occur at only very levels in natural waters.

Using the in-house QC materials to assess the wider range of elements in the ICP-MS suite was also reassuring, with slight deteriorations for some of the more amphoteric elements in QCA3 such as Al, Sn

and Pb, but in general very robust performance, in most cases significantly within the overall method uncertainty of approximately 15 %. Of particular note are the results for the rare earth elements contained in QCBC where overall uncertainty is almost without exception less than 4% and in many cases better than that. The major elements in QCMaj also demonstrate good and consistent recovery with only B (known to be more difficult using ICP) showing bias or precision above 10%.

3.4.2 AQC performance for IC anion analysis

For the IC CRM the data show excellent consistency between the two instrument channels with no systematic variation in precision and no significant bias observed between the two channels. This provides excellent confidence in the internal consistency of the entire dataset regardless of which channel a particular sample was analysed on.

The absolute performance of the IC method was also strong, with all the major anions consistently achieving both bias and precision of better than 5% for the higher concentrations (i.e. x10 and x 25 dilutions of the standard). The minor anions gave better than 10% across-the-board for the x 100 dilution used to assess the minor determinands, with the major determinands also better or close to 10% even when at the concentrations in the x100 dilution which are closer to the detection limits for the major anions.

3.4.3 AQC performance for NPOC analysis

For analysis of the NIST-traceable NPOC standard overall performance was generally sound, but there were occasional limit failures. Primarily these were due to lower than expected results believed to be associated with degradation of the standard material between preparation and to analysis and the observed overall bias and precision deteriorated correspondingly (-3.7% and 8.1% respectively). Where these failures occurred the results of the sample blocks affected were reconsidered. Samples were either re-run, or a subset of re-runs with acceptable QC performance was used to cross-validate the original data, or strong data from other QC checks already embedded in the run in question were used to establish validity. Consideration of the CRM data after rejection and reanalysis of these failures showed a much better overall performance with no significant overall bias or imprecision (-1.5% and 3.6% respectively).

4 Progress and reporting

4.1 OBSERVATIONS ON SAMPLING AND ANALYSIS

Analysis was commenced immediately on receipt of the first shipment of samples and continued uninterrupted at the full capacity of the laboratory until the entire programme was complete. The three methods have different time demands so could not be run absolutely in parallel. The ICP-MS analysis is fastest as the technique allows good quality data to be achieved for the full element suite for a sample aspiration time of only 3–4 minutes per sample. It was thus possible to achieve analysis of some 500 samples per week without difficulty. In contrast the IC elution time is nearer 25 minutes per sample, allowing only 50 injections per day on each channel, including standards, checks and controls. Using both instrument channels concurrently it was possible to achieve approximately 250 sample analyses per week. The NPOC instrument time is intermediate, but there is no second channel so the maximum throughput was similar to the IC at about 250 samples per week. The autosampler capacity for the NPOC instrument represents approximately 24 hours worth of samples, but exposure of samples for longer than that would risk sample degradation so it does not represent a major restriction in practice. Inevitably the instruments could not be maintained at theoretical maximum throughout the project as occasional breakdowns or performance drops had to be addressed, so the reporting timetable represents probably the maximum realistic throughput that could be delivered with the existing laboratory capacity and resourcing.

Samples were managed and reported in blocks of 500, with analytical data for each 500 being formally reported upon completion of all the analytical methods for the samples concerned. Monitoring of intermediate progress was maintained on a regular basis by means of summary progress charts circulated by the laboratory every two-three weeks, supplemented by telephone calls between the laboratory and GSI project managers roughly weekly to identify and resolve any difficulties emerging. The full progress of the batches of stream water samples through the facility from receipt to reporting is indicated by the dates shown in Table 6. It is unlikely that this rate of delivery could have been improved without compromising the standards of analysis.

A number of further reports were issued for each batch in response to reanalysis of specific samples requested by GSI in order to verify unexpected observations, or to address errors or invalidities identified after data release regarding small numbers of data. The identities, issue dates and reasons for these reports are provided in Table 7.

Table 6. Summary of progress and reporting for analysis of stream water samples.

