



**Technical Guidance Note
(Monitoring)**

M18

Monitoring of discharges to water and sewer

**Environment Agency
Version 6
September 2017**

M18: Monitoring of discharges to water and sewer

Foreword

This Technical Guidance Note (TGN) is one of a series providing guidance to Environment Agency staff and monitoring contractors, industry and other parties interested in the monitoring of discharges¹ to water. It is also a technical reference for our Operator Monitoring Assessment (OMA).

It describes an overall approach to operator self-monitoring (OSM) for discharges to the water environment and provides guidance on the selection of analytical methods used for regulatory purposes. The approach is also applicable to discharges to sewer, although caveats are given in the text where discharges of difficult matrices may cause additional problems.

It contains:

- quality assurance and quality control requirements
- different approaches to sampling
- guidance on selection and validation of analytical methods
- reporting requirements
- an index of common monitoring methods

The best way to have confidence in the quality and integrity of self-monitoring discharge data is for operators to use and adhere to a management system approach. Operators carrying out their own monitoring should develop a documented management system to cover all aspects of sampling and analysis of discharges. This will be based on ISO/IEC 17025, supported by accreditation as appropriate to provide additional reassurance.

This TGN will be particularly useful for operators with installations falling under OSM, the Industrial Emissions Directive (IED) and the Urban Waste Water Treatment Regulations (UWWTR) (SI 94/2841).

¹ In this document the term discharge will be used to describe a release or emission of substances to the water environment, including sewers.

Record of amendments

| Version number | Date | Amendments |
|----------------|----------------|--|
| 1 | July 2004 | First published. |
| 2 | April 2009 | Throughout the document sections have been updated to reflect additional and amended MCERTS schemes(1.2, 2.4, 3.5.) Definitions of validation criteria moved to a glossary (Appendix 1) Section 4.1 amended to emphasise that alternative methods to those listed in the Appendix may be used. Rewrite and update of introduction Appendices covering method validation protocol (3) and performance requirements (2) removed, as better placed in the appropriate MCERTS performance standard. List of methods updated, glossary of terms created as Appendix 1. Sampling requirements now Appendix 2. |
| 3 | March 2012 | General – Document restructured, reordered and updated and some sections simplified, deleted or inserted, to reflect experience gained during OMA audits of operator self-monitoring. Section1 - Deleted section1.1 legislative requirements and moved section 2.1 to section 1.2 Section 1.2 concerning MCERTS renumbered section 2 and updated. Section 2 monitoring strategy renumbered section 3 and updated Expanded section on quality assurance (2.5), moved from sub section 2.5 to its own section 4 Sections on Sampling and laboratory analytical systems updated and renumbered 5 and 6. Table 2: examples of best practice in sample preservation added. Added new section 7 on continuous water monitors, reflecting their increased availability and robustness. Other sections updated and renumbered. Appendix 2 on sampling requirements removed as covered elsewhere, two new appendices added on laboratory method performance requirements (A2) and using quality control charts (A3). Index of monitoring methods (now A4) updated. |
| 4 | November 2014 | General – Update of legislation references, hyperlinks, references and formatting where appropriate. Appendix 4 monitoring methods and standards updated. |
| 5 | October 2016 | Additional section (9) and appendix (A5) on load and average calculations General update of method references and clarification of accreditation requirements. |
| 6 | September 2017 | Update and reorganisation of method index and rewrite of section 5.5 to clarify sample storage temperature requirements. |

Status of this guidance

This TGN may be subject to review and amendment following its publication. The latest version of the TGN can be found on our web site at: www.mcerts.net.

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1. Introduction

1.1 Scope

This TGN provides guidance on the monitoring of effluent discharges to the water environment. It is aimed at operators of industrial plants and their monitoring contractors, and Environment Agency permitting and regulatory officers. It covers:

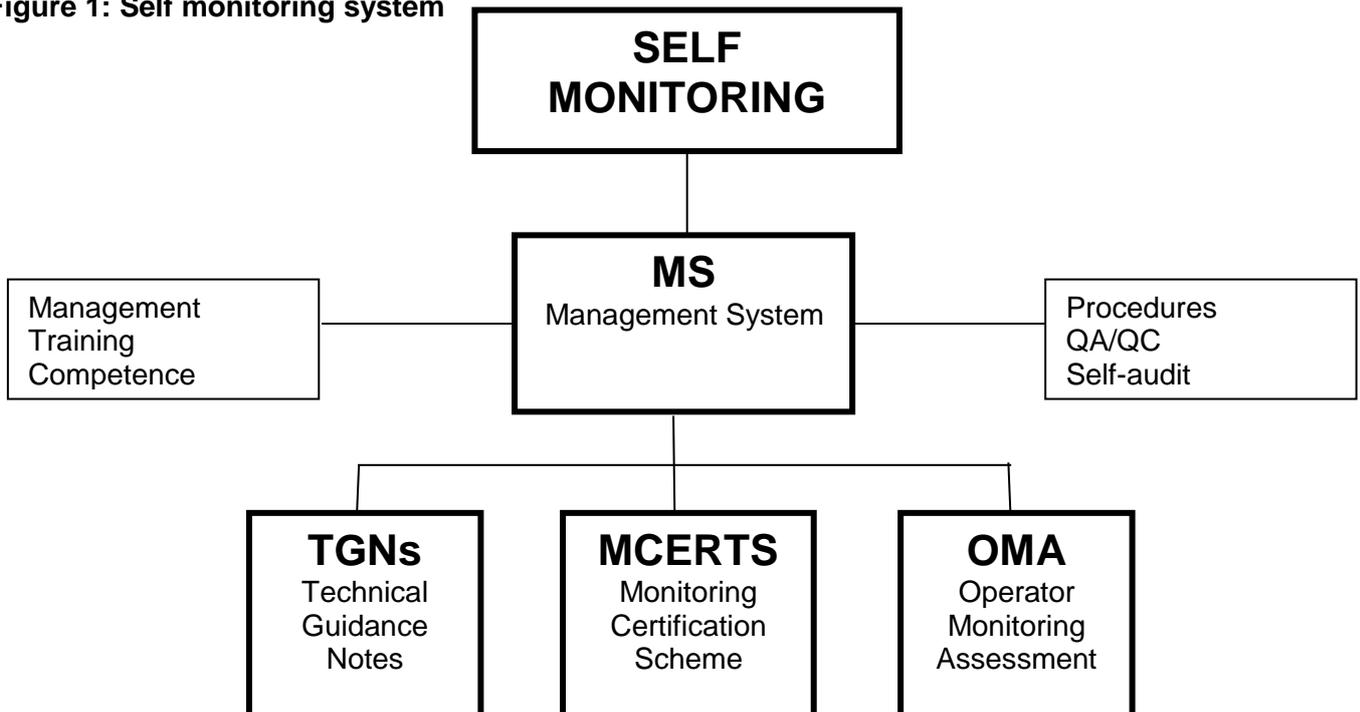
- management and quality assurance of monitoring activities
- the role of MCERTS
- sampling and sample collection
- laboratory analysis – selecting methods and quality control
- continuous and portable monitors/laboratory equipment – calibration and quality control
- what to look for when auditing (operator internal audits and our audits)

1.2 Operator self-monitoring

We must ensure that operator self-monitoring is performed correctly to an acceptable standard and to this end encourage operators to use and adhere to quality management systems. Operator self-monitoring is supported by a number of tools that give both regulator and regulated confidence in the accuracy and reliability of data (see Figure 1):

- Technical guidance notes, for example this document, provide a specification of the standards and procedures to be employed.
- The MCERTS scheme ensures that specific monitoring services and equipment are independently quality assured and therefore fit for purpose. MCERTS supports the requirements of EU Directives.
- The Operator Monitoring Assessment (OMA) scheme provides a consistent and transparent approach to the assessment of the management and performance of an operator’s monitoring arrangements, with a view to identifying areas that may require improvement.

Figure 1: Self monitoring system



2. MCERTS and discharges to water

MCERTS provides for the product certification of instruments, the competency certification of personnel and the accreditation of laboratories and on-site inspection in accordance with European and international standards. Some MCERTS applications are particularly relevant to the monitoring of discharges to water. These are:

a) 'Performance standard for organisations undertaking sampling and chemical testing of water: Part 1 - Sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents'

This scheme sets out what you must do if you carry out the sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents for sites regulated under OSM and IED, and have to send the results to the Environment Agency. Laboratories should be accredited to ISO 17025 for the MCERTS performance standard.

If an operator outsources monitoring to an external laboratory, we would expect that the laboratory holds appropriate accreditation for the analysis concerned.

b) 'Performance standards and test procedures for continuous water monitoring equipment'

This standard is in three parts:

Part 1 – 'Performance standards and test procedures for automatic water sampling equipment'

Part 2 – 'Performance standards and test procedures for on-line monitors'

This covers monitoring of: ammonia; COD; conductivity; dissolved oxygen; free cyanide; nitrates; orthophosphate; pH; temperature; TOC; total arsenic; total cadmium; total chlorine; total copper; total lead; total mercury; total nickel; total oxidised nitrogen; total phosphorus; turbidity

Part 3 – 'Performance standards and test procedures for water flowmeters' (See section 8 and d below for more details of the overall flow monitoring scheme)

c) 'Performance standards and test procedures for portable water monitoring equipment'

This covers monitoring of: ammonia; chlorophyll *a*; COD; conductivity; dissolved oxygen; free cyanide; nitrate; nitrite; orthophosphate; pH; temperature; total arsenic; total cadmium; total chlorine; total copper; total lead; total mercury; total nickel; turbidity

d) 'Minimum requirements for the self-monitoring of effluent flow'

The scheme sets the minimum standards that we require for operators that carry out self-monitoring of effluent flow. It also establishes a competency standard for independent MCERTS Inspectors who will inspect the operators' effluent flow monitoring arrangements.

Further information on these applications including copies of the performance standards, other guidance, and lists of certified instruments can be obtained from www.mcerts.net.

3. Monitoring strategy

3.1 Approaches to monitoring discharges

Monitoring can be conveniently classified into two types:

1) Periodic monitoring – In the context of discharges to water periodic monitoring usually occurs by removing a discrete sample from the effluent flow and sending the sample to a laboratory for analysis. Samples can be single spot samples or composite samples collected over a period of time, for example over 24 hours. This is discussed further in section 3. For a number of determinands portable instrumentation can be taken to the discharge site, examples are pH and dissolved oxygen measurements.

2) Continuous Water Monitoring systems (CWMs) – automatic measurements carried out continuously, with few if any gaps in the data produced. Measurement may be carried out *in situ* in the effluent flow or a sample taken from the effluent flow automatically to a permanently sited instrument. Continuous monitoring for certain determinands is specified in the IED². CWMs are often used to trigger alarms when permit limits are approached, so effluent can be diverted automatically to storage before the receiving water becomes polluted.

Some of the relative advantages and disadvantages of continuous and periodic monitoring are summarised in Table 1.

