



**Technical Guidance Note  
(Monitoring)**

**M18**

**Monitoring of discharges to water and sewer**

**Environment Agency  
Version 2  
April 2009**

M18: Monitoring of discharges to water and sewer

## Foreword

This Technical Guidance Note (TGN) is one of a series providing guidance to our staff and monitoring contractors, industry and other parties interested in the monitoring of discharges<sup>1</sup> to water. It is also a technical reference for our Operator Monitoring Assessment (OMA) scheme, which has been extended to include water.

Historically we have been responsible for carrying out monitoring of discharges. However, this is gradually being replaced by a system of self-monitoring, where the operator carries out the majority of the monitoring. This TGN describes our overall approach to self-monitoring 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 covers:

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

We consider that the best way for us to have confidence in the quality and integrity of self-monitoring discharge data is for operators to use and adhere to a quality management system (QMS) approach. We expect operators carrying out their own monitoring to develop a documented QMS to cover all aspects of sampling and analysis of discharges. This will be based on the requirements of proven international standards such as ISO/IEC 17025, supported by accreditation as appropriate to provide additional reassurance.

This TGN will be particularly useful for operators with installations falling under the Environmental Permitting Regulations (EPR), which implement the requirements of the Integrated Pollution Prevention and Control (IPPC) directive, the Urban Waste Water Treatment Regulations (UWWTR)(SI 94/2841), and operators with Water Resource Act 1991 numeric discharge consents transferring to self-monitoring. We plan to move the majority of operators to self-monitoring over the next few years.

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<sup>1</sup> 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,)
2	April 2009	Definitions of validation criteria moved to a glossary (Appendix 1)
2	April 2009	Section 4.1 amended to emphasise that alternative methods to those listed in the appendix may be used.
2	April 2009	Rewrite and update of introduction
2	April 2009	Appendices covering method validation protocol(3) and performance requirements (2)removed, as better placed in the appropriate MCERTS performance standard. List of methods (now appendix 3) updated , glossary of terms created as appendix 1. Sampling requirements now appendix 2.

## 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.environment-agency.gov.uk](http://www.environment-agency.gov.uk) by typing M18 into the search facility.

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# 1. Introduction

## 1.1 Legislative framework relevant to water discharge monitoring

The current legislative framework covering the monitoring of discharges is outlined below.

### 1.1.1 European Directives

The European Union (EU) has drawn up Directives stating objectives to be achieved in order to control pollution. The requirements of these Directives must be adhered to by member states of the EU. It is the responsibility of the member states to incorporate the requirements into the framework of their national legislation. Examples of relevant Directives include the Urban Waste Water Treatment Directive (91/271/EEC), the Waste Incineration Directive (2000/76/EC), and the Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC).

The Urban Waste Water Treatment (England & Wales) Regulations (UWWTR, SI 94/2841) implement the Urban Waste Water Treatment Directive in England and Wales. The UWWTR impose a duty on the us “to monitor or procure the monitoring by a competent authority or appropriate body of discharges from urban waste water treatment plants...” to which the Regulations apply. The Urban Waste Water Treatment Directive Implementation Group agreed that the sewerage undertakers shall be required to self-monitor their own processes for the determinands specified in the Regulations. In order to comply with the UWWTR flow-proportional or time-based 24-hour composite samples must be collected at a representative and well-defined point in the outlet of a treatment works and are used to monitor compliance with the requirements for discharged wastewater. Where compliance is to be based on percentage reduction in load in relation to the influent, samples of influent must be taken at an appropriate sample point. The detailed requirements for monitoring can be found in The Monitoring By Sewerage Undertakers Of Their Discharges Under The Urban Waste Water Treatment Regulations 1994: Guidance, Equipment Specification And Audit Strategy. EAS/2301/3/26.

The Waste Incineration Directive, 2000/76/EC (WID) incorporates and extends the requirements of the 1989 municipal waste incineration (MWI) Directives (89/429/EEC and 89/369/EEC) and the Hazardous Waste Incineration Directive (94/67/EC), forming a single Directive on waste incineration. The Waste Incineration Regulations came into force on 28<sup>th</sup> December 2002 together with directions issued at the same time to the regulators, that is the Environment Agency and Local Authorities. The Directive specifies a mixture of continuous and periodic monitoring for releases to water. Guidance can be found in: *Directive 2000/76/EC On the incineration of waste DEFRA 2002*.

