WAG Protocol	**ANALYTICAL GUIDELINES FOR WATER SAMPLES** _Version 1.1_ **(previously AG Protocol, updated Jan 2001)**
Aim	_To provide guidelines for the analysis of water samples from ECN terrestrial sites_

Rationale

Whilst each laboratory has full responsibility for managing its own analytical resources, participating laboratories have an obligation to conduct analyses under controlled conditions, and to provide documentation of methodology, information about significant changes in methodology, and information about validation procedures.

Procedures will be subject to annual review by an Analytical Working Group with representatives from each laboratory.

Appropriate methods are outlined below. Detection limits indicate targets for laboratories for their chosen method.

Method

Approved techniques

Alternative approved techniques for each determinand are given in the following Table (superscripts refer to Notes section below).

pH	[1]HMSO (1988) ('Blue book')		
Conductivity	[2]HMSO (1978) ('Blue book')		
Na^+	FES/AAS	ICP/OES	IC
K^+	FES/AAS	ICP/OES	IC
Ca^{2+}	AAS	ICP/OES	IC
Mg^{2+}	AAS	ICP/OES	
Fe^{2+}	AAS	ICP/OES	
Al^{3+}	AAS	ICP/OES	[4]Col-PCV
NH_4^+ N	[4]Col-indophenol blue		
Cl^+	IC	[4]Col-Hg/thiocyanate	
NO_3^- N	IC	([4]Col-Greiss/Illosvay)	
SO_4^{2-} S	IC	(ICP/OES)	
HCO_3^-	Alkalinity. [3]HMSO (1981) ('Blue book')		
PO_4^{3-} P	[4]Col-molybdenum blue		
DOC	Combustion	Colorimetry	
Total N	Kjeldahl/indophenol blue	Persulphate/NO_3	

Note: Techniques shown in brackets do not quantify directly the species of interest, but may be suitable following comparative tests. For pH and conductivity measurements, please see also the Initial Water Handling (WH) Protocol

[1]**HMSO**. 1988. _The determination of pH in low ionic strength waters_. London: HMSO.

[2]**HMSO**. 1978. _The measurement of electrical conductivity and the laboratory determination of the pH value of natural, treated and waste waters._ London: HMSO.

[3]**HMSO**. 1981. _The determination of alkalinity and acidity in water._ London: HMSO.(Method B)

[4]Col - colorimetry using continuous flow or flow injection analysis

Reference techniques

Changes and developments in analytical technology will inevitably occur during the lifetime of the ECN programme, and it is important to have a series of reference methods with which to compare and to assess alternative or innovative analytical methodologies. The methods listed below are the most suitable for use as primary references.

	Results expressed as	Species of interest	Reference technique	Ultimate detection limit
pH	pH		HMSO (1988)	
Conductivity	µS cm^{-1}		HMSO (1978)	1
Na$^+$	mg l^{-1}		AAS	0.02
K$^+$	mg l^{-1}		AAS	0.01
Ca^{2+}	mg l^{-1}		AAS	0.02
Mg^{2+}	mg l^{-1}		AAS	0.02
Fe^{2+}	mg l^{-1}		AAS	0.1
Al^{3+}	mg l^{-1}		AAS	0.1
NH$_4^+$ N	mg l^{-1} N		Indophenol blue	0.1
Cl$^-$	mg l^{-1}		IC	0.5
NO$_3^-$	mg l^{-1} N	Nitrate	IC	0.01
SO$_4^{2-}$	mg l^{-1} S	Sulphate	IC	0.1
Alkalinity	mg l^{-1} CaCO$_3$		HMSO (1981)	1
PO$_4^{3-}$	mg l^{-1} P	o-phosphate	Molybdenum blue	0.005
DOC	mg l^{-1} C		Combustion	0.1
Total N	mg l^{-1} N		Kjeldahl	0.1

Notes: HMSO references are given on previous page

For conductivity and pH measurement, please refer also to the Initial Water Handling (WH) Protocol. For pH measurement, a procedure should be used which is capable of quantifying low ionic strength solutions, with a separate glass and a recommended reference electrode.

Laboratories should report data on the fraction specified (eg SO$_4^{2-}$ by ion chromatography). If there is a strong preference by the laboratory to use a technique which quantifies a slightly different fraction (eg S by ICP/OES), then there is an obligation on the laboratory to monitor the two alternative techniques for the ECN samples in order to provide data to confirm the absence of bias.

