THE DRINKING WATER INSPECTORATE

GUIDANCE ON CALIBRATION AND ANALYTICAL QUALITY CONTROL FOR RESIDUAL CHLORINE MEASUREMENTS

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1 Introduction

1.1 Water companies in England and Wales are required to analyse for residual chlorine in the water leaving water treatment works, in service reservoirs and at consumer's taps in accordance with the requirements set out in the Water Supply (Water Quality) Regulations 2000 in England and 2001 in Wales (the Regulations).

1.2 The Inspectorate accepts that residual chlorine measurements are usually carried out as field tests, which means that the analysis is unlikely to meet the stringent quality control requirements expected of a laboratory analysis. However companies must still meet the requirements of regulation 16(2)(e) in terms of having a suitable system of analytical quality control in place. This means that the company or its contract laboratory must be able to demonstrate that:

- the method used for measuring residual chlorine is fit for purpose (i.e. produces results of the required trueness, precision and limit of detection) and has been performance tested;
- the equipment used for the measurement is fit for purpose; and
- the equipment is calibrated and working correctly at the time each sample is analysed.

1.3 The Inspectorate issued Interim Guidance on the Regulations in September 2003. Appendix 1 of the Guidance looked at regulation 16 and the analysis of samples, including those parameters such as residual chlorine that do not have a prescribed concentration, and therefore do not have method performance criteria specified in regulation 16(5) . Section A8.6 of the Appendix provided the following guidance in relation to residual disinfectant measurements:

> Satisfactory target values for limit of detection, precision and trueness need to be set by the laboratory. This should be done on the basis of fitness for purpose. Unless the water company is able to demonstrate that less stringent targets are appropriate the target values given below will be regarded as describing fitness for purpose for these parameters.
>
> | | |
> |---|---|
> | Trueness | The greater of 10% of the result or 0.05 mg Cl/l |
> | Precision | The greater of 10% of the result or 0.05 mg Cl/l |
> | Limit of Detection | 0.05 mg Cl/l or the minimum concentration specified as either a target value or an action level at any of the water company's treatments works or in its distribution system, whichever is the lower concentration. |

1.4 In 2003 residual chlorine was selected as a parameter for the vertical audits of non microbiological parameters that were carried out for all companies. These audits were carried out on behalf of the Inspectorate by Dr Peter Whittle, Consultant. Dr Whittle

produced a summary report of his findings, which was issued in May 2004 under the cover of Information Letter 7/04. He concluded for the residual chlorine audits that:

> 'Overall, the analytical control of residual chlorine monitoring was very poor. Calibration checks on photometers ranged from annually to twice daily, with the majority of companies undertaking daily checks. Nine of the twenty-three companies audited had no form of quality control or performance monitoring, and only seven companies practised a suitable regime at a monthly frequency or more often. The current situation cannot be considered adequate given that disinfection is the primary means of protecting public health.
> However some companies have given the matter serious thought and have developed innovative approaches, particularly involving the use of chlorine solutions sent out on a 'blind' basis giving checks on both systems and samplers.'

Dr Whittle recommended that the Inspectorate should review the requirements and guidance for the measurement of residual chlorine and that further inspections for this parameter should be undertaken at an early opportunity.

1.5 This guidance is in response to Dr Whittle's recommendation. It is intended to provide further guidance on best operational practice and should be read in conjunction with Appendix 1 of the Guidance to the Regulations.

2 Equipment and methodology

2.1 Equipment and methods used for measuring residual chlorine should be performance tested. Only methods and equipment that, in combination, meet the performance requirements specified in paragraph 1.3 above can be regarded as fit for purpose.

2.2 Either comparators or spectrophotometers may be used. The practical requirements for these techniques are different, even though both generally rely on the same chemistry. However this guidance applies only to equipment used for routine analysis. Full quality control procedures are not expected to be in place for emergency back up systems, although back up equipment, including comparator discs, should be properly calibrated before use.

2.3 Where comparators are routinely used, the samplers should be checked for colour blindness. If a problem is identified then the sampler should be issued with a spectrophotometer.

2.4 The most appropriate methods are likely to make use of the DPD reaction and be based on either the SCA 'Blue Book' or BS.EN ISO methods. Calibration and analytical quality control (AQC) practice should be appropriate to the required level of performance. Companies or their contract laboratories may use alternative fit for purpose criteria provided they are demonstrably appropriate to all regulatory samples. Alternative analytical quality control measures may also be used provided equivalent or better control of all methods and analyses can be demonstrated.

2.5 One of the key purposes of analytical quality control is to identify deterioration in the condition or performance of equipment before the problem becomes acute. Examples of deficiencies that have resulted in a deterioration in performance include a gradual reduction in performance of spectrophotometers as the battery begins to fail, dirty or damaged comparator discs, and poor housekeeping over the cleanliness of glassware. When such deficiencies are identified, immediate corrective action should be taken.