### 1.1.2 Water Resources Act 1991

Under the provisions of the Water Resources Act 1991 (WRA91) in England and Wales, a consent from us is required for any discharge of sewage effluent into “controlled waters”. “Controlled waters” include all inland watercourses, coastal waters and groundwater. A consent may also be required for any discharge into a soakaway or a self-contained pond. The holder of the discharge consent for a sewage treatment plant is responsible for ensuring that the plant is well maintained and that the effluent complies with the consent conditions. When numeric conditions are placed on the discharge they must be monitored to enable compliance to be assessed.

We currently monitor compliance with WRA91 numeric discharge consents using our own in-house sampling and analysis, but from April 2009, we will gradually move to an operator self-monitoring regime (OSM). OSM will be applied to water companies first, and will be introduced to other significant industrial and trade operators with WRA91 consents, after we have reviewed the overall success of the scheme. Operators will be required to comply with appropriate parts of our MCERTS scheme (see section 1.2 below).

### **1.1.3 Pollution Prevention and Control Regulations 2000**

The Pollution Prevention and Control (PPC) Regulations 2000 create the UK national framework for implementing the European Community directive on Integrated Pollution Prevention and Control (IPPC).

The IPPC Directive sets down the principle that industrial operators are responsible for carrying out monitoring of emissions from installations falling under IPPC. To support the implementation of the Directive the European IPPC Bureau in Seville has prepared a reference document (BREF) on the principles of monitoring under IPPC.

### **1.1.4 Environmental Permitting Regulations**

The Environmental Permitting (England and Wales) Regulations (EPR) came into force in April 2008. The new regulations replaced Pollution Prevention Control (PPC) and Waste Management Licensing (WML) regimes. All PPC Permits and WML automatically became environmental permits. WRA91 will also be replaced by the EPR regime in due course.

## **1.2 MCERTS and discharges to water**

We have established our Monitoring Certification Scheme (MCERTS) to provide a framework within which environmental measurements can be made to published quality requirements. 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 relevant to the monitoring of discharges to water. These are:

- 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 WRA91 and have to send the results to us. Laboratories should be accredited to ISO 17025 for the MCERTS performance standard.

At the time of publication of this MCERTS scheme has only been applied to effluent from sewage treatment works. The scheme may be extended to cover other OSM for water discharges over time e.g. EPR. We would also encourage operators and analytical laboratories to consider applying for accreditation under the scheme, ahead of any requirement to do so, as a means of demonstrating the required quality standards are being achieved. This will be reflected in the scores awarded under our Operator Monitoring Assessment (OMA) scheme.

- MCERTS 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.

- MCERTS certification of continuous water monitoring equipment

Performance standards and conformity testing procedures have been published for automatic wastewater samplers, on-line analysers covering turbidity, pH meters, ammonia, Chemical Oxygen Demand, Total Organic Carbon, dissolved oxygen, total phosphorus, nitrate and total oxidised nitrogen (TON), conductivity, total chlorine and free cyanide analysers, and flow meters.

Equipment covered has applications under various regulatory regimes including UWWTR, EPR and WRA91 for monitoring discharges.

- Performance standards and test procedures for portable water monitoring equipment

This scheme covers instruments for the determination of temperature, pH, conductivity, dissolved oxygen, turbidity, ammonia, nitrate, nitrite, orthophosphate, chlorophyll a, total chlorine and free cyanide, and will be amended to incorporate further determinands if required.