The analytical ranges in operation will differ between laboratories, producing different working detection limits. However, when the solution concentration is in the region of the working detection limit of the particular analytical system, there is a need to consider whether the quoted values at this detection limit provide data suitable for the purpose of the study, or alternatively whether the samples should be re-analysed using a lower analytical range. The defined limits provide a uniform guideline to be followed by each laboratory.

Priority listing of determinands

Sample volumes for soil solution and precipitation waters will be limited in periods of low rainfall. The following priority listing (where 1 indicates the highest priority) provides a working guideline to assist site operators and analysts in making decisions on handling and analytical options when sample volume is limiting.

1. pH, conductivity
2. Anions – NO$_3^-$, SO$_4^{2-}$, then PO$_4^{3-}$, Cl$^-$
3. Cations – Ca^{2+}, Mg^{2+}, then K$^+$, Na$^+$
4. NH$_4^+$ N
5. DOC
6. Cations requiring separate acidified portion – FE^{2+}, A^{3+}
7. Total-N, alkalinity

Please refer to the Initial Water Handling (WH) Protocol for information on solution handling, filtration, pH and acidification of samples.

WAG Protocol

Providing details of methodology

Details of analytical methods used by a laboratory should be kept at the laboratory for its operators, and summary information provided for the ECN database. This information will reside, one data record for each determinand for each ECN site, in the meta database, linked to the data by site, core measurement, determinand and date, to indicate the methodology in operation and its precision. The format is illustrated below, using nitrate as an example.

Performance characteristics of the method

Laboratory/site	Merlewood/Moor House
Substance determined	Nitrate
Basis of the method	Chemically suppressed ion chromatography
Types of sample	Rainwater (PC), stream water (WC), soil solution (SS)
Typical concentrations	PC: 0, WC: 0.50, SS: 3.2
Volume for analysis	10 ml
Calibration range	0.01 to 10 mg l^{-1} - slight deviation from linearity corrected for by using 3rd-order regression
Method of measurement	Peak area using integration / data system
Results reported	3 significant figures as N (mg l^{-1})
Detection limit	0.01 mg l^{-1}
Within batch standard deviation (mid-range) *	2% rsd
Interferences	None
Internal QC measure	CUSUM quality control chart
Accuracy measure	AQUACHECK

Notes: The detection limit is defined as 4.65 within-batch standard deviation* of the blank or a solution with a concentration close to the blank when no signal is detectable from the blank (n=10)
* A within-batch standard deviation in excess of 5% is unlikely to be acceptable

When any details change, a new record will be added to the database with a date 'stamp'. Aspects of the analysis such as instrument maintenance, calibration, drift, and training of staff will be controlled by the laboratory. The above information provides a record of changes in methodology and an assessment of 'suitability for the purpose' of the data.

Validation

Analytical data validation will be maintained through the application of approved techniques, adoption of uniform detection limits, and internal quality control, with an obligation to participate in regular interlaboratory analysis, eg AQUACHECK. The two main measures of quality are accuracy and precision.

Accuracy

Accuracy describes closeness to the true value, but in practical terms it reflects the agreement of values amongst the wider analytical community. Agreement can be established through participation in a control sample scheme, such as AQUACHECK. However, the operational frequency of such schemes is necessarily less than that of the sampling events and it will therefore be necessary to record all accuracy check results to confirm conformity, as well as recording any correction procedures which may be applied.

WAG Protocol

Example of an accuracy record

Element	SO_4^{2-}
Fraction measured	Dissolved
Results reported as (eg SO_4 as S)	S
Date of analysis	23-Jan-1993
Method	Ion chromatography
Laboratory	ITE Merlewood
Scheme	AQUACHECK
Within error threshold	Y
Result	1.23
Mean	1.34
Percentage relative error	+8.9%
Corrective measures	None

Individual laboratories should send all accuracy results relevant to ECN samples, in the categories shown above, to the ECN Database Manager in machine-readable form.

Precision

Precision control will be ensured by the use of synthetic solutions as quality control (QC) samples for assessment of possible batch bias. QC data should be reported to Site Managers with each set of sample results. Laboratories should not submit data if the QC values indicate that the procedures are functioning unacceptably.

