Standing Committee of Analysts

The Stability and Preservation of Drinking, Ground and Surface Water Samples 2018

Methods for the Examination of Waters and Associated Materials

November 2018

The Stability and Preservation of Drinking, Ground and Surface Water Samples

Methods for the Examination of Waters and Associated Materials

This book contains the method used to reach a consensus on a stability period for the determinands listed in three matrices of drinking water, ground water and surface water.

Whilst this booklet may report details of the materials actually used, this does not constitute an endorsement of these products but serves only as an illustrative example. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate methods in their own laboratories.

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About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments, soils (including contaminated land) and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials" and their continuing revision is the responsibility of the Standing Committee of Analysts (established 1972 by the Department of the Environment). At present, there are seven working groups, each responsible for one section or aspect of water quality analysis. They are

1 General principles of sampling and accuracy of results
2 Microbiological methods
3 Empirical, Inorganic and physical methods, Metals and metalloids
4 Solid substances
5 Organic impurities
6 Biological, biodegradability and inhibition methods
7 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will be notified to the technical press. If users wish to receive copies or advanced notice of forthcoming publications or obtain details of the index of methods then contact the Secretary on the SCA's web-page:- http://www.standingcommitteeofanalysts.co.uk/Contact.html

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary. Users should ensure they are aware of the most recent version they seek.

Rob Carter
Secretary
June 2017

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety. These should be consulted and be readily accessible to all analysts. Amongst such publications are; "Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory", 1992, produced by the Royal Society of Chemistry; "Guidelines for Microbiological Safety", 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and "Safety Precautions, Notes for Guidance" produced by the Public Health Laboratory Service. Another useful publication is "Good Laboratory Practice" produced by the Department of Health.

1 Introduction

This book has been produced to combine the data from across laboratories within the UK drinking water industry in order to supplement and enhance the stability times available in ISO 5667-3 [1]. This may, in some instances, also provide a robust alternative to 5667-3 where many of the stability times are listed as unvalidated or 'best practice'.

The water types included within this document are drinking water, ground water and surface water. The definitions of these water types, taken from the UKAS technical bulletin[2], can be found below.

Drinking water

Basic Definition: Water of sufficiently high quality (wholesome) that it can be consumed or used without risk of immediate or long term harm. Water that is free from disease-producing organisms, poisonous substances, chemical, biological, and radioactive contaminants which would make it unfit for human consumption.

Notes/Exceptions: Statutory Private and Public waters and operational samples both fall within this category. The relevant regulations will be referred to in the 'Standard specifications/Equipment/Techniques used' column of the Accreditation Schedule for example DWTS or The Natural Mineral Water, Spring Water and Bottled Drinking Water Regulations.

Examples:

- Regulatory Tap water
- Bottled Water
- Tanker/Bowser water
- Treated surface or ground waters

Ground Water

Basic Definition: Water that does not run off, and is not taken up by plants, but soaks down beneath the ground surface into soil pore spaces and ultimately into the fractures of rock formations (called an aquifer when it can yield a usable quantity of water). The term is not applied to water that is percolating or held in the top layers of the soil, but to that below the water table and is generally restricted to water that has been drawn up from aquifers.

Notes/Exceptions: Many drinking water companies use ground water as a source because it is generally quite clean as a consequence of its very slow transition into the aquifers, which can be a good mechanism for filtering out contamination.

Examples:

- Well water
- Borehole water
- Spring Water

Surface Water

Basic Definition: Water which is open to the atmosphere and subject to surface runoff. Water that runs across the top of soil or bedrock without infiltrating though either material. Generally, it is accepted to be water collected on the surface of the earth for example in rivers, streams, lakes, reservoirs or wetlands.

Whilst it would naturally include seas and oceans too, these are dealt with later in this document (saline water). This category also does not include waters used for recreational purposes (e.g. lakes) which are covered under the recreational water category of this document.

Note/Exceptions: If both surface and ground waters are validated as the source of drinking water the term raw waters may be used on accreditation schedules.