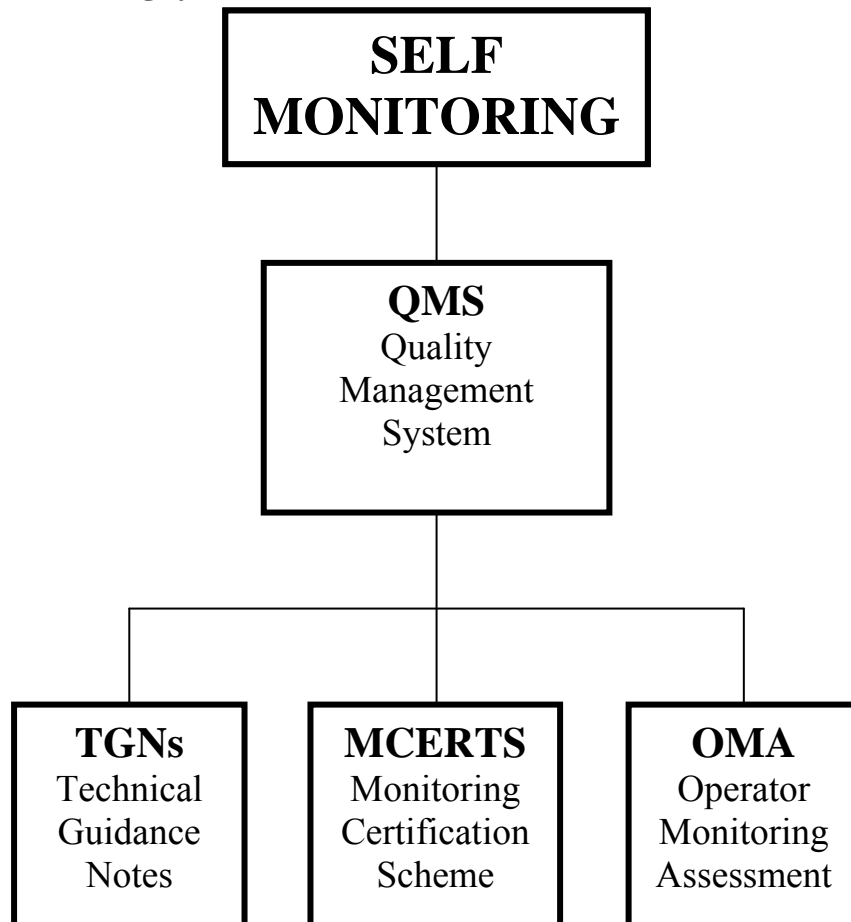
Further information on these applications including copies of the performance standards can be obtained from our web-site at [www.mcerts.net](http://www.mcerts.net).

## **2. Monitoring strategy**

### **2.1 Environment Agency self-monitoring policy**

We must ensure that operator self-monitoring is performed correctly to an acceptable standard and to this end encourages operators to use and adhere to quality management systems. Self-monitoring is supported by a number of tools that will 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 certain monitoring services and equipment are independently quality assured and therefore fit for purpose.
- The Operator Monitoring Assessment (OMA) scheme is used to provide 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**

## 2.2 Approaches to monitoring discharges

Monitoring approaches can be conveniently classified into two types:

- **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.
- **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 WID<sup>2</sup> and IPPC sector guidance (see appendix 2).

Although we would prefer to move to the use of continuous monitoring systems it is recognised that at present the availability of cost-effective systems is limited, and the use of periodic monitoring will predominate. This document reflects this situation. Some of the relative advantages and disadvantages of continuous and periodic monitoring are summarised in Table 1.

<sup>2</sup> The Waste Incineration Directive, 2000/76/EC

**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	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

### 2.3 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 the accuracy of result required (see section 2.4). 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, but are by no means exhaustive:

**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. The determination of total concentration may not be practical if great analytical effort required to determine all forms.

**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.

## 2.4 Specification of laboratory performance: tolerable error targets

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, the Environment Agency 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 standard<sup>3</sup>. Initial estimates of precision and bias are calculated during method validation studies (see section 4). 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.

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

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<sup>3</sup>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

the targets set in the MCERTS standard. If this situation arises the actual analytical performance that can be obtained should be reported to us. The MCERTS standard makes provision for this under “ongoing validation”. 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.

## **2.5 Quality assurance**

### **2.5.1 Quality management systems**

The operator responsible for self-monitoring must establish a Quality Management System (QMS) that covers all aspects of self-monitoring, including

- management of self-monitoring
- sampling programme design
- sampling procedures (see section 3)
- analysis and reporting procedures ( see section 4)
- staff training
- the process of audit and review of sampling and analysis operations.
- addressing non-conformities.

The system must be fully documented in a quality manual.

The use of a third party contractor for some or all aspects of sampling and analysis is acceptable. If the subcontractor is accredited to ISO 17025 or MCERTS, as appropriate, the operator will not require a quality system for those subcontracted 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 clearly split into two major parts, management requirements and technical requirements. The management requirements are written to ensure laboratory QMS comply with ISO 9001.