Table 1. Advantages and disadvantages of continuous monitoring and periodic monitoring approaches

| Characteristic | CWMs | Periodic monitoring |
|-----------------------------|--|--|
| Sampling period | Monitoring covers all or most of the period that substances are discharged | Snapshots of the long-term discharge profile |
| Speed of results generation | Almost always real-time output of results | Real-time results if portable instrumental analysers used; delayed results if laboratory end-method used |
| Stability | Sensors may be prone to fouling | Sample integrity needs to be maintained before analysis |
| Availability | Only available for a limited number of determinands | Comprehensive range of methods available |
| Applicability | May not be able to meet performance requirements at present | Methods that will meet the performance of most regulatory requirements are available |
| Reporting of results | Results continuously averaged over typically one hour or 24 hours | Results reported as daily average or instantaneous |
| Capital cost | Tends to be higher than equivalent periodic monitoring method, but long-term running costs should be considered. | Tends to be lower than equivalent CWMs |
| Certification of equipment | MCERTS product certification of equipment available for a number of determinands | MCERTS product certification of sampling equipment available Laboratory equipment use covered by ISO 17025 |
| Accreditation of monitoring | Not applicable | UKAS accreditation to MCERTS for ISO 17025 available for sampling and analysis |

3.2 Definition of substance to be measured

Before carrying out any monitoring it is essential to be able to define unambiguously the determinand to be measured in the discharge and also the accuracy of result required (see section 3.3). This will enable the selection of the most appropriate analytical system and its required performance characteristics in line with the regulatory requirements. If a third party

laboratory is used analytical requirements should be fully discussed before monitoring is started. For laboratories accredited to ISO 17025/MCERTS this will be part of the “contract review” procedure.

Substances may exist in various forms and a particular analytical method may not respond equally to all forms. The exact form to be determined should be carefully stated. Some examples are given below:

Dissolved, total or particulate - for metals and nutrients the dissolved portion of a sample is defined as that which will pass through a 0.45 micron membrane filter. Normally this filtration will take place immediately after sampling and the procedure employed should be fully documented (see section 3.4). Disposable single use filters can be used.

Total mercury - the method employed should be able to determine organo-mercury compounds as well as inorganic mercury, the effectiveness of sample digestion procedures to break down some compounds may need to be demonstrated.

Phosphorus - phosphorus can exist in various forms in the water environment, including orthophosphates, condensed phosphates and organophosphates. Recognised methods of analysis utilise an acid medium, as some of the condensed phosphates may be partially hydrolysed and labile organic phosphorus compounds broken down if present. It is therefore not possible to specify exactly the form of phosphorus being measured, so the term reactive phosphorus is employed. The fractions normally quoted are dissolved reactive phosphorus (sample filtered through 0.45 micron membrane), total reactive phosphorus (unfiltered sample) and total phosphorus (unfiltered sample pre-digested).

Phenols - individual phenols can be identified and determined chromatographically but a measure of the phenol content of a test sample can be obtained using the colorimetric phenol index method. Many common phenolic compounds will be detected by this method, but it is not equally sensitive to all. The system is calibrated using phenol itself, all other phenols will be determined as phenol, without regard to their relative sensitivity. The phenol index therefore only includes those phenolic compounds that can be determined under the specified conditions.

Groups or classes of determinand - some determinands are grouped into classes such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), which are large groups of chemicals and care must be taken to specify which individual species are to be monitored. Factors such as analytical response and harmfulness should be considered.

Non specific (empirical) methods - such methods should be carefully defined and applied, as the methods themselves define the determinand. An example is biochemical oxygen demand (BOD) where it is imperative to define length of test (5 days is normal) and whether or not allylthiourea (ATU) is to be added to suppress nitrification. Electrical conductivity is another example, the determination should be either made at a specified temperature or the measuring electrode must be temperature compensated to a standard value, usually 25°C.

3.3 Specification of analytical method performance

Analytical results are estimates of the true value or concentration. To ensure that results are fit for their intended purpose, we have set performance targets for analytical accuracy. For regulatory monitoring the results must show within acceptable limits of uncertainty that an operator is meeting the conditions of the permit. If errors are not known and under control, we will not be sure that permits are being complied with.

These performance targets are set in terms of both systematic errors (bias, trueness) and random errors (precision), and an up to date list can be found in the latest version of the MCERTS standard², and in Appendix 2 of this document. Initial estimates of precision and bias are calculated during method validation studies (see section 6). To obtain MCERTS accreditation a laboratory must not only show evidence of being able to achieve the performance for each determinand during method validation but must maintain the performance during routine operation. UKAS will check for continued compliance with MCERTS requirements during annual surveillance audits. However, in-house unaccredited laboratories should also meet these targets, and compliance will be assessed during OMA audits.

Some trade effluents and discharges to sewer may be more difficult to analyse due to the nature of the matrix, for example very high organic content, high solids etc. It may not be possible to attain the targets set in the MCERTS standard. If this situation arises, the actual analytical performance that can be obtained should be reported to us. We will then be able to decide if the reported result will allow proper assessment of compliance with permit, or whether further method development or even a change in analytical method is required.

4. Quality assurance

4.1 Management systems

The operator responsible for self-monitoring must ensure their management system covers all aspects of self-monitoring, including:

- management of self-monitoring
- sampling programme design
- sampling procedures (see section 5)
- analysis and reporting procedures (see section 6)
- staff training
- the process of audit and review of sampling and analysis operations
- addressing non-conformities

The system used should be fully documented, for example in a quality manual.

The use of a contractor for some or all aspects of sampling and analysis is acceptable. The contractor should be accredited to ISO 17025¹⁴ for the MCERTS standard, as appropriate. The operator will not require a quality system for those contracted parts but remains responsible for the overall quality of the results.

ISO 17025 is an international standard that specifies the general requirements for laboratories to demonstrate their technical competence. Laboratories are accredited to ISO 17025 by UKAS (United Kingdom Accreditation Service) for specified tests, to give independent recognition of competence to perform certain tests or calibrations. ISO 17025 is also the standard used to accredit sampling activities, and is not restricted to laboratories, so organisations that specialise in sampling may also gain accreditation.

ISO 17025 is clearly split into two major parts, management requirements and technical requirements. The management requirements are written to ensure laboratory management systems comply with ISO 9001.

²MCERTS Performance Standard for Organisations Undertaking Sampling and Chemical Testing of Water Part 1 - Sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents

As it only specifies requirements in general terms, ISO 17025 recognises that further explanations may be needed, elaborating on the general criteria to for specific fields of testing and calibration. MCERTS provides such an application for sampling and analysis of effluents.

4.2 Management

The quality manual must include a clear quality policy statement, endorsed by a senior executive. This should demonstrate the operators' commitment to quality. This policy must encompass all monitoring activities.

The person with overall responsibility for the self-monitoring quality policy (often termed quality manager) must be identified, as must the person or persons responsible for control and implementation of the self-monitoring process (technical management). Organisational charts must be available that includes defined lines of responsibility.

In order to preserve the independence of compliance monitoring, it is good practice that operation of the plant/process, wherever practical, is organisationally separate from sample scheduling and collection of samples. This is to promote independence of self monitoring from undue commercial pressures and influences. Appropriate evidence of such separation can be presented in the organisation's quality manual.

A clear document control system must be in place, to ensure only the latest versions of documents and procedures are in use. All documents and amendments to documents must be authorised.

The quality manual must contain a procedure to investigate complaints and anomalies regarding the self-monitoring process.

Records must be kept to provide an auditable trail from definition of sampling programme to results reporting.

4.3 Sampling programme design

The operator should set out a sampling schedule in advance of an assessment period, at frequencies stated in its permit. The schedule is usually annual on a calendar year basis, but this may not be suitable for batch processes or plants that operate seasonally. Best practice would include contingency arrangements for sampling event failures, for example malfunctioning autosamplers. The sampling schedule may need to be agreed with the Environment Agency in advance. Failure to comply with the agreed sampling schedule may lead to us taking enforcement action. However, in certain circumstances we will agree to a sampling event being rescheduled, due, for example, to adverse weather conditions or plant operational matters. For some regulatory regimes the Operator will need to report any missed samples within 24 hours of the scheduled event.

Sampling frequency will vary depending on the reason for sampling and the nature of the process being monitored.

4.4 Staff training

All staff involved in the self-monitoring process must be shown to be competent in carrying out their duties. Staff shall be trained in the necessary skills and a detailed record of training for

each individual must be maintained as part of the quality system. An appropriate trainer should sign off each documented procedure used by the staff. A programme of training updates should be detailed in the management system. Training records can include details of formal qualification, internal courses, instrument manufacturers training and in-house training.

4.5 Internal audit and review

The operator is required to carry out a series of audits of its management system. These should cover all aspects of the monitoring process and serve to verify that documented procedures are being adhered to. The audits should be pre-planned on an annual cycle, and, if possible, carried out by trained staff independent of the audited procedure. Audit findings and any corrective actions arising must be recorded, and follow up audits undertaken to ensure any corrective actions are effective.

A management review of the management system should take place at least annually. It should cover the results of internal audits and assessments by external bodies, and actions taken to correct non-conformances. It should also consider feedback or complaints from the Environment Agency and others. Details of management reviews should be recorded along with corrective actions taken.

Assessment of performance in interlaboratory proficiency tests and internal Analytical Quality Control (AQC) should be made, but this will not be required if a third party laboratory accredited to MCERTS/ISO 17025 is used. However, we may request information regarding a laboratory's performance in analytical quality control and participation in proficiency testing schemes.

4.6 Operator Monitoring Assessment (OMA) - Audit of Operators by the Environment Agency

A general assessment of the monitoring performance of an operator is made using the OMA scheme. This may include vertical audits of specific samples. This auditing scheme was developed to assess an operator's self monitoring arrangements and identify if any improvements are required. OMA covers:

- management, training and competence of personnel
- periodic and laboratory monitoring
- continuous monitoring
- quality assurance of monitoring

Guidance on what to expect in an audit and how to carry one out can be found at:

www.mcerts.net

5. Sampling

5.1 Choice of sampling point

Discharge sample points must be at a location that ensures that the sample is truly representative of the discharge.

- The sampling point location should be agreed with the Environment Agency, documented and clearly and permanently labelled.
- A sampling position in a pipe or channel must be sufficiently far downstream of the last inflow that mixing of the two streams is complete.

- Samples at an outfall should be taken from regions of high turbulence and good mixing, usually at the centre of the discharge. Solid materials will have little chance to settle out here.
- Samples in channels should be collected away from the sides and bottom of the channel to avoid contamination of the sample with sediment and biological growths.
- When sampling from chambers (for example manholes), avoid contamination of the sample by the disturbance of deposits from the cover when the cover is lifted and prevent contamination of the sample from the chamber walls and any bottom deposits.
- Samples may also be drawn off from effluent streams at a tap. Care should be taken to ensure any dead space is flushed out with effluent before the sample is collected.

Sampling staff should be aware that manholes and similar confined spaces are dangerous and must not be entered unless in accordance with a safe system of work and after appropriate training.

When automatic samplers are employed for composite sampling care should be taken to ensure the sample probe is deployed taking the above factors into consideration. Also it is important to ensure that the probe remains in the effluent flow during the entire period each sample aliquot is being taken i.e. variations in effluent flow should not result in the sample probe being left dangling in the air or in contact with the bottom of the channel.

Effluent may be discharged in batches from hold-up tanks, for example, discharge may only be permitted at high tides. Wherever possible, the tanks should be mixed, and in some cases, samples are taken from recirculation lines. If good mixing is not possible, it may be necessary to increase the frequency of sampling during discharge.

5.2 Composite or spot samples

There are two main sampling methods identified for wastewater, composite sampling and spot sampling:

Composite samples. Two types of composite sample are commonly used, flow-proportional and time-proportional. For a flow-proportional sample, a fixed amount of sample is taken for each pre-defined volume of effluent (for example every 10 m³). For time-proportional samples, a fixed amount of sample is taken from the effluent for each time unit (for example every hour). The analysis of a composite sample gives an average value of the determinand during the period over which the sample has been collected. It is normal to collect composite samples over 24 hours to give a daily mean value. Shorter times can be used with prior agreement from the Environment Agency.

Flow proportional sampling should be employed when the volume of effluent discharged varies significantly throughout the sampling period. When the volume of discharge is relatively constant then time proportional composites are appropriate.

Automatic sampling equipment is recommended (see section 5.3). However, it is necessary to consider the stability of the target substances over the total sample collection time, as samples may deteriorate while sitting in the automatic sampling device.