Examples:

- River water
- Lake/Open Reservoir water (Non Bathing)

2 References

1. **Water quality — Sampling** Part 3: Preservation and handling of water samples (ISO 5667-3)
2. UKAS water types technical bulletin **Guidance on Water Matrices Definitions for Sampling and Testing to ISO/IEC 17025** 06 June, 2014
3. DWI information letter 12/05
4. The Water Supply (Water Quality) Regulations 2016
5. Guidance on the implementation of the water supply (water quality) regulations 2016 in England and the water supply (water quality) regulations 2010 (as amended) in Wales
6. NS30 A Manual of Analytical Quality Control for the Water Industry (1989) M.J. Gardner, WRC
7. ISO/TS 13530:2009 Water quality -- Guidance on analytical quality control for chemical and physicochemical water analysis

A1 Methodology

The stability periods from 13 UK laboratories were gathered along with

a) Method Reference
b) Sample Matrix / Matrix Name
c) Matrix characteristics including hardness, pH, Total Organic Carbon and electrical Conductivity
d) Type of Container, including material, container colour and container cap
e) Storage Conditions (temp)
f) Preservative and / or dechlorinating agent
g) Spiked Sample or Natural Water (Used during trial)
h) Spiking level (where applicable)
i) Number of Replicates in trial

As part of the data gathering exercise laboratories also indicated whether the trial had been successful, or whether the trial had only been successful to a specific point. Where data is not provided in this book, for example metals (with the exception of mercury), this is due to no stability trial data being available. This is generally due to laboratories following 5667-3 information. All laboratories data that were used had been carried out using the guidance provided in DWI Information Letter 12/05[3] (see also Appendix 3) using the bias targets from the Water Supply Regulations[4] (see also Appendix 2).

The data outlined above was reviewed by a panel of industry experts to decide upon a common stability period for individual determinands for each water type where data was available. This decision process considered the different matrices characteristics together with other parameters such as preservative used and storage conditions.

Where a determinands stability was supported by only one laboratory's data this has been indicated in the table (see Appendix 1). Similarly, where a single laboratory's stability period was considered an 'outlier' in comparison to other laboratories data, this has also been indicated on the table. For example, if most laboratories data was between 14 to 21 days and showed no failure at a later point and one laboratory had obtained a stability of 37 days this has been highlighted to the user. This serves as an indicator to users that longer stability periods are possible but should be used with caution and verified on an individual basis. This approach was taken as the panel preferred to select the predominant and most robust value rather than simply accepting the longest stability period from the data available.

Where a determinands stability was supported by only one laboratory's data this has been indicated in the table (see Appendix 1) but has been produced using a robust statistical trial as outlined in this Bluebook. The characteristics of the sample matrix used in determining these stability times has been given in the table (see Appendix 1) which laboratories should compare to their own sample matrix characteristics and be able to justify use of the original laboratories data.

Laboratories looking to determine a longer stability than available in this book may also use the current data to provide the worst case matrix. For example, if ground water gave a stability of 4 days but surface and drinking water gave 7 days, stability testing may be carried out on ground water only as this has been shown to be the worst case scenario.

During the data review process, it was apparent that the variety of temperature ranges for storage of samples did not affect the stability period of the determinands assessed. These ranged from 1^{o}C to 8^{o}C and therefore any temperature within and including this range is

deemed acceptable when referencing stability periods within this blue book. Storage temperatures outside this range should have stability times verified by laboratories on an individual basis.

In addition laboratories have chosen different de-chlorinating agents typically, sodium thiosulphate and ascorbic acid were commonly used. Again, the data review process indicated that there was no difference in stability period obtained by the 13 laboratories and therefore users may de-chlorinate samples with either of these agents unless otherwise stated in the table. There were however, some key points to note with regards to specific preservative techniques and these have been highlighted in the table. The material of the bottle used is indicated in the table where there was a distinct single material. Where no material is specified this indicates that both plastic and glass were in use with no apparent difference between the two.