3 Reagents

3.1 Between batch checks of reagents are not required if the company or its contract laboratory can demonstrate that, for bought-in reagents, all new batches of reagent are adequately quality controlled by the manufacturer. In addition there should be no deterioration in the quality of the reagent over the maximum permitted storage period. The company or its contract laboratory will need to obtain such data with each batch of reagents. Otherwise, each new batch of reagents should be checked before use against the old batch, preferably using a standardised chlorine solution or an iodate solution.

3.2 All reagents should be used before their expiry date, or discarded. Further checks on reagents prior to their expiry date should not be necessary provided they are stored in cool, dark conditions or as specified by the manufacturer. Reagents (tablets, solutions etc) should not be stored in samplers' vans for more than a few days before use.

4 Comparators (including Nesslerisers)

Calibration

4.1 Each individual disc must be calibrated and calibrated discs must be stored in the dark when not in use.

4.2 A full calibration of each disc should be carried out at least annually. This may either be carried out by an appropriately accredited calibrating house, or in-house using potassium iodate solutions. A suggested procedure for in-house calibration is given in Annex 1. If full calibration is undertaken by an external calibrating house, each calibration must be accompanied by a certificate of calibration, which is traceable via the calibrating house to national and international standards.

4.3 A full calibration should also be carried out if results of proficiency checks (see section 6 below) indicate that it is needed.

AQC and analytical issues

4.4 The purpose of AQC for comparator methods is to check the suitability of reagents and the sampler's technique. Daily AQC checks using a known standard solution do not generally generate meaningful data with comparators and, provided the annual calibration of the disc is satisfactory, regular checking of calibration is not necessary.

However, the condition of the individual discs should be visually checked daily before use.

5 Spectrophotometric methods

Calibration

5.1 A number of instruments are available for use in the laboratory and in the field. Full calibration should be carried out at least annually or at such greater frequency as is recommended by the instrument manufacturer. Full calibration should also be carried out following significant maintenance or if calibration checks, proficiency checks or AQC results indicate that it is needed. If full calibration is undertaken by an external calibrating house, each calibration must be accompanied by a certificate of calibration, which is traceable via the calibrating house to national and international standards.

5.2 A calibration check should be carried out at the beginning of each day of use, before any samples are analysed. Calibration checks can be carried out using permanent colour standards (which may be gel or glass). Each standard must have a current certificate of calibration, which is traceable via the calibrating house to national and international standards. It should also be stored in the dark or under such other conditions as the manufacturer specifies. All checks should be within the stated tolerance of the standard. Failure to meet this tolerance should trigger recalibration and, if necessary, maintenance before the instrument is used again for regulatory analysis.

5.3 If daily AQC samples are not analysed, a second calibration check should be carried out at the end of each day.

AQC and analytical issues

5.4 AQC is intended to check the instrument calibration, the reagents and sampler's technique.

5.5 Ideally an AQC sample should be analysed daily and this should not be done immediately after calibration or calibration check. If this is not possible or practical, a further calibration check should be carried out at the end of each day and any change recorded. A calibration drift over the day of more than 10% should result in immediate checking of performance using AQC solutions and/or withdrawal of the instrument from use. Consideration may also have to be given to re-sampling. Companies may wish to consider using calibration drift as a means of monitoring instrumental performance, with a view to taking proactive action at, for example, 5% drift. Where a daily AQC check is not carried out, each sampler should be required to analyse an AQC sample at least once a month.

5.6 Ideally a separate control chart (Shewhart chart), with statistically derived control limits should be maintained for each instrument. As an alternative to using individual charts, a common chart may be used for identical instruments provided separate records are kept of the AQC results for each instrument, and the individual instrument record is checked for problems whenever a warning limit is breached. The records should also be checked periodically for instrument bias. Companies using a variety of instruments must produce separate control limits for each model.

5.7 A stable chlorine solution is the preferred QC material, but it is recognized that there could be difficulties with maintaining satisfactory stability. An iodate solution is a satisfactory alternative. The alternatives listed in paragraph 6.2 can also be used as control solutions, but they will not be appropriate in all circumstances. However, provided the solutions are stable and standardised before use, and the data interpreted in a way which demonstrates that the performance criteria are being met by all instruments and samplers on a day-to-day basis, they can be acceptable ways of achieving satisfactory control.