Lab No.	Field batch ID	Minimum sample number	Maximum sample number	Received at BGS	Reported to GSI
20002	5845xx	584501	584600	24-Apr-12	19-Jun-12
	5846xx	584601	584700		
	5847xx	584701	584800		
	5848xx	584801	584900		
	5849xx	584901	585000		
20003	5850xx	585001	585100	24-Apr-12	13-Jul-12
	5851xx	585101	585200		
	5852xx	585201	585300		
	5853xx	585301	585400		
	5854xx	585401	585500		
20004	5855xx	585501	585600	24-Apr-12	27-Jul-12
	5856xx	585601	585700		
	5857xx	585701	585800		
	5858xx	585801	585900		
	5859xx	585901	586000		
20008	5860xx	586001	586100	24-Apr-12	16-Aug-12
	5861xx	586101	586200	15-May-12	
	5862xx	586201	586300		
	5863xx	586301	586400		
	5864xx	586401	586500		
20010	5865xx	586501	586600	15-May-12	14-Sep-12
	5866xx	586601	586700		
	5867xx	586701	586800		
	5868xx	586801	586900		
	5869xx	586901	587000		
20012	5870xx	587001	587100	15-May-12	03-Oct-12
	5871xx	587101	587200		
	5872xx	587201	587300	13-Jun-12	
	5873xx	587301	587400		
	5874xx	587401	587500		
20014	5875xx	587501	587600	13-Jun-12	24-Oct-12
	5876xx	587601	587700		
	5877xx	587701	587800		
	5878xx	587801	587900		
	5879xx	587901	588000		
20016	5880xx	588001	588100	13-Jun-12	28-Nov-12
	5881xx	588101	588200		
	5882xx	588201	588300		
	5883xx	588301	588400		
	5884xx	588401	588500		
20018	5885xx	588501	588600	13-Jun-12	13-Dec-12
	5886xx	588601	588700	18-Oct-12	
	5887xx	588701	588800		
	5888xx	588801	588900		

Table 7. Details of analytical reports issued for each laboratory batch.

Lab No.	Report No	Report date	Reason
20002	20002-1I	1-Jun-12	ICP-MS and IC data complete. NPOC pending
	20002-2C	19-Jun-12	Analysis completed
	20002-3S	7-Aug-12	Repeat analyses requested by GSI. Data amended
	20002-4C	14-Sep-12	Correction of data transposed in error
	20002-5C	10-Jan-13	Repeat analyses requested by GSI. Data amended
20003	20003-1C	13-Jul-12	Analysis completed
	20003-2S	25-Oct-12	Some previous data (IC) found to be invalid.
	20003-3C	10-Jan-13	Repeat analyses requested by GSI. Data amended
	20003-4S	26-Apr-13	Some NPOC data previously reported uncensored
20004	20004-1C	27-Jul-12	Analysis completed
	20004-2C	14-Sep-12	Supplementary data for Mn with improved DL
	20004-3S	24-Oct-12	Correction of NPOC result found to be invalid
	20004-4C	10-Jan-13	Repeat analyses requested by GSI. Data amended
20008	20008-1C	16-Aug-12	Analysis completed
	20008-2S	10-Jan-13	Repeat analyses requested by GSI. Data amended
	20008-3S	26-Apr-13	Some NPOC data previously reported uncensored
20010	20010-1C	14-Sep-12	Analysis completed
	20010-2C	14-Jan-13	Repeat analyses requested by GSI. Data amended
20012	20012-1C	03-Oct-12	Analysis completed
	20012-2C	14-Jan-13	Repeat analyses requested by GSI. Data amended
	20012-3S	26-Apr-13	Some NO ₃ data previously reported uncensored
20014	20014-1C	24-Oct-12	Analysis completed
	20014-2C	14-Jan-13	Repeat analyses requested by GSI. Data amended
20016	20016-1C	28-Nov-12	Analysis completed
	20016-2C	17-Jan-13	Repeat analyses requested by GSI. Data amended
20018	20018-C	13-Dec-12	Analysis completed
	20018-2C	17-Jan-13	Repeat analyses requested by GSI. Data amended

5 References

BGS Technical Procedure AG 2.3.8. Determination of non-purgeable organic carbon in waters by combustion analysis using a Shimadzu TOC V CPH.