Spot samples. These are discrete samples taken at random time intervals from a discharge, and are not related to volume of discharge. They are best suited where:

- the composition of the waste water is relatively constant
- the discharge contains mineral oil or volatile substances, or when, due to decomposition, evaporation or coagulation, the target substances are not stable in the sample

- separate phases are present (for example an oil layer floating on water)
- there is a need to check the quality of the discharge at a particular moment, normally to assess compliance with the permit conditions
- the discharge is not continuous (from batch or hold-up tanks), but only when the effluent is well mixed
- collecting larger object and floating matter that is not representative of the discharge may be possible

Bulked composites. When a bulk sample is prepared by manually compositing a series of samples in a laboratory, it is important to consider the stability of the determinand being measured. For example, BOD will start to deteriorate significantly after 24 hours.

It may not be appropriate to collect composite samples for periods greater than 24 hours, due to the stability of some determinands, even when autosamplers are refrigerated. For example, BOD, pH, COD, VOCs and ammonia.

5.3 Automatic sampling equipment and MCERTS

We require that automatic sampling devices used for self-monitoring purposes have been tested and certified to the MCERTS performance standard:

‘Continuous Water Monitoring Equipment Part 1: Performance standards and conformity testing procedures for automatic wastewater sampling equipment’

This document and further information regarding the MCERTS scheme can be obtained at www.mcerts.net. A list of certified equipment is held by Sira Certification Services and can be accessed at www.siracertification.com/mcerts.

Note that the MCERTS standard only covers sampling from non-pressurised channels and vessels. Break tanks or other such devices may be installed to allow monitoring to take place.

5.4 Access, facilities and services

Access, facilities and services required for sampling will vary depending on the approach taken to monitoring, and the equipment used. However all require:

- a safe means of access to, and a safe place of work at the sampling position
- provision of shelter and weatherproofing of equipment
- space for the equipment and personnel
- essential services, for example, electricity and lighting

5.5 Sample bottles, storage and transportation

If preservation of samples by refrigeration is required, then during transportation of samples to the laboratory, including retention time in an automatic sampling device, the sample storage environment should maintain a temperature of between 1°C and 8°C. The average temperature over the period should be no more than 5°C. Ice packs, refrigerators or other appropriate methods may be used. An organisation carrying out sampling should have appropriate procedures for demonstrating this, for example using temperature loggers. It is recognised that some time may be required to bring the sample temperature to within this range during high ambient temperatures.

The temperature range is to allow for the cycling of the refrigeration devices, their opening and closing during normal operation, and effects of adding a number of warm samples.

Samples should be transported in sealed containers, which should be regularly cleaned and disinfected. Examination of the samples should be undertaken as soon as possible after collection. Every attempt should be made to start the examination within 24 hours of sample collection. Where logistics do not allow this, samples may be examined up to 48 hours after collection provided they are kept cool as above and in the dark.

When samples are stored at a laboratory, method specific storage requirements may need to be invoked, for example, laboratory storage temperatures may be 1 to 5°C. For most analytical purposes best practice is to keep the samples at a constant temperature of not more than 5 °C.

Sample containers should be appropriate for the determinand and analytical system employed. Wherever possible they should be supplied by the analysing laboratory. Sample containers should not be rinsed with sample before filling unless specified in the sampling procedures.

It is very important to take note of laboratory requirements regarding the filling of sample containers, for example, some test will require no air space be left after filling to stop loss of volatile components, while others need space left in the bottle to allow addition of extraction solvents when reaching the laboratory. Failure to carry out laboratory instructions on the use of sample bottles may lead to invalid analytical results. Laboratories accredited to ISO 17025 for an MCERTS standard should either reject improperly presented samples, or if the customer insists on analysing the samples then a disclaimer should accompany the results stating they may be invalid.

Where appropriate, add preservatives to ensure that there is no material change in the concentration of the determinands in question before analysis. Preservatives are often added to sample containers before they are dispatched from the laboratory, and these containers should not be rinsed. Some examples of best practice in storage and preservation are given in Table 2 below, and further guidance can be found in reference 16.

Table 2. Examples of best practice in sample preservation

| Determinand | Preservation | Notes |
|------------------|--|---|
| Ammonia (total) | Keep in the dark and cool at 5±3°C, target timescale for delivery to lab within 24hrs. | Samples with low concentrations should be analysed immediately. If acidified to pH 1 to 2 with sulfuric acid can be stored at < 5°C for 21 days. |
| BOD | Keep in the dark at 5±3°C, deliver to lab within 24hrs. | For best results start analysis within 24 hrs of sampling. If using a cooled composite sample, ensure analysis starts within 48 hrs of first aliquot. |
| COD | Keep in the dark, deliver to lab within 24hrs. | If unable to analyse immediately, stabilise with sulfuric acid to pH <2 and analyse within 6 months. |
| Cyanide | Sodium hydroxide, ensure pH >12 and keep cool in the dark. | Analyse within 14 days. |
| Sulfide | Sodium carbonate and zinc acetate. | Analyse within 7 days. |
| Suspended Solids | Cool to 5±3°C. | Analyse within 2 days of sampling. |

| | | |
|-----------------------------------|--|---|
| Mercury | Potassium dichromate and nitric acid. | Alternative preservation may be employed if specified in method. |
| Metals | If analysing dissolved fraction Immediate on-site filtration may be required. | Ensure that any material precipitated after filtration is re-dissolved in the laboratory. |
| Phenols by GC | Acidify with sulfuric acid to pH <4, use amber bottles. | Analyse within 21 days. |
| Phenols (colorimetric) | Phosphoric acid to pH <4. | Analyse within 21 days. |
| TOC | Acidify to pH 1 to 2 with sulfuric or phosphoric acid. Keep in the dark, at 5±3°C deliver to lab within 24hrs. | Analyse within 7 days. If samples can loses volatile components on acidification, then keep cooled and analyse immediately. |
| VOCs (volatile organic compounds) | Keep in the dark at 5±3°C at all times. Use appropriate sampling vials. | Analyse within 24hrs. Samples acidified to pH 1 to 2 with nitric or sulfuric acid, are stable for 7 days. |

5.6 Sampling procedures

Operators should fully document the procedures used in sampling, which should include:

- the precise location of the discharge, spot sampling point and automatic sampler installation as appropriate
- the sampling process
- the conditions of storage and transport of samples
- the types of bottles or containers and their closures
- the cleaning procedure for each type of bottle, container and closure
- details of any sample preservation measures
- calibration and maintenance of automatic samplers, timers and thermometers etc
- provision of records and information, including records of training of those who take the samples, and the automatic sampler installation and testing record
- actions to be taken in the event of automatic sampler failure
- procedure for notification of sampling event failure to Environment Agency
- quality assurance procedures for sampling activities

These procedures should be part of the management system and be made available to all staff that undertake sampling and if requested should be submitted to the Environment Agency for approval. The procedures should include examples of:

- the sampling event record sheets to be presented to the analysing laboratory
- sample results forms returned from the laboratory plus format of any computer generated data
- sampling staff training records
- calibration and maintenance records
- sample event failure reports

Having a well controlled sampling methodology is essential to ensure the contribution of sampling to the overall uncertainty budget is minimised.

5.7 Sampling quality control

The initial sampling process can make a substantial contribution to the overall uncertainty of a measurement result. The performance of field procedures can be verified for each batch of samples taken. Control samples should be taken and analysed with the batch of samples they are associated with.

The following types of control sample may be suitable:

- Blank samples - can be used to assess levels of contamination in the sampling process, and investigate contamination of different areas of the process, such as filtration or bottles.
- Spiked sample - a known quantity of a determinand standard solution is added to a sample. Can be used to assess different areas of the sampling process, such as sample bottles, pre-treatment (filtration, preservation), transport. Standards used for spiking the sample should be from a different source or lot number to that used for calibration.
- Duplicate samples - as far as practical, the entire sampling procedure is repeated and 2 separate samples are submitted to the laboratory for analysis.
- Reference materials/samples - can be used to carry out quality assurance checks on field instruments used for on-site tests.

To monitor the variation of sampling control samples, results should be recorded or plotted on control charts, see section 6.6 and Appendix 3. The data collected can be used as part of an estimate of sampling uncertainty.

6. Laboratory analysis

6.1 Choosing a method

Standard methods are developed by various national and international organisations. It has been suggested that choosing measurement methods published by the organisations listed below will form the foundation for better reliability and comparability:

- standard methods required by relevant EU Directives
- CEN standard for the relevant determinand
- ISO standards
- alternative methods, such as SCA blue books, in house methods, modified methods or test kits, with prior approval from the Environment Agency (extra requirements may be imposed)

However, the degree of validation detailed in standard methods is variable, especially with regard to the matrix the method is employed in. Therefore it is extremely important that the measuring method is evaluated to check that it is fit for purpose, and that the laboratory employing the method is itself able to verify any performance criteria that may be stated in the appropriate standard or specified by the Environment Agency, for example in an MCERTS standard. If the sample to be analysed is of a matrix that has not been the subject of suitable validation tests, then further tests will need to be carried out to ascertain the suitability of the method. We may require proof of method suitability and details of how matrix problems are addressed.

A list of CEN and ISO analytical methods is given in Appendix 4, and some alternatives in Appendix 5. The list is neither mandatory nor exhaustive, and other appropriate methods may be acceptable with satisfactory validation. CEN, ISO and British Standards can be obtained

from the British Standards Institute at www.bsi-global.com, SCA blue books can be obtained from the Environment Agency. ISO methods can also be obtained from www.iso.ch.

6.2 Laboratory equipment

Any equipment used in the analytical systems must be shown to be fit for purpose:

- Instrument operation instructions, calibration procedures and performance checks must be fully documented and available to users as part of the management system.
- Instrument performance checks and calibration procedures must be carried out at appropriate intervals and a record kept showing that calibration is maintained.
- All instruments must be correctly maintained and records of this maintenance are kept, whether or not carried out by a third party, such as the instrument manufacturer.
- Traceability of calibration of equipment such as balances, thermometers, timers, auto-pipettes, ovens, heating blocks etc. to national measurement standards must be demonstrated, and any corresponding certificates or other records must be available.
- Calibrated equipment must be clearly labelled and identified to the user.

6.3 Test kits

The majority of appropriate test kits involve colorimetric methods. They come in two main formats, those using visual comparators and those using portable or bench top spectrometers.

Generally, the use of visual comparators is not acceptable, as these systems are very dependent on the operator and environmental conditions. They often lack the accuracy required for assessing regulatory permits. If they are employed the users must demonstrate that they are fit for purpose.

Test kit methods using spectrometers have increased in sophistication and quality in recent years, and many are based on standard laboratory methods. Traceability of the data can be achieved due to electronic result storage capabilities.

Test kits offer some advantages as the methods may benefit from reagents being pre-packaged, ease and convenience of use, and built in calibration routines. However, they should undergo a full evaluation before use, ensuring appropriate performance characteristics and matrix suitability, and be treated the same as a standard method in terms of documentation and QA/QC procedures.

Test kits are employed for many determinands, COD, ammonia, phosphate and iron included. Comprehensive guidance to test kit usage is given in reference 19.

6.4 Validation

Analytical methods must be supported by the assessment of the following performance criteria, obtained in an appropriate matrix, to demonstrate that it is fit for purpose:

- selectivity and interference effects
- range of applicability
- linearity
- calibration and traceability
- bias (recovery)
- precision (repeatability, intermediate reproducibility)
- limit of detection (LOD)
- uncertainty estimates

These performance tests should be carried out before a method is put into routine use, but only when the analytical system has been optimised. If an analytical system is modified, it may be necessary to revalidate, for example when a piece of equipment is replaced. A typical protocol for validation is given in:

'MCERTS Performance standard for organisations undertaking sampling and chemical testing of water Part 1 - Sampling and chemical testing of untreated sewage, treated sewage effluents and trade effluents', which can be downloaded from www.mcerts.net

6.5 Methods and procedures

The measuring method must be fully documented and must include details of:

- scope/performance characteristics/estimate of uncertainty
- principles
- hazards and disposal of waste materials
- reagents and standards
- equipment
- sample collection, preservation and preparation
- calibration and procedure
- quality control
- calculation and reporting
- references

Detailed guidance can be obtained in references 4 and 17.