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.

Some operators may already be certified to ISO 9001, which is a generic standard for the QMS approach that is applicable to all organisations irrespective of size, type of field of operation, including laboratories. Unlike ISO 17025 it does not contain reference to the technical requirements of laboratories, so it cannot be assumed that laboratories holding ISO 9001 certification will produce results fit for our purpose.

## **2.5.2 Management**

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

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, operation of the plant/process should be wherever practical 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 must 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.

Further details of requirements may be obtained from international standard ISO 17025.

## **2.5.3 Sampling programme design**

The operator must set out a rigid 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. The sampling schedule may need to be agreed with us in advance. Failure to comply with the agreed sampling schedule may lead to the us taking enforcement action, although 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 inform us of 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. The requirements of each of the regulations are summarised in Appendix 2.

## **2.5.4 Staff training**

All staff involved in the self-monitoring process should be shown to be competent in carrying out their duties. Staff should be trained in the necessary skills, and a record of training for each individual should be maintained as part of the quality system. A programme of training updates should be detailed in the quality system.

### **2.5.5 Internal audit and review of Quality System**

The operator is required to carry out a series of audits of its quality system. These should cover all aspects of the quality management system and serve to verify that the procedures documented in it are being adhered to. The audits should be pre-planned on an annual cycle, and 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 quality 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 us 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.

### **2.5.6 Audit of Operators by the Environment Agency**

A general assessment of the monitoring performance of the operator will be made using the OMA scheme. Alongside this, vertical audits of specific samples may be required.

## **3. Sampling**

### **3.1 Choice of sampling point**

Discharge sample points must be at a location that ensures that the sample is truly representative of the discharge. For example, 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. The sampling point location should be agreed with us, documented and clearly and permanently labelled.

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 (e.g. manholes), it is necessary to ensure that measures are taken to avoid contamination of the sample by the disturbance of deposits from the cover when the cover is lifted and to prevent contamination of the sample from the chamber walls and any bottom deposits. 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.

### 3.2 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 (e.g. every 10 m<sup>3</sup>). For time-proportional samples, a fixed amount of sample is taken from the effluent for each time unit (e.g. 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 us. Automatic sampling equipment is recommended (see section 3.3). 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;
- when 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);
- to check the quality of the discharge at a particular moment, normally to assess compliance with the permit conditions.
- when the discharge is not continuous (from batch or hold-up tanks), but only when the effluent is well mixed.

You should avoid collecting larger object and floating matter that is not representative of the discharge.

Details of the sampling methods required can be found in Appendix 2.

### 3.3 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 from our web-site at [www.mcerts.net](http://www.mcerts.net). A list of certified equipment is held by Sira Certification Services and can be accessed at [http://www.sira.co.uk/mcerts\\_prod.html](http://www.sira.co.uk/mcerts_prod.html) or via [www.mcerts.net](http://www.mcerts.net).

### **3.4 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.

### **3.5 Sample storage and transportation.**

If preservation of samples by refrigeration is required, then during transportation and subsequent storage of samples, including retention time in an automatic sampling device, the sample storage environment should maintain a temperature of  $5\pm 3^{\circ}\text{C}$ , using ice packs, refrigerators or other appropriate methods. An organisation carrying out sampling should have appropriate procedures for demonstrating this. It is recognised that some time may be required to bring the sample temperature to within this range.

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 ( $1-5^{\circ}\text{C}$ ) and in the dark.

Sample containers should be appropriate for the determinand and analytical system being 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, preservatives may be added 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. Guidance can be found in:

BS EN ISO 5667-3: Water Quality-Sampling-Part 3: Guidance on the preservation and handling of samples.

### **3.6 Sampling procedure manual**

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. This to include 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 us;
- quality assurance procedures for sampling activities.

These procedures should be part of the QMS and be made available to all staff that undertake sampling and if requested should be submitted to us 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, e.g. the Customer Self Monitoring (CSM) data import formats provided by the Environment Agency (see section 4.8);
- sampling staff training records;
- calibration and maintenance records;
- sample event failure reports.

### **3.7 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 two 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 4.5. The data collected can be used as part of an estimate of sampling uncertainty.