BGS Technical Procedure AG 2.3.18. Determination of major and trace elements in aqueous samples using inductively coupled plasma-mass spectrometry (Agilent 7500CX)

BGS Technical Procedure AG 2.3.19. Determination of major and trace anions by ion chromatography (ICS5000)

Breward, K.M., Chenery, S.R.N. and Barlow, T.S. 2009. Validation report for the analysis of aqueous solutions by Agilent 7500 series ICP-MS. British Geological Survey Internal Report, IR 09/049.

Cheeseman, R V, and Wilson, A L. 1989. A Manual on Analytical Quality Control for the Water Industry, WRc, NS30

Harrison, H M, Milne, C J, and Gowing, C J B. 2012. Validation of the Determination of Major and Trace Anions by Ion Chromatography (ICS5000), BGS Internal Report IR/12/057.

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.

Appendix 1 Analytical Quality Control data and summary statistics

The following tables present the observed measurements for the Certified Reference Materials used by the laboratory during analysis. The summarised data are those used to control reported analytical data; QC data and associated analyses which were rejected are not included.

Values are presented for the certified value, and the observed maximum, minimum, mean, median and standard deviation. The mean is then used to determine the relative bias (compared to the certified value) and the relative standard deviation.

Where practical (for ICP-MS) values presented have been compared against expected performance and colour-highlighted to aid interpretation:

- Values without highlight have fully satisfied both method performance and CRM certification in all respects.
- For values highlighted in blue (■), either the observed mean value is below the stated LLD and therefore analyses can be expected to show increased relative uncertainty.
- For values highlighted in green (■), either the observed mean value is below the threshold of 3 x LLD and therefore analyses can be expected to show increased relative uncertainty.
- Values highlighted in red (■) show relative bias or imprecision outside the nominal method expanded uncertainty but at mean concentrations above the specified LLR thresholds.

No Upper Limit or Lower Limit are quoted when suppliers certificates of analysis do not include estimates of uncertainty in the reference value.

Table 8. Summary performance statistics for analysis of certified reference material NIST 1643e by ICP-MS.

	7 Li µg L ⁻¹	9 Be µg L ⁻¹	11 B µg L ⁻¹	23 Na mg L ⁻¹	24 Mg mg L ⁻¹	27 Al µg L ⁻¹	39 K mg L ⁻¹	42 Ca mg L ⁻¹	51 V µg L ⁻¹	52 Cr µg L ⁻¹	55 Mn µg L ⁻¹	56 Fe µg L ⁻¹	59 Co µg L ⁻¹	60 Ni µg L ⁻¹
Method LLD	1	0.01	10	0.2	0.01	1	0.02	0.3	0.1	0.05	0.2	1	0.01	0.1
Certificate value	17	13.64	154	20.23	7.841	138.33	1.984	31.5	36.93	19.9	38.02	95.7	26.4	60.89
Upper spec limit	20.4	16.6	194	23.4	9.41	185.2	2.38	37.0	42.8	23.1	45.2	125.6	33.0	78.7
Lower spec limit	14.4	11.3	121	18.0	6.67	98.4	1.69	27.6	32.9	17.7	32.7	70.6	21.1	46.2
Max	21.9	16.0	209	23.8	9.18	167.9	2.23	33.9	42.2	23.5	50.8	114.3	29.8	66.2
Mean	18.6	13.5	161	20.7	7.98	146.1	2.03	31.0	37.8	20.5	38.6	100.1	26.6	59.5
Median	18.7	13.5	161	20.8	7.95	146.0	2.04	31.0	37.7	20.5	38.5	99.5	26.5	59.4
Std deviation	1.4	0.8	16	1.1	0.44	7.8	0.09	1.1	1.6	1.0	2.1	4.9	1.1	2.8
Min	14.1	11.4	120	18.1	6.97	130.8	1.81	25.9	33.2	18.3	32.2	89.1	22.8	51.3
No of analyses	180	180	180	180	180	176	180	180	180	180	180	180	180	180
No of limit failures	20	0	4	1	0	0	0	2	0	1	4	0	0	0
% mean bias	9.4	-0.8	4.6	2.2	1.8	5.6	2.5	-1.6	2.2	3.2	1.5	4.6	0.7	-2.2
% RSD	7.3	6.0	10.1	5.1	5.6	5.3	4.4	3.7	4.2	4.7	5.4	4.9	4.2	4.7