6.6 Quality control

Laboratories should have established and fully documented analytical quality control (AQC) procedures that should be part of its quality management system. These procedures must provide a continuing check on the day to day performance of analytical systems, and the laboratory must subscribe to an external proficiency scheme (where available and appropriate).

Internal quality control procedures relate to ensuring the quality of specific samples or batches of samples and may include:

- analysis of reference materials/measurement standards
- analysis of blind samples
- use of quality control samples and control charts
- analysis of blanks
- analysis of spiked samples
- analysis in replicate
- system suitability checks

As a minimum the use of Shewhart control charts is recommended for routine analysis of effluent and water samples, as they easily identify at a glance when an analytical system is out of statistical control.

A method is said to be in statistical control when the variability within the analytical system arises from a stable set of what can be considered as sources of random analytical variability. That is, the precision of the method fall within expected limits, a list of which can be found in

Appendix 2. These limits are those that must be achieved by MCERTS accredited laboratories, and give a good guide to what is achievable by a well run laboratory. These causes of variation can be assumed to be equally likely to result in analytical errors in a positive or negative direction and will affect all measurements. Loss of statistical control is characterised by the introduction of sources of systematic error (bias, trueness), or by a change in the size of the random error (precision) operating in the analytical method.

Laboratories must have fully documented procedures for actions to be taken when a system is identified as out of control. Records of breaches should be kept, and also of remedial measures taken. A procedure for re-evaluating and updating the control limits should also be present.

An example detailed procedure can be found in Appendix 3, and further information can be found in references 2, 3, 6, 7 and 8.

Proficiency Testing (PT) schemes are interlaboratory comparisons of analytical performance. They consist of a regular distribution of homogeneous samples to a number of participating laboratories. The concentration of target determinands in the samples should reflect the concentrations of determinands in permits and consents, but should not be known by participating laboratories. The matrix of test samples should be as near as possible to that analysed by participating laboratories. The results of the analysis are statistically evaluated and give an assessment of the analytical performance of participants. Again laboratories should have a fully documented procedure, including methods for investigating and recording actions taken when poor performance occurs.

Examples of PT schemes, which are designed to comply with BS EN ISO/IEC 17043⁹ can be seen on the following websites:

www.lgc.co.uk/, www.eptis.bam.de

6.7 Measurement uncertainty

Measurement uncertainty is the range of values, within which the true value of an analytical result lies, with a specified level of confidence. Every measurement has an uncertainty associated with it, resulting from errors arising in the various stages of sampling and analysis and from imperfect knowledge of factors affecting the result. For measurements to be fit for purpose some knowledge of these errors is required. The Environment Agency may request a statement of the uncertainty associated with a reported result.

Two general approaches are used to estimate measurement uncertainty:

In the first approach all individual sources of uncertainty must be identified and listed. Sources include random and systematic errors, volumetric equipment, balances and weights, calibration, sample pre-treatment, temperature effects and interferences. Each independent contribution should be estimated. Some data will be available, some may be available from literature (certificates, equipment specifications etc.), and some may require further experimental studies. This approach may lead to an underestimate of measurement uncertainty, as it is difficult to assign all causes or an overestimate, as it is difficult to be sure all identified contributions of uncertainty are fully independent.

The second approach is probably more appropriate for routine analysis of discharges. Measurement uncertainty is estimated using an overall estimate of precision obtained from validation studies and long term AQC data (intermediate reproducibility). Again all possible sources of uncertainty should be considered. It may be necessary to incorporate a contribution to uncertainty from bias (recovery) measurements, sample homogeneity, matrix, concentration etc. If a source of uncertainty is identified and found to be inherently accounted

for in precision and bias studies uncertainty may not require further evaluation. For example, if data is drawn from a whole year then the variations in the laboratories environmental temperature will be adequately represented and if a variety of different volumetric apparatus has been used their effects on calibration etc. will be taken into account.

Bias (recovery) is usually studied by analysing certified reference materials or spiked samples during method validation and/or longer-term evaluation. Every effort should be made to eliminate or reduce the bias effect. Bias needs only to be included in estimates of uncertainty if it is considered to be significant. If an analytical procedure is considered empirical, then bias need only be evaluated for laboratory performance, and not for the method, as the result obtained is defined by the method applied, and depends solely on it.

Once all the important sources of uncertainty have been identified and estimated they should be converted to standard uncertainties, which are expressed as standard deviation. If based on single measurements then intermediate reproducibility data is usually already a standard deviation, but if based on replicate determinations then standard deviation of the mean should be calculated.

Individual standard uncertainties should then be used to calculate the combined standard uncertainty using an appropriate method. These methods are fully discussed in the references below.

Uncertainty should be expressed as an expanded uncertainty, by multiplying the combined uncertainty by a coverage factor (k), which is derived from student t values. This gives an appropriate level of confidence to the uncertainty estimation. It is envisaged that a value for k of 2 will be used, giving a 95% confidence in most cases. This will not be true when the combined degrees of freedom of the estimate is small, but this situation should not arise.

Results should be reported in the form $R \pm U$, where R is the result and U is the expanded uncertainty. If k has a different value than 2 then it needs to be stated with the result.

Further details and worked examples can be found in references 5, 10, 11, 12, and 18.

6.8 Collection and reporting of data

The routine test report must contain the following information:

- name and address of laboratory where analysis took place
- a reference to the method or standard used
- any deviations from the standard used, or options employed
- full identification of the sample, including date and time taken, date and time received
- the results of the determinations and expanded uncertainties if requested
- any factors which may have affected the results including recovery factors

6.9 Electronic data reporting

The results of self-monitoring may be reported in an electronic format. For example, the Generic Operator Returns (GOR) which is a web based portal, the file format required by the system is XML. Full traceability is required.

7. Continuous water monitors

Many of the topics covered in section 5 for sampling and section 6 for laboratory analytical methods apply to CWMs.

7.1 Location of sensor

This can be in situ, directly in the effluent flow, or remote from the effluent flow with sample pumped to it. When positioning the sensor and/or the sample intake section 5.1 applies.

Access, facilities and services mentioned in section 5.4 apply, and provision should be made for cleaning of sampling pipes and tubes where necessary.

7.2 Type of CWM

Method employed by the CWM must be appropriate in terms of the exact determinand specified in the permit, and measured by an appropriate technique. Some examples are given below. Instruments with MCERTS certification should be employed where available and suitable for the application.

- direct electrochemical, for example pH, DO, conductivity
- specific ion electrodes, for example nitrate and ammonia
- metals, for example anodic stripping voltammetry
- colorimetric (spectrometry), for example ammonia, phosphate, total phosphorus, iron
- TOC
- turbidity

7.3 Calibration and maintenance

Regular calibration and maintenance of CWMs is vital to ensure that monitoring data of an appropriate quality is produced with minimum data loss from breakdowns.

CWMs should be installed, commissioned and validated by their manufacturers or manufacturers' agents.

Maintenance procedures should be documented and carried out as per manufacturers instructions and recommended frequencies. Major servicing is best carried out by manufacturers or specialist companies. Suitably trained staff can undertake interim (daily, weekly) calibration and maintenance checks.

A written schedule of maintenance and calibration tasks should be followed, and records of all maintenance and calibration activities should be kept.

An appropriate quantity of spare parts and consumables should be held on site to ensure the CWM is in continuous operation. A call out contract is recommended for emergency repairs.

8. Flow measurement

The uncertainties associated with flow measurement can have a significant effect on the calculation of emission loads. Small fluctuations in flow measurements can lead to large differences in load calculations.

Two MCERTS standards cover the inspection of effluent flow monitoring arrangements including the monitoring installations and the associated quality assurance systems. The standards are:

‘Minimum requirements for the self-monitoring of effluent flow’ - this specifies our requirements for permit holders to measure the flow of sewage and/or trade effluent discharging to controlled waters or public sewer. It also includes the relevant quality systems and the collection/reporting of monitoring data.

‘Competency Standard for MCERTS inspectors – effluent flow monitoring’ – this specifies the competency standard required for independent technical specialists who will undertake the assessment process on behalf of the consent holder.

The scheme operates as follows:

- MCERTS Inspectors are appointed by CSA Group (as Sira Certification Service) who operate this scheme on our behalf. The scheme is delivered through a number of companies operating in a commercially competitive market. Operators place a contract with one of the companies employing MCERTS Inspectors. Details of companies employing MCERTS Inspectors can be found via the MCERTS Self monitoring of effluent flow web page.
- A total daily volume target of better than +/- 8% uncertainty for effluent flow monitoring systems has been set. MCERTS Inspectors will check this during their inspection. This uncertainty target covers the whole monitoring system, not just the performance of the flow meter. For example, deviations in construction of V-notch weirs and other installation issues.
- Following the inspection, the MCERTS Inspector prepares a report, including a recommendation based on their expert opinion as to whether the flow monitoring arrangements meet the MCERTS requirements. This includes an assessment of the flow application, type of flow measurement device and maintenance.
- The QMS (quality management system) for flow monitoring also needs to be assessed. The assessment is performed by a UKAS accredited Certification Body that has MCERTS for flow included in its scope. This can be Sira or an Operators existing ISO 9000/14001 auditor if they have appropriate accreditation.
- Sira will then check the MCERTS Inspector's report and the QMS auditor's report. If the MCERTS requirements are met they will issue an MCERTS Site Conformity Inspection Certificate, valid for five years.
- An annual QMS surveillance visit is also required by the QMS auditor. The frequency may be reduced once it can be demonstrated to the Auditor that the QMS is able to guarantee performance.

Operators are also required to use MCERTS certified flow meters. Meters that comply with the requirements of the MCERTS performance standard for flow meters are capable of producing results of the required quality and reliability, when operated within the MCERTS flow scheme.

Detailed guidance on what is expected can be found in the MCERTS standard “Minimum requirements for the self-monitoring of effluent flow”, via www.mcerts.net. Additional guidance can be found in MCERTS bulletins at www.siracertification.com/mcerts

9. Calculating results as averages and specific load

9.1 Averages from continuous and periodic measurements

For continuous monitoring, averages may be required to be calculated at different time periods, for example one hour, two hours or 24 hours, depending on sector requirements. The same time period should be used for averaging the results of the flow measurements.

Where flow-proportional composite samples are collected for periodic monitoring, results are already representative averages, as the sampling method already considers the flow. This is the preferred sampling method for estimation average and load.

Time-proportional composite samples are not suitable when a single composite sample is collected for the period, as there will be no relation to flow, unless the flow is constant. If discrete samples are collected (say hourly samples over 24-hours) additional calculations can be made to relate to the flow at the time of the sample to be representative of the discharge of a pollutant for a specific time period. Total discharge volume for each time interval must be calculated.

To calculate a representative concentration over a longer time period, the individual measurement results need to be averaged and weighted by the related waste water flow:

$$C_w = \frac{\sum_{i=1}^n c_i q_i}{\sum_{i=1}^n q_i} \quad \text{Equation 9.1}$$

Where C_w = flow weighted average concentration of determinand

n = number of measuring periods

c_i = average concentration of determinand during i^{th} measurement period

q_i = average flow rate during i^{th} measurement period

For a yearly average concentration based on 24-hour flow-proportional composite samples, the measurement result of each 24-hour flow-proportional composite sample obtained during the observed year has to be multiplied with the corresponding daily average flow, summed up and divided by the sum of all daily average flows.