## 4. Analytical systems

### 4.1 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 pollutant or parameter
- ISO standards
- national standards (SCA blue books + BSI)
- alternative methods, such as in house methods and modified methods, with prior approval from us. We may also impose extra requirements.

**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 fully validated 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 us, 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 were addressed.**

A list of analytical methods is given in Appendix 3. The list is neither mandatory nor exhaustive, and other appropriate methods may be acceptable with satisfactory validation. For example, automated methods of analysis have been listed for ammonia that use continuous flow methods. However, in larger laboratories these methods have been superseded by discrete analysers that use essentially the same method and can operate with the required performance, but are more cost effective.

CEN, ISO and British Standards can be obtained from the British Standards Institute at [www.bsi-global.com](http://www.bsi-global.com), SCA blue books can be obtained from us, details can be found on our website at [www.environment-agency.gov.uk/](http://www.environment-agency.gov.uk/) by typing SCA into the search facility. ISO methods can also be obtained from [www.iso.ch](http://www.iso.ch).

### 4.2 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 quality 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, autopipettes 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.

### 4.3 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

Further information on and procedures for method validation can be found in:

*A Manual on Analytical Quality Control for the Water Industry*, NS30, Water Research Centre, UK, 1989, ISBN 0 902156 85 3

*The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics* - EURACHEM Guide

*In-House Method Validation – A Guide for Chemical Laboratories* LGC ISBN 094892618X

### 4.4 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 from:

*The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics* - EURACHEM Guide.

ISO 78-2:1999. *Layout for Standards - Part 2: Methods of chemical analysis.*

## 4.5 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 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. 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 or by a change in the size of the random error operating in the analytical method. The level of variation is estimated during method validation studies (as a standard deviation), and if acceptable is used to construct the control charts. Any breaches of control limits are assumed to be the result of assignable causes that should be identified and eliminated or reduced.

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. Further details can be found in:

*A Manual on Analytical Quality Control for the Water Industry*, NS30, Water Research Centre, UK, 1989, ISBN 0 902156 85 3

ISO TR 13530:1997 *Water Quality - A Guide to Analytical Quality Control for Water Analysis*

ISO 7870:1993 *Control charts - General guide and introduction*

ISO 8258:1991 *Shewhart control charts*.

*Quality Control Charts in Routine Analysis*, WRc Report CO4239, M J Gardner, 1996.

**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. Further details can be found in the following:

ISO/IEC Guide 43 Part 1 (1997): *The Development and Operation of Proficiency Testing Schemes*'.

[ILAC](#) Guide G13 *Guidelines for the Requirements of Providers of Proficiency Testing Schemes*'

Examples of PT schemes, which are designed to comply with ISO/IEC Guide 43 Part 1, can be seen on the following websites;

<http://www.lgc.co.uk/>, <http://www.vam.org.uk/>, [www.eptis.bam.de](http://www.eptis.bam.de)

## 4.6 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 seen to be fit for purpose some knowledge of these errors is required. We 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.), 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 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:

*EURACHEM/CITAC Guide to Quantifying Uncertainty in Analytical Measurement*  
EURACHEM/CITAC Guide CG 4 (2000 2<sup>nd</sup> ed), S L R Ellison(UK) M Rosslein (Switzerland)  
A Williams (UK) (eds.)

*EURACHEM/EUROLAB/CITAC/Nordtest/AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches* EURACHEM (2007). ISBN 978 0 948926 26 6.  
M H Ramsey and S L R Ellison (eds.)

*In-House Method Validation: A Guide for Chemical Laboratories* LGC ISBN 094892618X

*Vocabulary of metrology —Part 3: Guide to the Expression of Uncertainty in Measurement (GUM)* PD 6461-3: 1995 BSI 2002

*Guide to the expression of uncertainty in analytical measurement*, ISO, Geneva, 1995.  
(Identical to PD 6461 – 3, above)

*Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories* 2<sup>nd</sup>  
Edition Nordtest ref TR 537:2004

## **4.7 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, 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.

## **4.8 Electronic data reporting**

The results of self-monitoring can in many cases be supplied to us in an electronic format. At present the WIMS Customer Self Monitoring (CSM) Database is used for UWWTR returns. It is a system designed to import, convert and then export the customer supplied sample data to our data archives.