	63 Cu µg L ⁻¹	66 Zn µg L ⁻¹	75 As µg L ⁻¹	78 Se µg L ⁻¹	85 Rb µg L ⁻¹	88 Sr µg L ⁻¹	95 Mo µg L ⁻¹	107 Ag µg L ⁻¹	111 Cd µg L ⁻¹	121 Sb µg L ⁻¹	137 Ba µg L ⁻¹	205 Tl µg L ⁻¹	208 Pb µg L ⁻¹	209 Bi µg L ⁻¹
Method LLD	0.4	0.5	0.02	0.1	0.01	0.1	0.03	0.05	0.01	0.005	0.1	0.01	0.02	0.01
Certificate value	22.2	76.5	58.98	11.68	13.8	315.1	118.5	1.036	6.408	56.88	531	7.623	19.15	13.75
Upper spec limit	28.9	101.4	68.9	14.1	16.3	372.6	139.7	1.20	7.56	65.9	604.3	8.79	22.8	15.9
Lower spec limit	16.6	55.6	52.0	9.8	12.0	269.6	103.1	0.71	5.58	50.7	484.1	6.10	16.5	12.6
Max	26.9	84.1	62.4	12.8	16.6	343.7	154.3	2.05	6.78	66.5	623.1	8.65	23.9	15.7
Mean	21.2	74.5	56.4	11.1	14.3	314.5	123.1	0.90	6.28	57.5	544.1	7.06	19.0	14.1
Median	21.0	74.4	56.3	11.2	14.3	314.6	122.7	0.87	6.27	56.9	543.2	6.95	18.8	14.2
Std deviation	1.3	4.1	2.1	0.6	0.5	10.2	7.2	0.22	0.20	3.0	18.9	0.45	1.2	0.6
Min	16.6	62.8	50.1	9.5	12.9	289.7	104.6	0.58	5.77	51.7	504.0	6.11	16.3	12.3
No of analyses	180	180	180	180	180	180	180	188	180	180	180	180	180	180
No of limit failures	1	0	2	4	2	0	7	30	0	2	2	0	5	4
% mean bias	-4.6	-2.7	-4.3	-4.6	3.8	-0.2	3.9	-13.5	-2.0	1.1	2.5	-7.4	-1.0	2.7
% RSD	6.3	5.6	3.7	5.8	3.7	3.2	5.9	24.7	3.3	5.2	3.5	6.4	6.4	4.2

Table 9. Summary performance statistics for analysis of laboratory QC solution QCA3 by ICP-MS.

	7 Li $\mu\text{g L}^{-1}$	9 Be $\mu\text{g L}^{-1}$	27 Al $\mu\text{g L}^{-1}$	51 V $\mu\text{g L}^{-1}$	52 Cr $\mu\text{g L}^{-1}$	55 Mn $\mu\text{g L}^{-1}$	59 Co $\mu\text{g L}^{-1}$	60 Ni $\mu\text{g L}^{-1}$	63 Cu $\mu\text{g L}^{-1}$	66 Zn $\mu\text{g L}^{-1}$	75 As $\mu\text{g L}^{-1}$
Method LLD	1	0.01	1	0.1	0.05	0.2	0.01	0.1	0.4	0.5	0.02
Nominal target	5	5	5	5	5	5	5	5	5	5	5
Upper spec limit	6.65	5.95	6.5	5.65	5.65	5.8	6.1	6.3	6.35	6.39	5.7
Lower spec limit	3.35	4.05	3.5	4.35	4.35	4.2	3.9	3.7	3.65	4.25	4.3
Max	6.68	7.36	7.47	5.69	5.68	11.67	5.57	5.75	10.42	10.90	5.81
Mean	5.22	5.06	5.23	5.14	4.94	5.12	4.98	5.11	5.28	5.47	5.06
Median	5.20	5.05	5.20	5.15	4.94	5.10	4.99	5.11	5.21	5.35	5.05
Std deviation	0.43	0.34	0.68	0.19	0.23	0.62	0.21	0.23	0.58	0.80	0.19
Min	3.66	4.17	3.27	4.28	4.37	3.15	4.11	4.54	3.92	3.33	4.52
No of analyses	309	309	307	309	309	309	309	309	309	309	309
No of limit failures	1	5	17	2	1	13	0	0	7	29	1
% mean bias	4.3	1.3	4.6	2.8	-1.2	2.5	-0.3	2.3	5.6	9.5	1.3
% RSD	8.3	6.7	13.0	3.7	4.7	12.1	4.2	4.5	11.0	14.6	3.8