A2 Outcome

Following the review process, each determinands stability period was tabulated for the three water types (where available) and a spreadsheet with the aim of allowing users to filter, search and sort the data as required for review. It should be noted that the master copy entitled [The Stability and Preservation of Waters November 2018] and is held on the SCA website http://www.standingcommitteeofanalysts.co.uk. Once downloaded the accompanying spreadsheet should be considered an uncontrolled document.

A3 Future work

The stability of determinands may well change in the future as development in preservatives and analysis techniques occurs. The data within the table will be regularly updated via the SCA Inorganic and Organic committees as and when new data become available.

Appendix 1

Table of stability periods

This is held as a separate document and can be found by following this link: http://www.standingcommitteeofanalysts.co.uk.

7 Appendix 2

Targets for bias (taken from The Water Supply (Water Quality) Regulations 2016)

Parameters	Trueness % of prescribed concentration or value or specification
Aluminium	10
Ammonium	10
Antimony	25
Arsenic	10
Benzene	25
Benzo(a)pyrene	25
Boron	10
Bromate	25
Cadmium	10
Chloride	10
Chromium	10
Colour	10
Conductivity	10
Copper	10
Cyanide(i)	10
1,2-dichloroethane	25
Fluoride	10
Iron	10
Lead	10
Manganese	10
Mercury	20
Nickel	10
Nitrate	10
Nitrite	10
Pesticides and related products(ii)	25
Polycyclic aromatic hydrocarbons(iii)	25
Selenium	10
Sodium	10
Sulphate	10
Tetrachloroethene(iv)	25
Tetrachloromethane	20
Trichloroethene(iv)	25
Trihalomethanes Total(iii)	25
Turbidity(v)	10
Turbidity(vi)	25

(i) The method of analysis must determine total cyanide in all forms.
(ii) The performance characteristics apply to each individual pesticide and depends on the pesticide concerned.

(iii) The performance characteristics apply to the individual substances specified at 25% of the
parametric value in Part I of Table B in Schedule 1.
(iv) The performance characteristics apply to the individual substances specified at 50% of the
parametric value in Part I of Table B in Schedule 1.
(v) The performance characteristics apply to the prescribed value of 4 NTU.
(vi) The performance characteristics apply to the specification of 1 NTU for water leaving treatment works.

8 Appendix 3

Extract from DWI information letter 12/05

Specification of requirement

For regulatory analysis the appropriate target value is one half of the maximum permitted trueness error. For most parameters this is 5% of the value at the PCV. For many organic parameters it is 12.5%. Significance is at the two-sided 95% confidence level, and the power is set at 90%. Each sample matrix type of interest must be tested separately. The specification, design, calculation and interpretation given in this document are all derived from NS30 pages 113 to 120, 137 to 139 and 148.

Note: see table in Appendix 2 for the bias targets

Design of Trial

The trial should consist of spiking of a pre-determined number of samples to the PCV. All samples must be collected by filling a series of bottles from the same source (e.g. a single tap). The true concentrations of the parameter must show negligible variation from one sample to another. If filling a series of bottles directly from the tap may not yield such samples, a bulk sample should be taken which is then mixed and sub-divided into a series of bottles. Precision of spiking is of paramount importance and more important than the absolute value spiked. If precision of spiking is likely to cause problems, consideration should be given to spiking a bulk sample, which can then be sub-divided into a series of bottles.