However, a new system will be available soon, the Generic Operator Returns (GOR) which is a web based portal. It should be ready for phase 2 of OSM for WRA91 sites in April 2010. The file format required by the new system will be XML. It will be finalised by April 2009. Our aim is to use the same new file format for other data returns, such as abstraction licences. Where possible we will be consulting with customers to ensure it is easy to use. Until the GOR system is ready, we will be using the existing CSM route, where applicable.

## **5. Flow measurement**

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

We have therefore produced two MCERTS standards to 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 the Environment Agency 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 Sira Certification Service who run 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.
- We have set a total daily volume target of better than +/- 8% uncertainty for effluent flow monitoring systems. MCERTS Inspectors will check this during their inspection.
- 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 for flow monitoring also needs to be assessed. This is done by a UKAS accredited Certification Body that has MCERTS for flow included in its scope. This can be, for example, your existing ISO 9000/14001 auditor or Sira.
- Sira 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.

Detailed guidance on what is expected can be found in the MCERTS standard “Minimum requirements for the self-monitoring of effluent flow”, via the Self monitoring of effluent flow web page at [www.mcerts.net](http://www.mcerts.net). Additional guidance can be found in MCERTS bulletins at [www.sira.co.uk/download.html](http://www.sira.co.uk/download.html)

The initial focus of this scheme was our requirements for consent holders under the WRA91 to measure the flow of final effluents and collect and report the monitoring data. It has now been extended to most EPR installations with effluent flow monitoring specified in their permits.

## 6. References

### 6.1 General

1. *The Chemical Analysis of Water – General principles and techniques 2<sup>nd</sup> edition 1986* D.T.E.Hunt and A.L.Wilson ISBN 0851867979
2. *NS30 - A Manual on Analytical Quality Control for the Water Industry* R.V.Cheeseman and A.L.Wilson revised M.J.Gardner June 1989 ISBN 0902 156853
3. ISO TR 13530:1997 *Water Quality - A Guide to Analytical Quality Control for Water Analysis.*
4. *The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics* EURACHEM Guide
5. *In-House Method Validation – A Guide for Chemical Laboratories* LGC ISBN 094892618X
6. *Quality Control Charts in Routine Analysis*, WRc Report CO4239, M J Gardner, 1996.
7. ISO 7870:1993 *Control charts - General guide and introduction*
8. ISO 8258:1991 *Shewhart control charts.*

9. ISO/IEC Guide 43 Part 1 (1997): *The Development and Operation of Proficiency Testing Schemes*.
10. [ILAC](#) Guide G13 *Guidelines for the Requirements of Providers of Proficiency Testing Schemes*
11. EURACHEM/CITAC *Guide to Quantifying Uncertainty in Analytical Measurement*  
EURACHEM / CITAC Guide CG 4
12. *Vocabulary of metrology —Part 3: Guide to the Expression of Uncertainty in Measurement (GUM)* PD 6461-3: 1995 BSI 2002
13. *IPPC Reference Document on the General Principles of Monitoring* July 2003 (the monitoring BREF)
14. BS EN ISO/IEC 17025 *General requirements for the competence of testing and calibration laboratories*
15. BS EN ISO 9001 *Quality management systems - Requirements*
16. BS EN ISO 5667-3: *Water Quality-Sampling-Part 3: Guidance on the preservation and handling of samples*.
17. ISO 78-2:1999. *Layout for Standards - Part 2: Methods of chemical analysis*.
18. *Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories 2<sup>nd</sup> Edition* Nordtest ref TR 537:2004