	78 Se $\mu\text{g L}^{-1}$	88 Sr $\mu\text{g L}^{-1}$	95 Mo $\mu\text{g L}^{-1}$	107 Ag $\mu\text{g L}^{-1}$	111 Cd $\mu\text{g L}^{-1}$	118 Sn $\mu\text{g L}^{-1}$	121 Sb $\mu\text{g L}^{-1}$	137 Ba $\mu\text{g L}^{-1}$	205 Tl $\mu\text{g L}^{-1}$	208 Pb $\mu\text{g L}^{-1}$	238 U $\mu\text{g L}^{-1}$
Method LLD	0.1	0.1	0.03	0.05	0.01	0.02	0.005	0.1	0.01	0.02	0.002
Nominal target	5	5	5	1.25	5	5	5	5	5	5	5
Upper spec limit	5.9	5.8	5.75	1.75	5.75	5.65	5.55	5.9	5.8	5.8	5.8
Lower spec limit	4.1	4.2	4.25	0.75	4.25	4.35	4.45	4.1	4.2	4.2	4.2
Max	5.88	5.81	5.44	2.82	5.52	4.08	5.38	6.27	5.27	44.50	5.94
Mean	5.19	5.01	4.95	1.27	5.18	3.63	4.98	4.86	4.89	5.16	5.03
Median	5.21	5.00	4.95	1.22	5.17	3.65	5.00	4.89	4.89	5.05	5.03
Std deviation	0.23	0.19	0.18	0.27	0.15	0.17	0.14	0.24	0.15	2.25	0.20
Min	4.35	4.04	4.15	0.01	4.31	3.03	4.48	4.02	4.36	4.40	4.23
No of analyses	309	309	309	328	309	318	309	309	309	309	309
No of limit failures	0	2	1	10	0	0	0	8	0	1	1
% mean bias	3.7	0.1	-1.0	1.6	3.5	-27.4	-0.3	-2.7	-2.2	3.2	0.7
% RSD	4.4	3.8	3.7	21.6	2.9	4.8	2.7	4.9	3.1	43.6	4.0

Table 10. Summary performance statistics for analysis of laboratory QC solution QCBC by ICP-MS.

	47 Ti µg L ⁻¹	85 Rb µg L ⁻¹	89 Y µg L ⁻¹	90 Zr µg L ⁻¹	93 Nb µg L ⁻¹	118 Sn µg L ⁻¹	133 Cs µg L ⁻¹	139 La µg L ⁻¹	140 Ce µg L ⁻¹	141 Pr µg L ⁻¹	146 Nd µg L ⁻¹	147 Sm µg L ⁻¹	151 Eu µg L ⁻¹
Method LLD	0.05	0.01	0.005	0.05	0.02	0.02	0.005	0.002	0.002	0.002	0.01	0.002	0.002
Nominal target	5	5	5	5	5	5	5	5	5	5	5	5	5
Upper spec limit	5.75	5.75	5.75	5.75	5.65	5.75	5.8	5.75	5.75	5.75	5.85	5.8	6
Lower spec limit	4.25	4.25	4.25	4.25	4.35	4.25	4.2	4.25	4.25	4.25	4.15	4.2	4
Max	5.65	6.63	5.33	6.75	5.24	10.34	6.51	5.31	5.54	5.48	5.51	5.42	5.92
Mean	5.05	5.00	4.97	4.79	4.88	5.12	4.94	4.99	5.02	4.94	4.97	5.03	5.04
Median	5.07	5.01	4.98	4.81	4.91	5.00	4.94	5.00	5.02	4.94	4.99	5.04	5.04
Std deviation	0.24	0.31	0.14	0.25	0.18	0.84	0.30	0.17	0.16	0.17	0.17	0.17	0.21
Min	3.66	0.76	3.92	3.45	3.79	1.59	0.77	3.90	3.98	3.75	3.89	3.96	3.95
No of analyses	291	291	291	291	291	299	291	291	291	291	291	291	291
No of limit failures	2	3	1	5	2	11	3	3	1	2	1	2	1
% mean bias	1.0	0.0	-0.6	-4.2	-2.5	2.4	-1.3	-0.3	0.4	-1.2	-0.5	0.6	0.8
% RSD	4.8	6.1	2.9	5.2	3.6	16.4	6.1	3.3	3.2	3.5	3.5	3.3	4.2