9.2 Specific load

A monthly or yearly average load based on a daily measurement frequency can be calculated using the following equation:

$$l_{\text{specific}} = \frac{\sum_{i=1}^n \frac{c_i q_i}{p_i}}{n} \quad \text{Equation 9.2}$$

where l_{specific} = average specific load of the parameter

M18: Monitoring of discharges to water and sewer

- n = number of measurement periods
- c_i = average concentration of determinand during i^{th} measurement period
- q_i = average flow rate during i^{th} measurement period
- p_i = production output during i^{th} measurement period (or raw material consumed)

If a limit is given as a specific yearly load based on 24-hour flow proportional composite sampling, the measurement result of each 24-hour flow proportional composite sample obtained during the year is multiplied with the corresponding daily flow and then divided by the daily production output to calculate the specific daily load. The specific daily loads are summed up and divided by the number of measurements to calculate the specific load for the year. The same approach can be taken for monthly loads.

The calculation of specific loads based on a measurement frequency less than daily can be done in a similar way, but it needs to be ensured that the measurement results are representative for the examined time period. However, the average should be reported as an average over the samples obtained during the period, to avoid any confusion.

See appendix 5 for some example calculations.

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Appendix 1: Glossary of terms

Bias and Recovery

Bias is the systematic error of an analytical system and can be expressed as the difference between the mean of a significant number of determinations and the true or accepted value. Certified reference materials can be useful here, but are not always available. Sources of bias include sample instability, interference and matrix effects, calibration, blanks and inability to recover all forms of the defined determinand.

Recovery tests using real samples are carried out to estimate bias from some sources. A sample is spiked with a known amount of a determinand, portions of sample and spiked sample are analysed a number of times (11 batches of 2 duplicates is typically used, which will guarantee 10 degrees of freedom), and the percentage of spiked determinand recovered is calculated:

$$\text{Recovery (spiked samples)} = \frac{(S(V+W) - UV)}{CW} \times 100 \%$$

where: U = measured conc. in unspiked sample
 S = measured conc. in spiked sample
 C = conc. of spiking solution
 W = volume of spiking solution added
 V = volume of sample to which spike is added

Recovery or bias for general and metals determinations is usually acceptable where the true mean recovery lies between 95% and 105% with 95% confidence, or 90% to 110% for organic determinands. Outside of this, it may be necessary to correct results, for example with trace organic analysis. The correction factors applied should be reported with the results.

Calibration and traceability

Calibration is the process that relates the output from an analytical system to the concentration of the substance being measured. Usually a series of standards of known concentration that are prepared from or relate to the substance being measured, are subjected to the analytical procedure. The output from the analytical system can then be related to the concentration of the substance being measured, for example by use of a calibration curve.

Most laboratory analytical procedures rely at some stage on measurements of such properties as weight, volume, temperature and time, for example volumetric flasks, analytical balances that are used to weigh out materials to prepare calibration standards, thermometers, etc. All such devices should be calibrated.

All calibrations should be documented and traceable to national or international reference standards, through an unbroken chain of comparisons with known uncertainties.

Linearity

Ideally, an analytical system will, within the working range, respond with a test result that is directly proportional to the concentration of the determinand being measured. This is easily checked by measuring a blank and range of standards (minimum 6) spread evenly across the calibration range and plotting a calibration curve, which can be inspected for outliers and general shape. Regression coefficients can then be calculated. If the response is non-linear then it may be possible to employ a suitable non-linear calibration function.

Limit of Detection (LOD)

A key aspect of monitoring is the limit of detection (LOD) of an analytical system; because the uncertainty associated with a measurement increases the closer the result is to the LOD.

Good analytical practice dictates that the LOD of a method should not exceed 10% of the concentration of interest, which is usually the emission limit defined in the permit. This should not be confused with the working range of the method, as an LOD can often be below 1% of the analytical system's range of applicability. The estimation of the LOD required provides a guide for the selection of an appropriate method and helps minimise the uncertainty associated with a measurement result that is close to the emission limit.

Several methods of calculating the LOD are in use, the most appropriate for discharges is a statistically based approach. LOD can be defined as the concentration at which 95% probability of detection of the determinand occurs, which gives a suitably small probability of failing to detect.

Precision

Precision is the distribution of a number of repeated determinations, expressed as the standard deviation of results. It estimates errors of a random nature. Total standard deviation is calculated from a combination of within analytical batch and between analytical batch standard deviations and is measured under a number of conditions:

Under repeatability conditions, a sample is analysed by the same method, equipment, laboratory and analyst within a short time interval. This is precision data that would be produced during method validation studies, and would be used to derive internal quality control charts. Typically, 11 batches of two duplicates is used, in order to guarantee 10 degrees of freedom. An in-house or intermediate reproducibility condition is where the method has been put into routine use, has been used by a variety of analysts using different equipment over a longer time and would reflect variations caused by environmental condition (for example laboratory temperature).

Precision may vary across the concentration range, and should be tested at a minimum of two different concentrations, one of these should be at the level of interest, such as the permit limit. Laboratories often use 20% and 80% of the highest concentration determined by the method.

Range of applicability (working range)

This is the range of concentration that the method has been shown to provide analytical results of the required accuracy and precision.

Selectivity and interference effects (matrix effects)

Ensure that the method not only measures the determinand specified, but that the measurement is not affected by the presence of other chemical species in the sample. This is achieved by analysing standards with a range of potential interferences added at varying concentrations, which should include the highest possible concentration that may be found in the sample. As the extent of interference may depend on determinand concentration, study at least two different concentrations of determinand.

Appendix 2: Performance characteristics of analytical methods

| | precision ¹ | bias ² | | precision ¹ | bias ² |
|------------------------|------------------------|-------------------|---|------------------------|-------------------|
| Aluminium | 5 | 10 | Fluoride | 5 | 10 |
| Antimony | 7.5 | 10 | Formaldehyde | 5 | 10 |
| Arsenic | 7.5 | 10 | Nitrite nitrogen | 5 | 10 |
| Beryllium | 5 | 10 | Nitrogen total oxidised | 5 | 10 |
| Boron | 5 | 10 | Nitrogen kjeldahl | 5 | 10 |
| Cadmium | 5 | 10 | Nitrogen total | 5 | 10 |
| Chromium | 5 | 10 | pH | 0.2 | 0.2 |
| Chromium (VI) | 5 | 10 | Phosphorus total | 5 | 10 |
| Cobalt | 5 | 10 | Phosphate | 5 | 10 |
| Copper | 5 | 10 | Sulfide | 7.5 | 10 |
| Iron | 5 | 10 | Sulfate | 5 | 10 |
| Lead | 5 | 10 | Suspended solids (105°C) | 7.5 | 10 |
| Manganese | 5 | 10 | Turbidity | 5 | 10 |
| Mercury | 7.5 | 10 | Acid herbicides ³ | 15 | 20 |
| molybdenum | 5 | 10 | Alcohols/Ketones | 10 | 15 |
| Nickel | 5 | 10 | Hexachloro-1,3-butadiene | 15 | 20 |
| Selenium | 7.5 | 10 | Hydrocarbon oils(IR) | 10 | 12.5 |
| Silver | 7.5 | 10 | Nitroaromatics ³ | 15 | 20 |
| Thallium | 5 | 10 | Nonyl phenols ³ | 15 | 20 |
| Tin | 5 | 10 | Organochlorine compounds ³ | 15 | 20 |
| Titanium | 5 | 10 | Organophosphorus compounds ³ | 15 | 25 |
| Vanadium | 5 | 10 | Organotin compounds ³ | 15 | 20 |
| Zinc | 5 | 10 | Phenols ³ | 15 | 20 |
| Alkalinity (to pH 4.5) | 5 | 10 | Phenols Monohydric colorimetric | 6 | 10 |
| Ammonia | 5 | 10 | Polyaromatic hydrocarbons ³ | 15 | 20 |
| BOD | 10 | 10 | Polychlorinated biphenyls ³ | 15 | 20 |
| COD | 5 | 10 | Volatile organic compounds ³ | 15 | 20 |
| Chloride | 5 | 10 | Pyrethroids ³ | 15 | 20 |
| Chlorine (all forms) | 10 | 10 | Triazines ³ | 15 | 20 |
| Cyanide(all forms) | 5 | 10 | Urons/carbamates ³ | 15 | 20 |

1. Precision expressed as percent relative standard deviation, except pH, which is in pH units.

2. Bias expressed in percentage terms, except pH which is in pH units

3. Performance targets are for individual compounds within these groups. If a total (for example total PAH) result is requested, then each individual component should be determined and reported with the total.

Appendix 3: Preparing and interpreting simple AQC charts

A3.1 Introduction

Having verified or validated the appropriate performance criteria for an analytical method, on-going performance must be monitored for the following reasons:

- To demonstrate that the method performance maintained in a statistically controlled manner.
- To identify at an early stage any changes (especially deterioration) in method performance.
- So this performance can be verified historically (i.e. records are kept).
- To enable aspects of measurement uncertainty to be estimated.

These objectives can be fulfilled by monitoring on-going precision and trueness (bias) by using control charts.

The performance of each analytical method should be verified for each batch of samples analysed. Control samples should be run within the analytical batch they have been prepared with.

A3.2 Laboratory Control (AQC) Samples

Best practice dictates that laboratory control samples should be incorporated into each analytical batch, but a lower frequency could be appropriate (say weekly) if a small number of samples are being measured each day. Laboratory control samples should be traceable, and can be certified reference materials, in-house reference materials, spiked effluents or aqueous standards.

At least one blank sample per batch should be taken through the entire analytical method. A result above the normal method reporting limit would show evidence of contamination which should be investigated and may require analysis of the entire batch of samples to be repeated. Laboratories should have written procedures that prescribe and justify the way blank samples are utilised.

A3.3 Treatment of results for Laboratory Control Samples

The interpretation of results from the analysis of internal Laboratory Control Samples is usually carried out by the use of control charts. They compare the current results against limits set after estimating the variability of an analytical system, while under statistical control. A method is said to be in statistical control when the variability within the analytical system arises from a stable set of what can be considered as sources of random analytical variability. Various forms of control chart may be appropriate for use:

- Shewhart charts – Probably the most common in use
- Cusum charts – more sensitive to bias detection than Shewhart charts
- zone control chart (J-Chart) – Combines Shewhart and Cusum charts capabilities

As a minimum, a Shewhart chart should be used, as described below.

A3.4 Setting Up and Updating Control Charts

Control charts should be set up using estimates of mean (M) and standard deviation (sd) obtained from results of at least 20 control samples analysed obtained when the analytical

system is under statistical control. This data can initially have been obtained during method validation procedures. As more data are obtained, it should be incorporated into the estimates of M and sd , until 60 to 100 data points have been used, depending on frequency of analysis. The precision and bias should ideally not be greater than the targets given in Appendix 2 for a given determinand. As a general rule, the following performance standards should never be exceeded:

| | |
|------------|--|
| Metals | – 5% RSD (relative standard deviation) |
| Inorganics | – 10% RSD |
| Organics | – 15% RSD |

If required, statistical significance tests are applied, which are described in the MCERTS Performance Standard for Organisations Undertaking Sampling and Chemical Testing of Water.

A senior member of staff should review charts on a regular basis. The timescale will depend on frequency and nature of analysis, but at least monthly.

At least annually, mean and standard deviation should be estimated from new data. If any of the data points have breached the control rules and a definite cause can be assigned, then the data points shall not be used. However, since some results, which are part of the normal distribution, will breach even the 'action' limits, then these should be used where no specific reason for the breach could be assigned.