5.8 Ideally rules for interpretation and action should be the same as those for other chemical analyses. However it is recognized that this is likely to be impractical. If control limits are correctly calculated, the likelihood of an action limit breach arising by chance is about 0.3%. Therefore an action limit breach should be taken as adequate evidence of an acute failure of the method or equipment. Such breaches should, in the absence of a demonstrable cause, result in immediate cessation of use of the instrument and rejection of the associated results.

5.9 Successive warning limit failures by an instrument are also indicative of failure, with similar probability of a false warning. However the evidence of acute failure is less certain. Therefore while such a failure should always result in immediate cessation of use of the instrument, given the difficulties of re-sampling the associated results may be accepted in the absence of other evidence of acute failure. In all cases instruments should not be returned to use until they have been demonstrated to be operating satisfactorily. The quality of reagents and technique of the sampler should also be investigated and appropriate remedial action taken, as necessary.

6 Proficiency checks

6.1 Equipment, reagents and samplers' techniques should be checked periodically by requiring samplers to test 'blind' solutions at three different concentrations within the range of concentrations of interest, plus a blank, presented in random order. Ideally this should be carried out quarterly either in-house, or using an external proficiency testing scheme. The Inspectorateis not currently aware of a scheme providing this service.

6.2 Alternatively a single 'blind' sample (covering over time a wide range of concentrations, including blanks) may be distributed to all samplers for testing once a month. Preferably standardised chlorine solutions should be used for the 'blind' tests,

although iodate solutions may be used. Alternatives such as permanganate solutions; iodine solutions; and fixed taps at water treatment works or service reservoirs with a stable residual chlorine could be used, but they will not be suitable in all circumstances. However, provided the solutions are stable and standardised before use, and the data interpreted in a way which demonstrates that the performance criteria are being met by all instruments and samplers, they can be acceptable ways of achieving satisfactory control.

6.3 The results of all 'blind' tests should be recorded and any 'flagged' results (ie results outside permitted limits) should be investigated. Where necessary remedial action, including refresher training, should be taken and the outcome noted. Deviations from the assigned value, or z-scores, should be plotted for each sampler to identify trends.

Annex 1

This is an example of an acceptable in-house procedure for calibrating a comparator disc in the range 0 to 1.0 mg Cl/l using potassium iodate solution. As an alternative to preparing a stock iodate solution, standard potassium iodate solutions are commercially available.

SCOPE; The method produces a coloured solution equivalent to a known concentration of total residual chlorine against which the comparator discs can be calibrated. The procedure is based on BS.EN ISO 7393-2:2000 and BS 6068: Section 2:26 1986.

REAGENTS AND EQUIPMENT:

Potassium Iodate Stock Solution: Dissolve 1.006 ± 0.0006 g of potassium iodate (AR dried at 120°C to constant weight) in about 250 ml water in a 1000 ml volumetric flask. Make up to the mark with water and mix.

Potassium Iodate Standard Solution: Pipette 10.0 ml of stock solution (2.1 above) into a 1000ml volumetric flask, add 1.0 ± 0.01g of potassium iodide and make up to the mark with water. Prepare the solution on the day of use.
1ml of this solution contains 10.06 µg of potassium iodate, equivalent to 0.141µmol or 10 µg chlorine.

1 molar Sulphuric acid: In a 1000ml volumetric flask containing about 800ml water, add 54±2 ml concentrated sulphuric acid (AR s.g. 1.84). Cool to room temperature and then make up to the mark with water.

2 molar Sodium Hydroxide: Weigh 80.O ± 0.5g of pellets and add to circa 800ml water in a 1000ml volumetric flask. When dissolved and cool make up to the mark with water.

Glassware: Ensure glassware is clean and chlorine demand free before use by filling with sodium hypochlorite solution (approx 0.1 g/L) and leaving to stand for one hour. Then rinse copiously with water before use

Class B volumetric glassware is suitable for this procedure.

METHOD:

In a series of 100ml volumetric flasks place increasing volumes of potassium iodate standard solution (2.2) to give concentrations of chlorine equivalent to the colour discs on the comparator (see table below).

Volume added to 100 ml flask	**mg/l chlorine equivalent**
10	1.0
8	0.8
6	0.6
4	0.4
2	0.2

Add 1 ml of sulphuric acid (2.3) to each flask, and after 1 ± 0.1 minute add 1 ml of sodium hydroxide (2.4) and dilute to the mark with water.

Take 10 ml of freshly prepared iodate solution and place in the comparator cell together with DPD no 1 tablet. Crush the tablet, mix and allow the colour to develop for 30 ± 3 seconds. Read the standard solution against the comparator disc and confirm that the colour intensity of the disc is correct at the concentration tested. Repeat for each colour disc on the comparator disc.
Record the results in the calibration record for the disc. Label the disc with either the date that the calibration was carried out or the date the next calibration is due.
Store the comparator disc in the dark when not in use.