	159 Tb µg L ⁻¹	160 Gd µg L ⁻¹	163 Dy µg L ⁻¹	165 Ho µg L ⁻¹	166 Er µg L ⁻¹	169 Tm µg L ⁻¹	172 Yb µg L ⁻¹	175 Lu µg L ⁻¹	178 Hf µg L ⁻¹	181 Ta µg L ⁻¹	184 W µg L ⁻¹	232 Th µg L ⁻¹
Method LLD	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.01	0.02	0.05	0.005
Nominal target	5	5	5	5	5	5	5	5	5	5	5	5
Upper spec limit	5.9	5.95	6	5.95	6.1	5.95	5.85	5.95	6.05	5.8	6.05	5.8
Lower spec limit	4.1	4.05	4	4.05	3.9	4.05	4.15	4.05	3.95	4.2	3.95	4.2
Max	5.74	5.40	5.55	5.39	5.50	5.47	5.52	5.42	5.60	5.34	5.44	5.55
Mean	4.99	5.00	5.05	4.97	5.03	5.01	4.98	4.99	4.83	4.83	4.92	4.97
Median	4.98	5.01	5.07	4.99	5.04	5.01	5.00	5.01	4.83	4.84	4.93	5.00
Std deviation	0.20	0.17	0.16	0.21	0.16	0.19	0.16	0.20	0.22	0.25	0.17	0.20
Min	3.73	3.90	3.97	3.69	3.97	3.80	3.93	3.73	3.51	3.60	3.91	3.77
No of analyses	291	291	291	291	291	291	291	291	291	291	291	291
No of limit failures	1	1	1	1	0	1	1	1	1	1	1	1
% mean bias	-0.3	-0.1	1.0	-0.5	0.6	0.2	-0.4	-0.1	-3.4	-3.5	-1.6	-0.5
% RSD	3.9	3.3	3.2	4.2	3.1	3.7	3.2	4.0	4.5	5.1	3.5	3.9

Table 11. Summary performance statistics for analysis of laboratory QC solution QCMaj by ICP-MS.

	7 Li µg L ⁻¹	11 B µg L ⁻¹	23 Na mg L ⁻¹	24 Mg mg L ⁻¹	27 Al µg L ⁻¹	28 Si µg L ⁻¹	31 P mg L ⁻¹	34 S mg L ⁻¹	39 K mg L ⁻¹	42 Ca mg L ⁻¹	56 Fe µg L ⁻¹	66 Zn µg L ⁻¹	88 Sr µg L ⁻¹	137 Ba µg L ⁻¹
Method LLD	1	10	0.2	0.01	1	50	0.01	1	0.02	0.3	1	0.5	0.1	0.1
Nominal target	50	50	30	3	50	3000	3	10	3	30	100	50	100	50
Upper spec limit	59.9	72.9	33.9	3.51	65	3630	3.84	13.5	3.51	34.2	128	64.5	116	55.5
Lower spec limit	43.9	38.4	26.1	2.49	35	2370	2.16	6.5	2.49	25.8	72	35.5	84	44.5
Max	60.6	78.4	36.8	3.66	99.9	3753	3.52	13.1	3.47	33.2	118	64.9	111	56.2
Mean	52.2	56.6	30.2	3.06	51.3	3258	3.14	10.7	3.10	30.5	103	51.5	102	49.6
Median	52.6	56.3	30.3	3.08	50.9	3259	3.13	10.6	3.12	30.7	103	51.6	102	49.6
Std deviation	3.8	5.8	1.9	0.18	4.7	154	0.15	0.6	0.14	1.3	5	3.1	4	2.4
Min	33.7	40.6	20.1	1.84	31.1	2231	2.13	7.00	2.09	20.3	69.4	36.7	66.3	33.1
No of analyses	288	288	288	288	288	288	288	288	288	288	288	288	288	288
No of limit failures	10	2	8	4	3	4	1	0	2	2	1	1	3	7
% mean bias	4.4	13.2	0.6	2.0	2.5	8.6	4.7	6.5	3.5	1.6	3.1	2.9	1.6	-0.9
%RSD	7.2	10.3	6.2	5.9	9.1	4.7	4.8	5.4	4.6	4.4	5.3	6.0	4.3	4.8