The new values should be tested to see if any significant change in precision (expressed as standard deviation) has occurred, using an F test at the 95% confidence level. A student's t test, again at the 95% confidence level, should be used to see if the mean has changed significantly.

If a statistically significant change has occurred, then the new values are used in the control rules, and new control lines should be drawn on control charts. If no significant changes are detected then no changes should be made.

All significant changes should be investigated, even if precision and bias are still within the targets set.

A3.5 Control Rules and Failure Investigation

Rules should be set to indicate whether the analytical method is in control. A laboratory should have documented procedures that define loss of statistical control and procedures to specify actions to be taken when control limits are breached. All breaches should be investigated, and the findings and actions should be recorded. It is required that samples in an analytical batch where AQC samples breach the control rules be reanalysed.

The investigation should include at least the following:

- check for changes in concentration of stock standard solutions and reagents and that all are in date
- check calibration of all instruments used in the analytical process
- check methods were followed as written
- check that system suitability check data meets requirements
- check that no significant drift has occurred for automated runs
- check service/faults log

Records should include:

- identification of control sample and all associated sample results
- control limits in force at time of breach and breach result
- investigation details, conclusions and actions taken
- what happened to the sample results

A3.6 Reporting

Results associated with failed QC samples should not be reported. However In some circumstances, (for example where it may be impossible to repeat the sampling or analysis), their may be no alternative. Whenever results associated with failed QC are reported should only be issued under the direct authority of an appropriate manager, and with agreement with the Agency.

Any report issued, which contains results associated with failed QC must include a note to identify the result.

A3.7 Example: Shewhart Chart

The results of repeat analysis of a single sample should be normally distributed around the mean. In the unlikely event that this is not the case then the Shewhart control chart is not appropriate.

Given the availability of sufficient QC data produced when the method of analysis is in a statistically controlled state, comparison with on-going results will show whether the data continue to comply with fitness for purpose or departs from expected values. Onset of drift can also be promptly detected.

Statistical analysis of the 60 or more previous results produced while the method was in control gives a standard deviation (sd) and mean (M).

The properties of the Normal Distribution allow the prediction that for on-going analysis, 95% of results will fall within ± 2 times sd and that 99.7% of results will fall within ± 3 times sd of the mean (M), given no deterioration in method performance.

An example is shown in Figure 1. The chart is constructed as follows:

The y-axis is concentration, the x-axis time (date of analysis)

The Mean AQC Standard value **M** is plotted as a line ("mean")

2 Warning Limits are plotted as lines at $\mathbf{M} \pm 2 \times \mathbf{sd}$ ("2SD")

2 Action limits are plotted as lines at $\mathbf{M} \pm 3 \times \mathbf{sd}$ ("3SD")

The AQC Standard nominal value may be plotted as a line ("value").

As AQC results become available, they are plotted individually and consecutively against time. They shall not be averaged before plotting.

Control rules to indicate a system failure should include:

- 1 QC result outside a control chart action limit
- 2 consecutive QC results outside a control chart warning limit.

In addition, 9 successive QC results on the same side of the chart mean could indicate a change in the trueness (bias) of the analytical system, and should be investigated.

However, this may be due to a small insignificant change, laboratories should use other methods of identifying significant changes in bias.

Appendix 4: Index of CEN and ISO monitoring methods

General determinands

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|--|--|----------------------------|---|-------------------------------------|------------------------------------|
| Ammonia See also BS ISO 15923-1 on page 34 | Water quality. Determination of ammonium nitrogen by flow analysis (CFA and FIA) and spectrometric detection | BS EN ISO 11732 | LOD and range can be varied by different instrument configuration. | 0.1 - 1 mg/l | 0.1 - 10 mg/l |
| | Method for the determination of ammonium: manual spectrometric method | BS 6068-2.11 ISO 7150-1 | Many laboratories use an automated version of this method employing a discrete analyser (BS ISO 15923 – 1). | 0.01 mg/l | 0 - 0.5 mg/l |
| | | | | 0.03 mg/l | 0 - 50 mg/l |
| | Water quality. Determination of ammonium-Distillation and titration method | BS 6068-2.7 ISO 5664 | | 0.2 mg/l | 0 -10 mg/l extended by dilution |
| Water quality. Determination of ammonium-Potentiometric method | BS 6068-2.10 ISO 6778 | | 0.2 mg/l | 0 - 50 mg/l extended by dilution | |

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|---|---|------------------|--|--------------|-----------------|
| BOD | Determination of biochemical oxygen demand after n days (BOD _n) –Part 1: Dilution and seeding method with allylthiourea addition | BS EN 1899-1 | Procedures for 5 and 7 day incubation periods are presented. In the UK the 5 day test is normal. | 3 mg/l O | 0 - 6000 mg/l O |
| | Determination of biochemical oxygen demand after n days (BOD _n) –Part 2: Method for undiluted samples | BS EN 1899-2 | Procedures for 5 and 7 day incubation periods are presented. In the UK the 5 day test is normal. | 0.5 mg/l O | 0.5 - 6 mg/l O |
| Chloride See also BS ISO 15923-1 on p34 | Water quality: Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection | BS EN ISO 15682 | Range and LOD depends on configuration of the analyser. | 1 – 10 mg/l | Up to 1000 mg/l |
| Chlorine | Water quality. Determination of free chlorine and total chlorine. Iodometric titration method for the determination of total chlorine | BS EN ISO 7393-3 | | | 0.7-15 mg/l |
| | Water quality. Determination of free chlorine and total chlorine. Colorimetric method using N,N-diethyl-1,4-phenylenediamine for routine control purposes | BS EN ISO 7393-2 | | 0.05 mg/l | 0.03-5 mg/l |
| | Water quality. Determination of free chlorine and total chlorine. Titrimetric method using N,N-diethyl-1,4-phenylenediamine | BS EN ISO 7393-1 | | 0.05 mg/l | 0.03-5 mg/l |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|---------------------|---|----------------------------------|---|--------------|---------------------------------------|
| COD | Water quality. Physical, chemical and biochemical methods. Method for the determination of the chemical oxygen demand | BS 6068-2.34 Same as ISO 6060 | If chloride concentration in the sample is >1000mg/l then it should be diluted until it is below. This will effect the limit of detection that can be quoted. | 30 mg/l O | 30 - 700 mg/l O, extended by dilution |
| | Water quality. Determination of the chemical oxygen demand index (ST-COD). Small-scale sealed-tube method | BS ISO 15705 | If chloride concentration in the sample is >1000mg/l then it should be diluted until it is below. This will effect the limit of detection that can be quoted. | 6–15 mg/l O | 0 -1000 mg/l O extended by dilution |
| Conductivity | Water quality. Method for the determination of electrical conductivity | BS EN 27888 ISO 7888 | | | |
| Cyanide | Water quality. Determination of total cyanide and free cyanide using flow analysis (FIA and CFA). Method using flow injection analysis (FIA) | BS EN ISO 14403-1 | | | 20-200 µg/l Can extend by dilution |
| | Water quality. Determination of total cyanide and free cyanide using flow analysis (FIA and CFA). Method using continuous flow analysis (CFA) | BS EN ISO 14403-2 | Free CN results by EN ISO 14403-1 are not equivalent | | 10-100 µg/l Can extend by dilution |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|---|--|-------------------------|--|-----------------------------------|--|
| Cyanide | Water quality. Determination of available free cyanide (pH 6) using flow injection analysis (FIA), gas-diffusion and amperometric detection | BS ISO 17690 | | | 5-500 µg/l |
| Nitrate, nitrite and TON See also BS ISO 15923 – 1 and BS EN ISO 10304-1 on page 34 | Water quality. Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection | BS EN ISO 13395 | | TON 0.2mg/l NO2 0.01mg/l | 0 - 20 mg/l 0 - 1 mg/l can be varied |
| | Water quality. Determination of nitrite: Molecular absorption spectrometric method | BS EN 26777 ISO 6777 | | 0.002 mg/l | 0 - 0.25 mg/l |
| Nitrogen (Total) | Water quality. Determination of nitrogen. Method using oxidative digestion with peroxodisulfate | BS EN ISO 11905-1 | Will not oxidised all organonitrogen compounds completely, will not adequately recover some common compounds found in crude sewage such as creatinine. | 0.02 mg/l | 0 - 5 mg/l, extended by dilution. |
| | Water quality. Determination of nitrogen - Determination of bound nitrogen (TNb), following oxidation to nitrogen oxides | BS EN 12260 | As above | typically 0.5mg/l | 1 - 200mg/l |
| | Water quality. Determination of total nitrogen after UV digestion. Method using flow analysis (CFA and FIA) and spectrometric detection | BS ISO 29441 | | | 0 – 20mg/l |

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|--|---|-------------------|--|--|--|
| Orthophosphate and total phosphorus | Water quality. Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) —Part 1: Method by flow injection analysis (FIA) | BS EN ISO 15681-1 | Method recommends manual digestion procedure for total phosphorus using ISO 6878. | Ortho P 0.01 mg/l Total P 0.1 mg/l | Ortho P 0.01 - 1.0 mg/l Total P 0.1 - 10 mg/l. |
| | Water quality. Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) —Part 2: Method by continuous flow analysis(CFA) | BS EN ISO 15681-2 | Method includes digestion procedure for total phosphorus using an integrated UV digestion and hydrolysis unit alternatively suggests manual method using ISO 6878. | Ortho P 0.01 mg/l Total P 0.1 mg/l | Ortho P 0.01 - 1.0 mg/l Total P 0.1 - 10 mg/l. . |
| | Water quality, Determination of phosphorus. Ammonium molybdate spectrometric method See also BS ISO 15923 – 1 on page 34 For total phosphorus, see also BS EN ISO 11885 – page 38 | BS EN ISO 6878 | | | |
| pH | Water quality. Physical, chemical and biochemical methods. Determination of pH | BS ISO 10523 | Covers laboratory and on-line instruments. | | |
| Suspended Solids | Water quality. Determination of suspended solids. Method by filtration through glass fibre filters | BS EN 872 | Method does not specify filter size and filter type, UK practice is to use a Whatman GF/C paper or equivalent. | 2 mg/l | |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|---|--|-------------------|---|----------------------|--|
| A selection of anions by ion chromatography | Water quality. Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate | BS EN ISO 10304-1 | | | Up to 20 mg/l or up to 50 mg/l depending on anion. |
| | Part 3: Determination of chromate, iodide, sulfite, thiocyanate, thiosulfate | BS EN ISO 10304-3 | | | Up to 50 mg/l |
| A selection of inorganic parameters by discrete analyser | Water quality. Determination of selected parameters by discrete analysis systems. Part 1: Ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate and silicate with photometric detection | BS ISO 15923-1 | This method is favoured by high throughput laboratories as it carries out multiple colorimetric determinations simultaneously. The individual methods for each determinand usually follow a standard. | | |
| Sulfate | See BS ISO 15923 – 1 and EN ISO 10304-1 on this page | | | | |
| TOC and DOC | Water analysis. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC) | BS EN 1484 | Results obtained will be influenced by instrument dependant considerations.. | Instrument dependant | Up to 1000 mg/l |
| Turbidity | Water quality. Determination of turbidity | BS EN ISO 7027-1 | | | 0 -40 FNU |