One set of samples is analysed on day 0, with a further set analysed at each selected time interval with all sample preservation and storage conditions applied exactly as it is intended to apply them to regulatory samples. It would be prudent to also include times less than the full period desired for routine storage of samples in the trial. The estimated minimum number of samples (n) required to be analysed on each day of testing to show whether the change is significant is given below:

Standard deviation %PCV)	Number of samples to detect 12.5% change	Number of samples to detect 10% change	Number of samples to detect 5% change
1	2	2	2
2	2	2	5
3	2	3	10
4	3	7	17
5	5	**7** (mercury)	**26**
6	6	10	38
7	9	13	51
8	11	17	67
9	14	22	85
10	17	**26 (**tetrachloromethane)	104
11	21	32	126
12	24	38	150
12.5	**26**	41	163
38	38	59	234
20	67	104	416

These figures are minimum values of n for which the equation $(t_\alpha + t_\beta)\, s\sqrt{(2/n)} \leq \delta$ is true, where δ is the target change, subject to a minimum of 2 for a statistical comparison to be made. This indicates that the test will probably be sufficiently powerful to identify the target change as being a statistically significant difference. Figures in bold relate to the maximum permitted precision relevant to the maximum permitted change. These numbers are only estimates of the actual numbers required because the actual distribution of data will not be known until after the test is completed, and either more or fewer replicates may be needed in practice. Reasons for large deviations from the expected standard deviation should be investigated to determine if there is any reason for the unexpected change in performance, which may invalidate the trial. Large within batch variations can also lead to wrong conclusions being drawn. Prior to undertaking trials steps should be taken to ensure that between batch errors are not significant. The most common cause of significant between batch errors is variation in the true value of calibration standards. If it is not possible to reduce such errors to a magnitude which will not adversely affect the trial, means should be adopted to measure and compensate for such errors, such as those described in NS30 or DD ISO ENV 13530:1998

The same design can also be used to test alternative preservation and pre-treatment methods. In these cases, storage times should be the same and between batch errors can be eliminated by analysing both sets of samples in the same analytical batch.

Calculation

The significance of any observed difference is determined using a t-test. The following is an example calculation, with expected standard deviation of 2% and target change 5%

	Day zero	Day x
	101	94
	100.3	93.2
	98.8	92.9
	101.2	96.5
	99.9	92.8
Mean	100.225	94.05
Standard deviation	1.11	1.72
Pooled standard deviation	1.45	
Mean difference	6.175	
Standard Error (of differences)	1.024	
t statistic (calc)	6.032	
Degrees of freedom	6	
Critical value (.05) (from tables)	2.447	

Conclusion: there is a real difference between the means.

Interpretation

$t_{0.05}$ for 6 degrees of freedom = 2.447 (from tables). The observed value is greater than the tabulated value and therefore there is a real difference between the two means. The numerical value of the change is also greater than the target value and therefore there is a significant change.

If the observed value of t is greater than the tabulated value and the change was less than or equal to the target change, the change is less than (or equal to) the target and samples may be stored for up to the tested period under the conditions tested.

If the observed value of t is less than the tabulated value and the change was equal to or greater than the target change, the trial was not sufficiently powerful to show a significant change and must be repeated with more replicates.

If the change is less than the target change and the observed value of t was less than the tabulated value then, provided the trial was sufficiently powerful and would have identified any difference in excess of the target change as being significant, there has been no significant change and samples may be stored for up to the tested period under the conditions tested. The test is sufficiently powerful if the target change is substituted for mean difference in the formula for the t test and the value of t then calculated is greater than the tabulated value. If it is not greater then the trial was not sufficiently powerful to show a significant change and must be repeated with more replicates.
In summary:

Mean difference greater than target?	Observed t greater than tabulated value?	Would difference equal to target change have observed t greater than tabulated value?	Proposed new storage arrangements satisfactory?
Yes	Yes	N/A	No
Yes	No	N/A	No*
No	Yes	N/A	Yes
No	No	No	No*
No	No	Yes	Yes

* Trial not sufficiently powerful to test the original hypothesis. Repeat trial using more replicates.

Address for correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts at the address given below. In addition, if users wish to receive advance notice of forthcoming publications, please contact the Secretary.

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Drinking Water Inspectorate
Standing Committee of Analysts

Members assisting with these methods

Without the good will and support given by these individuals and their respective organisations SCA would not be able to continue and produce the highly valued and respected blue book methods.

Member	Organisation
Shagufta Banaras	Thames Water
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