Table 12. Summary performance statistics for anion analysis by ion chromatography of dilutions of NIST-traceable certified standard Spex ICMIX6. All data combined.

	Chloride mg L ⁻¹	Sulphate mg L ⁻¹	Nitrate mg L ⁻¹	Bromide mg L ⁻¹	Nitrite mg L ⁻¹	o-Phosphate mg L ⁻¹	Fluoride mg L ⁻¹
LOD	0.05	0.05	0.03	0.01	0.005	0.01	0.005
x 10 dilution							
Certified value	5.03	15.1	11.1				2.0
Max	5.49	16.1	11.99				2.23
Mean	5.08	14.98	11.35				2.01
Median	5.07	14.95	11.33				2.00
Std deviation	0.15	0.39	0.32				0.08
Min	4.636	13.97	10.60				1.80
No of analyses	332	334	321				334
% mean bias	1.0	-0.8	2.5				0.6
% RSD	2.9	2.6	2.8				3.9
x 25 dilution							
Certified value	2.01	6.04	4.43				0.800
Max	2.20	6.4	4.87				0.91
Mean	2.01	5.94	4.46				0.81
Median	2.01	5.96	4.46				0.81
Std deviation	0.08	0.17	0.20				0.04
Min	1.819	5.48	3.96				0.72
No of analyses	355	362	356				363
% mean bias	-0.3	-1.6	0.7				1.3
% RSD	3.9	2.9	4.4				4.7
x 100 dilution							
Certified value	0.503	1.51	1.11	1.00	0.821	1.50	0.200
Max	0.67	1.7	1.41	1.188	1.061	1.73	0.23
Mean	0.50	1.43	1.07	1.045	0.822	1.52	0.19
Median	0.50	1.43	1.06	1.05	0.82	1.52	0.19
Std deviation	0.06	0.08	0.11	0.046	0.069	0.08	0.02
Min	0.37	1.22	0.86	0.927	0.612	1.22	0.13
No of analyses	338	350	360	355	372	357	367
% mean bias	-0.8	-5.2	-3.8	4.5	0.0	1.1	-6.5
% RSD	11.5	5.7	10.5	4.4	8.4	5.2	9.4

Table 13. Summary performance statistics for anion analysis by ion chromatography of dilutions of NIST-traceable certified standard Spex ICMIX6. Data for instrument channel 1 only.