Trace Metals

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|----------------|---|-------------------------|---|----------------------------------|-------------------------------------|
| Arsenic | Water quality. Determination of Arsenic. Atomic absorption spectrometric method (hydride technique) | BS EN ISO 11969: | WITHDRAWN: replaced by 17378-2 | | |
| | Water quality. Determination of arsenic and antimony. Method using hydride generation atomic fluorescence spectrometry (HG-AFS) | BS ISO 17378 -1 | Will need to be fully validated for waste water | | 0.02 -100 µg/l |
| | Water quality. Determination of arsenic and antimony. Method using hydride generation atomic absorption spectrometry (HG-AAS) | BS ISO 17378 -2 | Will need to be fully validated for waste water | | 0.5-20 µg/l |
| | Water quality. Determination of total arsenic: Silver diethyldithiocarbamate spectrophotometric method | BS EN 26595 ISO 6595 | Extra digestion step required if effluent likely to contain silicon fluoride or difficult to decompose organic arsenic compounds. | | 1- 100 µg/l |
| Cadmium | Water quality. Determination of cadmium by atomic absorption spectrometry | BS EN ISO 5961 | Two methods given, flame atomic absorption spectrometry (FAAS) and electrothermal atomisation atomic absorption spectrometry (EAAAS). | FAAS 0.05 mg/l EAAAS 0.3 µg/l | FAAS 0.05-1mg/l EAAAS 0.3-3 µg/l |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|--------------------|---|---------------------------|---|--------------|---------------------------------------|
| Chromium | Water quality. Determination of chromium. Atomic absorption spectrometric methods | BS EN 1233 | Two methods given, flame atomic absorption spectrometry (FAAS) and electrothermal atomisation atomic absorption spectrometry (EAAAS). | | FAAS 0.5-20 mg/l EAAAS 5-100 µg/l |
| Chromium VI | Water quality. Determination of chromium (VI). Spectrometric method using 1,5-diphenylcarbazide | BS 6068-2.47 ISO 11083 | Susceptible to interference, sample to be analysed as soon as possible after sampling. | | 0.05-30mg/l |
| | Water quality. Determination of chromium (VI). Photometric method for weakly contaminated water | BS EN ISO 18412 | For weakly contaminated waters | | |
| | Water quality. Determination of Chromium (VI). Method using flow analysis (FIA and CFA) and spectrometric detection | BS EN ISO 23913 | Best for large numbers of samples. Samples may be stored for a maximum of 24 h at 2 °C to 5 °C. | | 20 to 2000 µg/l flow system dependent |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|-----------------|---|-------------------|---|--------------|----------------|
| Mercury | Water quality. Determination of mercury | BS EN 1483 | WITHDRAWN: replaced by 12846 | | |
| | Water quality. Determination of mercury. Enrichment methods by amalgamation | BS EN 12338 | WITHDRAWN: replaced by 12846 | | |
| | Water quality. Determination of mercury — Method using atomic absorption spectrometry (AAS) with and without enrichment | BS EN 12846 | | | 0.01-1 µg/l |
| | Water quality. Determination of mercury, method using a combined preservation and digestion step followed by atomic fluorescence spectrometry | BS EN ISO 17852 | Highly sensitive method that may require an additional digestion step for wastewater samples. | 1-10ng/l | 0.01 - 10µg/l |
| Selenium | Water quality. Determination of selenium. Method using hydride generation atomic fluorescence spectrometry (HG-AFS) | PD ISO/TS 17379-1 | | | 0.02-100 µg/l |
| | Water quality. Determination of selenium. Method using hydride generation atomic absorption spectrometry (HGAAS) | PD ISO/TS 17379-2 | | | 0.5-20 µg/l |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|---|---|--|--|--------------------------------------|--|
| <p>Trace metals (Multi determinand methods)</p> | <p>Water quality. Determination of selected elements by inductively coupled plasma optical emission spectroscopy (ICPOES)</p> <p>Water quality. Application of inductively coupled plasma mass spectrometry (ICP-MS)— Part 1: General guidelines and basic principles</p> <p>Water quality. Application of inductively coupled plasma mass spectrometry (ICP-MS) —Part 2: Determination of 62 elements</p> <p>Water quality. Determination of trace elements using atomic absorption spectrometry with graphite furnace</p> | <p>BS EN ISO 11885</p> <p>BS EN ISO 17294-1</p> <p>BS EN ISO 17294-2</p> <p>BS EN ISO 15586*</p> | <p>ICPOES is also known as ICPAES. LOD may not be adequate for some elements, for example Cadmium and arsenic. Will be the method of choice at many laboratories.</p> <p>Very low detection limits possible</p> <p>Method covers Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, and Zn. Validation data limited on wastewaters for some elements.</p> <p>*This method tends not be used for routine samples due to low throughput but is acceptable.</p> | <p>0.1 - 10µg/l in clean samples</p> | <p>linear over several orders of magnitude</p> |

Organics

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|--|--|-----------------|---|--------------|---------------------|
| Acid herbicides | Water quality. Determination of selected phenoxyalkanoic herbicides, including bentazones and hydroxybenzonnitriles by gas chromatography and mass spectrometry after solid phase extraction and derivatization. | BS EN ISO 15913 | Not tested on effluents LOD and range depends on linear range of calibration curve, and instrument used. | | |
| AOX | Water quality. Determination of adsorbable organically bound halogens (AOX) | BS EN ISO 9562 | | | |
| Chlorophenols | Water quality. Gas chromatographic determination of some selected chlorophenols in water | BS EN 12673 | Includes pentachlorophenol. | | 0.1 µg/l - 1mg/l |
| Complexing agents (EDTA, NTA, etc.) | Water quality. Determination of six complexing agents. Gas-chromatographic method | BS EN ISO 16588 | Includes EDTA, NTA, DTPA, MGDA, β-ADA, 1,3 - PDTA | | 0.5 µg/l – 200 µg/l |
| Dioxins/Furans | Water quality. Determination of tetra to octa-chlorinated dioxins and furans —Method using isotope dilution HRGC/HRMS | BS ISO 18073 | LOD and range very dependant on interference levels in the sample. | | |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|------------------------------------|---|------------------|---|---|----------------|
| Dioxin-like PCBs | Water quality. Determination of dioxin-like polychlorinated Biphenyls. Method using gas-chromatography/mass spectrometry | BS ISO 17858 | | | |
| Hydrocarbon Oil index | Water quality. Determination of hydrocarbon oil index — Method using solvent extraction and gas chromatography | BS EN ISO 9377-2 | The total peak area between <i>n</i> -decane and <i>n</i> -tetracontane is measured. The concentration of mineral oil is quantified against an external standard consisting of two specified mineral oils, and the hydrocarbon oil index is calculated. | | Above 0.1mg/l |
| Organochlorine compounds | Water quality. Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes — Gas chromatographic method after liquid-liquid extraction | BS EN ISO 6468 | May not be suitable for samples with high suspended solids (>50 mg/l). | 1 - 50ng/l with waters of low organic content | |
| Organotin compounds | Water quality. Determination of selected organotin compounds. Gas chromatographic method | BS EN ISO 17353 | | | |
| Organo-phosphorus compounds | Water quality. Determination of parathion, parathion-ethyl and some other organophosphorus compounds in water by dichloromethane extraction and gas chromatographic analysis | BS EN 12918 | | | up to 1µg/l |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|--|---|-----------------|--|---|----------------|
| Organic nitrogen and phosphorus compounds | Water quality. Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods | BS EN ISO 10695 | Atrazine, Fenpropimorph, Dimethoate, Vinclozolin, Metolachlor, Isochloridazon, Metazachlor, Simazine have been tested. Samples should contain <50 mg/l suspended solids. | 0.5µg/l or 0.05µg/l depending on extraction | |
| Nonylphenols | Water quality. Determination of individual isomers of nonylphenols. Methods using solid phase extraction (SPE) and gas chromatography / mass spectrometry (GC/MS) | BS ISO 24293 | | 0.1µg/l | 0.1 - 50µg/l |
| PAH | Water quality. Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction | BS EN ISO 17993 | No performance data for effluents. Can be modified for determining PAH in wastewater, and for other PAHs. Will need validating when modified | | |
| | Water quality. Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water. Method using gas chromatography with mass spectrometric detection (GC-MS) | BS ISO 28540 | As above. | | |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|------------------------|--|--------------------------|--|--------------------|---|
| PFOS & PFOA | Water quality. Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry | BS ISO 25101 | If used for wastewaters will need to be matrix validated. | | 2 - 10000 µg/l PFOS 10 - 10000 µg/l PFOA |
| Phenol Index | Water quality. Determination of phenol index by flow analysis (FIA and CFA) | BS EN ISO 14402 | Relative response of the method to substituted phenols depends on their molecular structure and is usually less than response for phenol itself. Hence the term phenol index, results reported as mg/l phenol. | | 0.01 - 1mg/l |
| Phenol Index | Water quality. Physical, chemical and biochemical methods Determination of phenol index: 4-aminoantipyrine (4-aminophenazone) spectrometric methods after distillation | BS 6068-2.12 ISO 6439 | Two methods presented. Relative response of the method to substituted phenols depends on their molecular structure and is usually less than response for phenol itself. Hence the term phenol index, results reported as mg/l phenol. | 0.1 or 0.01mg/l | |
| Phthalates | Water quality. Determination of selected phthalates using gas chromatography/mass spectrometry | BS EN ISO 18856 | | | 0.02-0.15 µg/l |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Standard method | Comments | Reported LOD | Reported Range |
|--|---|-----------------|--|---|-------------------------|
| Volatile halogenated hydrocarbons | Water quality. Determination of highly volatile halogenated hydrocarbons. Gas-chromatographic methods | BS EN ISO 10301 | Highly volatile halogenated hydrocarbons are defined as fluorinated, chlorinated, brominated and/or iodinated mainly nonaromatic hydrocarbons composed of one to six atoms of carbon, whose boiling points generally fall within the range of 20 °C to 220 °C. | | |
| VOCs | Water quality. Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption | BS EN ISO 15680 | | Typically 10µg/l, depends on detector used and matrix | Typically up to 100µg/l |