Author   *A.P. Rowland*

WAG Protocol

ANALYTICAL GUIDELINES FOR WATER SAMPLES

APPENDIX 1

Quality Control Procedures for the Analysis of Water Samples within the ECN Terrestrial Network

A separate QC system is added for ECN participants to use for their purpose. Laboratories are encouraged to continue their independent assessment of QC to validate each batch of analyses and to join an accredited interlaboratory sample exchange scheme to test their performance independently. This approach replaces the requirement for occasional interlaboratory studies at a similar overall cost.

Assuming that all sites use the same solutions and procedure, there is an opportunity to compute between site correction factors. This protocol also offers the possibility of detecting rogue batches and detecting analytical trends over the long-term.

This additional measure will be managed by the analysts. Two concentrated solutions (one for cation analysis, one for anion analysis), prepared at Merlewood Research Station, will be distributed to site managers at the end of the year for use in the following calendar year.

Procedure

- accurately dilute 2ml of each concentrate to 200ml separately with deionised water (or 1ml to 100ml, as experience shows the amount of QC soln. required with each batch of samples). These solutions should be prepared by the analyst, just prior to analysis of the first determinand. A sub-sample of the cation solution should be immediately acidified to the same matrix as the acidified sub samples. There should be no need to filter the diluted QC solutions. Where pH and Conductivity measurements are routinely carried out by the ECN site manager rather than at the analytical laboratory, then a separate QC dilution will need be made by the site manager for this purpose.

- analyse the cation solution for cations and DOC, the anion solution for pH, conductivity, anions, ammonium, total N and total P, yielding one value for each determinand in a batch. Analyse the QC samples in an identical manner to the other solutions.

- a new concentrate will be prepared annually at Merlewood during December. In January in future years, analyse the QC solutions from the previous year together with the 'new' solution to provide a continuity check.

Data Transfer

The QC data should be submitted to the ECN CCU in the same format as for water samples, but with the solution preparation date substituted for sampling and filtration date fields, as indicated below. Note that there should be a <u>single</u> QC data record for each batch of samples, holding both the anion and cation results. The QC data records can be submitted in the same physical dataset as the samples.

The format of the data record should be in <u>free-format, comma-separated</u> and consist of the following variables, in the order given below:

	Variable	Units	Format/Storage precision
1	Measurement code:	2-char code	QC
2	Site ID:	2-digit code	e.g. 04 (Moor House)
3	Local QC sample code:	2-digit code	01
4	[1]Preparation date for QC solution to measure pH and Conductivity	Day-Month-Year	DD-MON-YYYY
5	Date of pH measurement:	Day-Month-Year	DD-MON-YYYY
6	Time of pH measurement:	(this field not relevant in QC context, please include only the colon separator :)	
7	[1]Preparation date for QC solution to measure rest of determinands	Day-Month-Year	DD-MON-YYYY
8	Date analysis complete	Day-Month-Year	DD-MON-YYYY
9	pH AQC Unstirred	pH scale	precision: 0.01
10	pH AQC Stirred	pH scale	precision: 0.01
11	pH	pH scale	precision: 0.01
12	Conductivity	μS/cm	precision: 0.1
13	Alkalinity	mg/l	
14	Na	mg/l	
15	K	mg/l	
16	Ca	mg/l	
17	Mg	mg/l	
18	Fe	mg/l	
19	Al	mg/l	3 significant figures
20	PO_4-P	mg/l	
21	NO_3-N	mg/l	
22	NH_4-N	mg/l	
23	Cl	mg/l	
24	SO_4-S	mg/l	
25	DOC	mg/l	
26	Total N	mg/l	
27	Quality code separator	1-character code	Q

Quality fields follow on if required:
28 onwards:

	Quality codes	3-fig codes	e.g. 506

Note[1]: Preparation date fields for two sets of QC solutions are necessary where ECN site managers perform pH and Conductivity locally. Where all analyses are performed together at the analytical lab using a single QC solution, simply repeat the preparation date in field 7 above.

Example Moor House QC record:

QC,04,01,16-Dec-1997,17-Dec-1997,:,20-Jan-1998,27-Jan-1998,4.06,3.94,4.33,91.6…..(etc)..0.095,Q,000

AP Rowland
C Woods
M Lane
(Revised) 6th August 1998