	Chloride mg L ⁻¹	Sulphate mg L ⁻¹	Nitrate mg L ⁻¹	Bromide mg L ⁻¹	Nitrite mg L ⁻¹	o-Phosphate mg L ⁻¹	Fluoride mg L ⁻¹
LOD	0.05	0.05	0.03	0.01	0.005	0.01	0.005
x 10 dilution							
Certified value	5.03	15.1	11.1				2.0
Max	5.39	15.8	11.97				2.22
Mean	5.01	14.87	11.17				2.01
Median	5.01	14.81	11.15				2.01
Std deviation	0.14	0.41	0.28				0.08
Min	4.636	13.97	10.60				1.80
No of analyses	155	159	155				156
% mean bias	-0.4	-1.5	0.9				0.7
% RSD	2.7	2.7	2.5				4.2
x 25 dilution							
Certified value	2.01	6.04	4.43				0.800
Max	2.15	6.2	4.83				0.91
Mean	1.96	5.84	4.33				0.81
Median	1.95	5.82	4.34				0.81
Std deviation	0.07	0.15	0.16				0.04
Min	1.819	5.48	3.96				0.72
No of analyses	170	175	178				171
% mean bias	-2.7	-3.3	-2.2				1.0
% RSD	3.6	2.6	3.6				5.5
x 100 dilution							
Certified value	0.503	1.51	1.11	1.00	0.821	1.50	0.200
Max	0.67	1.6	1.33	1.188	1.061	1.73	0.23
Mean	0.46	1.38	1.00	1.041	0.835	1.51	0.18
Median	0.45	1.37	0.96	1.03	0.83	1.51	0.18
Std deviation	0.05	0.07	0.09	0.058	0.079	0.09	0.02
Min	0.37	1.22	0.86	0.927	0.612	1.22	0.13
No of analyses	152	162	173	174	177	176	171
% mean bias	-8.2	-8.8	-10.0	4.1	1.6	0.6	-8.9
% RSD	10.9	5.0	9.0	5.6	9.5	5.9	10.9

Table 14. Summary performance statistics for anion analysis by ion chromatography of dilutions of NIST-traceable certified standard Spex ICMIX6. Data for instrument channel 2 only.

	Chloride mg L ⁻¹	Sulphate mg L ⁻¹	Nitrate mg L ⁻¹	Bromide mg L ⁻¹	Nitrite mg L ⁻¹	o-Phosphate mg L ⁻¹	Fluoride mg L ⁻¹
LOD	0.05	0.05	0.03	0.01	0.005	0.01	0.005
x 10 dilution							
Certified value	5.03	15.1	11.1				2.0
Max	5.49	16.1	11.99				2.23
Mean	5.14	15.08	11.52				2.01
Median	5.14	15.04	11.55				2.00
Std deviation	0.13	0.35	0.25				0.07
Min	4.826	14.39	10.68				1.82
No of analyses	177	175	166				178
% mean bias	2.2	-0.1	4.1				0.6
% RSD	2.5	2.3	2.2				3.6
x 25 dilution							
Certified value	2.01	6.04	4.43				0.800
Max	2.20	6.4	4.87				0.91
Mean	2.05	6.04	4.59				0.81
Median	2.04	6.03	4.60				0.81
Std deviation	0.06	0.12	0.14				0.03
Min	1.868	5.80	4.18				0.75
No of analyses	185	187	178				192
% mean bias	1.9	0.0	3.7				1.6
% RSD	2.8	2.1	3.0				3.9
x 100 dilution							
Certified value	0.503	1.51	1.11	1.00	0.821	1.50	0.200
Max	0.65	1.7	1.41	1.108	0.984	1.689	0.23
Mean	0.53	1.48	1.13	1.050	0.810	1.52	0.19
Median	0.52	1.48	1.12	1.05	0.81	1.53	0.19
Std deviation	0.04	0.06	0.09	0.028	0.057	0.07	0.01
Min	0.403	1.37	0.87	0.966	0.66	1.22	0.15
No of analyses	186	188	187	181	195	181	196
% mean bias	5.2	-2.1	1.9	5.0	-1.4	1.5	-4.3
% RSD	8.2	4.1	8.0	2.7	7.0	4.4	7.4

Table 15. Summary performance statistics for analysis of dilutions of NIST-traceable certified NPOC standard (100 mg L⁻¹ potassium hydrogen phthalate solution, ERA).

For further details of all and accepted data please see main text.

	NPOC mg L ⁻¹	NPOC mg L ⁻¹
LOD	0.5	0.5
Certified value	10.0	10.0
	All data	Accepted data
Max	11.34	10.68
Mean	9.63	9.85
Median	9.71	9.87
Std deviation	0.78	0.35
Min	4.86	9.20
No of analyses	122	95
% mean bias	-3.7	-1.5
% RSD	8.1	3.6