Appendix 5: Index of some alternative monitoring methods

| Determinand | Title | Method | Comments | Reported LOD | Reported Range |
|--|--|--------------------------------------|--|--------------|--------------------------------------|
| Ammonia | Ammonia in Waters 1981 | SCA blue book 48 ISBN 0117516139 | Several suitable methods presented. LOD and range can be varied by different instrument configuration. | 0.5 mg/l | 0 0 - 40 mg/l |
| BOD | 5 Day Biochemical Oxygen Demand (BOD5) Second Edition 1988 (with Amendments to Dissolved Oxygen in Waters) | SCA blue book 130 ISBN 0117522120 | Procedure for 5 day incubation period, with addition of allylthiourea | 2 mg/l | 0 - 6 mg/l O extended by dilution |
| Chemical disinfecting agents including chlorine | Chemical disinfecting agents in waters and effluents 2008 | SCA blue book 218 | Methods for all forms of chlorine plus some procedures for determining other disinfecting agents used in water treatment, including chlorine dioxide, ozone, bromine and iodine. If samples cannot be analysed immediately in a laboratory on-site methods should be considered. | | |
| Chloride | Chloride in Waters, Sewage and Effluents 1981 | SCA blue book 51 ISBN 0117516260 | Several methods presented, not all suitable for wastewater. LOD and range can be varied by different instrument configuration. | 1 – 10 mg/l | Up to 1000 mg/l |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Method | Comments | Reported LOD | Reported Range |
|---------------------------------|---|----------------------------------|--|--|--|
| COD | Determination of Chemical Oxygen Demand in waters and effluents (2207) | SCA blue book 215 | Contains 5 methods 3 of which do not use mercury compounds. | 10 mg/l O | Up to 400 mg/l O, extendable by dilution |
| Conductivity and pH | The measurement of Electrical Conductivity and the Laboratory Determination of the pH value of natural, treated and waste waters 1978 | SCA blue book 14 ISBN 0117514284 | | | |
| Cyanide | The determination of cyanide in waters and associated materials (2007) | SCA blue book 214 | Methods presented for easily liberated and complex cyanides, utilising colorimetry, potentiometry and continuous flow. | 0.003 to 0.4 mg/l, depending on method | Depends on method employed |
| | Water quality. Physical, chemical and biochemical methods. Methods for the determination of easily liberatable cyanide | BS 6068-2.18 | Three methods presented | | 0.02 - 0.25 mg/l as CN |
| | Water quality. Physical, chemical and biochemical methods. Methods for determination of total cyanide | BS 6068-2.17 | Three methods presented | | Up to 100 mg/l |
| Nitrate, nitrite and TON | Oxidised Nitrogen in Waters 1981 | SCA blue book 40 ISBN 0117515930 | Covers several methods for both nitrite and TON. | TON 0.2mg/l NO2 0.01mg/l | 0 - 40 mg/l 0 - 1 mg/l |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Method | Comments | Reported LOD | Reported Range |
|-------------------------------|---|--------------------------------------|---|---|----------------------|
| Phosphorus and Silicon | Phosphorus and Silicon in Waters, Effluents and Sludges 1992 | SCA blue book 147 ISBN 0117523771 | Compendium of methods for both P and Si. | | |
| Suspended Solids | Suspended, Settleable and Total Dissolved Solids in Waters and Effluents 1980 | SCA blue book 105 ISBN 011751957X | Paper filtration method should be used (Whatman GF/C paper or equivalent). | 2 mg/l | |
| Sulfate | Sulfate in Waters, Effluents and Solids 1988 (2nd Edition.) | SCA blue book 136 ISBN 0117522406 | Contains 5 methods reported as suitable for wastewater | 0.1 – 5 mg/l | Up to 5000 mg/l |
| TOC and DOC | The Instrumental Determination of Total Organic Carbon and Related Determinands 1995 | SCA blue book 157 ISBN 0117529796 | Results obtained will be influenced by instrument dependant considerations. Two methods presented. | Instrument dependant nominally 0.05 to 0.2 mg/l | Instrument dependant |
| Turbidity | Colour and Turbidity of Waters 1981 | SCA blue book 103 ISBN 0117519533 | | | |
| Arsenic | Arsenic in potable waters by atomic Absorption Spectrophotometry (Semi Automatic method) 1982 | SCA blue book 69. ISBN 0117516791 | No method performance data for wastewater. | | 0.05 - 5µg/l |
| Mercury | Mercury in waters, effluents, and sludges by flameless atomic absorption spectrophotometry 1978 | SCA blue book 10 ISBN 0117513261 | | 0.1- 0.2µg/l | 0 - 2µg/l |
| | Mercury in Waters, Effluent, Soils and Sediments etc (additional methods) 1985 | SCA blue book 92 ISBN 0117519073 | Includes amalgamation and atomic fluorescence methods. | 1 - 2ng/l | |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Method | Comments | Reported LOD | Reported Range |
|---|---|-----------------------------------|---|-----------------------------|---------------------|
| Silver | Silver in Waters, Sewages and Effluents by Atomic Absorption Spectrophotometry 1982 | SCA blue book 68. ISBN 0117516783 | | 0.03 mg/l | Up to 6mg/l |
| Trace metals (Multi determinand methods) | Inductively Coupled Plasma Spectrometry 1996 | SCA blue book 163 ISBN 0117532444 | ICPAES and ICPMS both covered. ICPMS may be the most appropriate method for very low concentrations. | | |
| Hydrocarbon Oils | The Determination of Hydrocarbon Oils in Waters by Solvent Extraction, Infra Red Absorption and Gravimetry 1983 | SCA blue book 77 ISBN0117517283 | Solvents recommended no longer in use, tetrachloroethene now used, so quoted LOD may not be achieved. | 0.2mg/l has been achieved . | |
| Steroid Oestrogens | The determination of steroid oestrogens in waters using chromatography and mass spectrometry (2008) | SCA blue book 220 | Several methods presented. | typically 0.1ng/l | typically to 25ng/l |
| Organotin compounds | The Determination of Organic, Inorganic, Total and Specific Tin Compounds in Water, Sediments and Biota 1992 | SCA blue book 142 ISBN0117523607 | No performance data presented for effluents. | | |
| Phenols and phenol Index | Phenols in Waters and Effluents by Gas Chromatography, 4-aminoantipyrine and 3-methyl-2-benzothiazolinehydrazone 1981 | SCA blue book 50 ISBN 0117516171 | GC method gives results for individual phenols, the 4 colorimetric procedures are of the phenol index type. | | |

M18: Monitoring of discharges to water and sewer

| Determinand | Title | Method | Comments | Reported LOD | Reported Range |
|-------------|--|-------------------|--|--------------|----------------|
| VOCs | The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998 | SCA blue book 170 | Covers many volatile compounds including halogenated hydrocarbons. Applicable to (diluted) Wastewater, no performance data presented for wastewater. | | |

Appendix 6: Examples of calculation of flow-weighted average concentrations and specific loads ³

Table 5.1: Monthly average from a determinand measured daily – flow-weighted average concentration and specific load for COD

| Date | Flow rate (daily) | Production (daily) | COD (daily average) | | COD Specific load (daily average) | |
|----------------------|-------------------|--------------------|--|-----|---|------|
| | q_i | p_i | c_i | | $\frac{c_i q_i}{p_i}$ | |
| | m ³ | t | mg/l | | kg/t | |
| 1 st May | 7656 | 1527 | 223 | | 1.12 | |
| 2 nd May | 7358 | 1575 | 235 | | 1.10 | |
| 3 rd May | 7554 | 1453 | 237 | | 1.23 | |
| 4 th May | 7303 | 1425 | 226 | | 1.16 | |
| 5 th May | 7474 | 1534 | 220 | | 1.07 | |
| 6 th May | 8038 | 1345 | 219 | | 1.31 | |
| 7 th May | 7275 | 1585 | 233 | | 1.07 | |
| 8 th May | 8028 | 1224 | 244 | | 1.60 | |
| 9 th May | 8012 | 1291 | 235 | | 1.46 | |
| 10 th May | 6453 | 1465 | 235 | | 1.03 | |
| 11 th May | 8566 | 1434 | 232 | | 1.39 | |
| 12 th May | 8085 | 1478 | 276 | | 1.51 | |
| 13 th May | 7141 | 1532 | 232 | | 1.08 | |
| 14 th May | 7294 | 1532 | 236 | | 1.12 | |
| 15 th May | 8596 | 785 | 247 | | 2.71 | |
| 16 th May | 7104 | 577 | 194 | | 2.39 | |
| 17 th May | 4208 | 554 | 146 | | 1.11 | |
| 18 th May | 2899 | 975 | 117 | | 0.35 | |
| 19 th May | 7606 | 1408 | 174 | | 0.94 | |
| 20 th May | 6904 | 1071 | 184 | | 1.19 | |
| 21 st May | 6172 | 1454 | 189 | | 0.80 | |
| 22 nd May | 7242 | 1422 | 194 | | 0.99 | |
| 23 rd May | 6585 | 1504 | 201 | | 0.88 | |
| 24 th May | 7083 | 1536 | 217 | | 1.00 | |
| 25 th May | 7068 | 1294 | 230 | | 1.26 | |
| 26 th May | 7307 | 1554 | 229 | | 1.08 | |
| 27 th May | 6577 | 1504 | 224 | | 0.98 | |
| 28 th May | 7171 | 1460 | 241 | | 1.18 | |
| 29 th May | 6717 | 1530 | 239 | | 1.05 | |
| 30 th May | 7449 | 1541 | 240 | | 1.16 | |
| 31 st May | 7068 | 1325 | 251 | | 1.34 | |
| | | | Monthly average (weighted, equation 9.1) | 233 | Monthly average load (not weighted, equation 9.2) | 1.21 |
| | | | Monthly average (not weighted) | 219 | | |

³ Taken from draft JRC Reference Report on Monitoring of emissions from IED-installations 2013 (MONREF)

Table 5.2: Annual average from a determinand measured periodically - flow-weighted average concentration and specific load for AOX

| Date | Flow rate (daily) | Production (daily) | AOX concentration (daily average) | AOX Specific load (daily average) |
|------------|-------------------|--|-----------------------------------|-----------------------------------|
| | q_i | p_i | c_i | $\frac{c_i q_i}{p_i}$ |
| | m ³ | t | mg/l | kg/t |
| 04/01/2011 | 7857 | 1413 | 0.13 | 0.00072 |
| 11/01/2011 | 8405 | 1552 | 0.28 | 0.00152 |
| 19/01/2011 | 7445 | 1378 | 0.24 | 0.00130 |
| 27/01/2011 | 7642 | 1526 | 0.15 | 0.00075 |
| 02/02/2011 | 8351 | 1411 | 0.13 | 0.00077 |
| 10/02/2011 | 8218 | 1576 | 0.20 | 0.00104 |
| 14/02/2011 | 6764 | 934 | 0.12 | 0.00087 |
| 20/02/2011 | 6517 | 1393 | 0.14 | 0.00066 |
| 08/03/2011 | 7035 | 1508 | 0.22 | 0.00103 |
| 16/03/2011 | 7764 | 1575 | 0.35 | 0.00173 |
| 24/03/2011 | 7442 | 1541 | 0.32 | 0.00155 |
| 31/03/2011 | 8141 | 1520 | 0.36 | 0.00193 |
| 03/04/2011 | 7461 | 1510 | 0.24 | 0.00119 |
| 12/04/2011 | 7455 | 1424 | 0.18 | 0.00094 |
| 19/04/2011 | 8331 | 1388 | 0.22 | 0.00132 |
| 27/04/2011 | 8038 | 1327 | 0.28 | 0.00170 |
| 05/05/2011 | 7474 | 1534 | 0.06 | 0.00029 |
| 24/05/2011 | 7083 | 1536 | 0.68 | 0.00314 |
| 08/06/2011 | 7493 | 1366 | 0.24 | 0.00132 |
| 16/06/2011 | 7790 | 1524 | 0.22 | 0.00112 |
| 24/06/2011 | 7868 | 1476 | 0.30 | 0.00160 |
| 27/06/2011 | 7873 | 1554 | 0.18 | 0.00091 |
| 04/07/2011 | 8258 | 1581 | 0.21 | 0.00110 |
| 12/07/2011 | 7704 | 1446 | 0.28 | 0.00149 |
| 20/07/2011 | 7871 | 1534 | 0.34 | 0.00175 |
| 23/08/2011 | 7573 | 1577 | 0.25 | 0.00120 |
| 30/08/2011 | 8512 | 1498 | 0.23 | 0.00131 |
| 06/09/2011 | 7527 | 1397 | 0.32 | 0.00172 |
| 19/09/2011 | 7881 | 933 | 0.29 | 0.00245 |
| 04/10/2011 | 8485 | 1561 | 0.25 | 0.00136 |
| 11/10/2011 | 7462 | 1452 | 0.22 | 0.00113 |
| 18/10/2011 | 7971 | 1554 | 0.19 | 0.00097 |
| 25/10/2011 | 7371 | 1298 | 0.26 | 0.00148 |
| 02/11/2011 | 6873 | 1565 | 0.24 | 0.00105 |
| 07/11/2011 | 7858 | 1537 | 0.25 | 0.00128 |
| 16/11/2011 | 8591 | 1070 | 0.23 | 0.00185 |
| 01/12/2011 | 8318 | 1550 | 0.34 | 0.00182 |
| 07/12/2011 | 8418 | 1385 | 0.17 | 0.00103 |
| 12/12/2011 | 7899 | 1508 | 0.25 | 0.00131 |
| 21/12/2011 | 7474 | 1243 | 0.24 | 0.00144 |
| | | Average of samples obtained during one year (weighted, equation 9.1) | 0.24 | 0.00133 |
| | | Average of samples obtained during one year (not weighted) | 0.24 | |
| | | Average of samples obtained during one year (not weighted, equation 9.2) | | |

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