## 6.2 Legislative

1. European Commission 1991. *The Urban Waste Water Treatment Directive* (91/271/EEC)
2. *The Urban Waste Water Treatment (England and Wales) Regulations 1994* (S.I. No. 2841)
3. *The Urban Waste Water Treatment (England & Wales) 1994, Working Document for Dischargers and Regulators - A Guidance Note* Issued by the Department of the Environment, Transport and the Regions and the Welsh Office, July 1997
4. DETR, 1995. *Urban Waste Water Treatment Directive Implementation Group, Agreed papers*.
5. Environment Agency, 1999. *The monitoring by sewerage undertakers of their discharges under the Urban Waste Water Treatment Regulations 1994: Guidance, Equipment specification and Audit strategy*. (EAS/2301/3/26)
6. Directive 96/61/EC, *A European Community system for Integrated Pollution Prevention and Control (IPPC)*, Official Journal No. L257, 10.10.96.
7. *Integrated Pollution prevention and Control (IPPC) Reference document on the general principles of monitoring* (the monitoring BREF), July 2003, European Commission, European IPPC Bureau.
8. 89/369/EEC, *Directive on air pollution from new municipal waste incinerators*, Official Journal No. L163, 14.6.89.
9. 89/429/EEC, *Directive on air pollution from existing municipal waste incinerators*, Official Journal No. L203, 15.07.89.
10. 94/67/EC, *Directive on the incineration of hazardous waste*, Official Journal No. C365, 31.12.94.
11. 2000/76/EC, *Directive on the incineration of waste*.
12. 2001/80/EC, *Directive on limiting emissions of certain pollutants into the air from large combustion plants*
13. *Pollution Prevention and Control Regulations* SI 2000 no 1973
14. *Environmental Protection Act* 1990

## **Appendix 1: Glossary of terms**

### **Selectivity and interference effects (matrix effects)**

It must be ensured 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, at least two different concentrations of determinand should be studied in this way.

### **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.

### **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.

### **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 e.g. 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.

### **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.

### **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 (e.g. 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, e.g. the permit value. Laboratories often use 20% and 80% of the highest concentration determined by the method.

### **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 must 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 one 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.

## Appendix 2: Detailed sampling requirements

The sampling requirements in terms of frequency and method for each of the regulations are reproduced below. Whereas the WID, WRA91 and UWWTR requirements are very specific the EPR regulations require a more risk based approach.

### Waste Incineration Directive

The WID requires a variety of sampling frequencies and methods depending on the determinand being measured.

Determinand	Number of samples per year	Sampling method employed
pH	Continuous	CWM
Flow	Continuous	CWM
Temperature	Continuous	CWM
Total Suspended Solids	365	Daily spot sample or flow proportional sample over 24-hours
Mercury	12	24-hours flow proportional sample
Cadmium	12	24-hours flow proportional sample
Titanium	12	24-hours flow proportional sample
Arsenic	12	24-hours flow proportional sample
Lead	12	24-hours flow proportional sample
Chromium	12	24-hours flow proportional sample
Copper	12	24-hours flow proportional sample
Nickel	12	24-hours flow proportional sample
Zinc	12	24-hours flow proportional sample
Dioxins and Furans (TEQ)	2 but 4 during the first year of operation	
Other pollutants e.g.PAH's	As appropriate based on site specific assessment	

### Water Resources Act

For WRA91 spot samples are required, and the sampling frequency is as summarised in the table below:

Number of Samples Per Year	Population Equivalent	Maximum Daily Volume m <sup>3</sup> /d
At Environment Agency discretion	<25	5
4	25-250	>5-100
12	250-20,000	100-10,000
24	20,000-100,000	10,000-50,000
48	>100,000	>50,000

Population Equivalents are based on the daily biochemical oxygen demand load, i.e. influent BOD multiplied by average flow (grams/day) divided by 60 (i.e. 60g of BOD per head of population). It is anticipated that the discharger will provide this information.

For sewage treatment works final effluents:

- the maximum daily volume is the flow to full treatment;
- where no maximum daily volume is specified in the consent, but an average daily flow is given, the maximum daily volume shall be taken to be 2.4 times the average daily flow;
- if a daily dry weather flow only is specified, the maximum daily volume shall be taken to be 3 times the daily dry weather flow.

For trade effluents:

- the maximum daily volume is the flow to full treatment;
- where no maximum daily volume is specified in the consent, but a daily dry weather flow is given, this shall be taken to be the maximum daily volume except where the discharge may contain rainfall when the maximum daily volume shall be taken to be 3 times the daily dry weather flow.

The samples in the schedule should be taken at “regular but randomised intervals”. The sampling should be spread evenly over the period of interest (usually a calendar year) and the dates / times of individual samples within that regular framework should be chosen randomly or according to a pre-determined schedule. For example, if an effluent is to be sampled at a frequency of 12 p.a., then one sample should be scheduled for each month, but randomised within each month. Failed sampling events should be rescheduled before the end of the time period it is intended to represent. If this proves impossible the sample must be taken before the end of the next period. The exception being for a frequency of four samples per year where the catch-up must be within the same period to avoid potentially a significant delay.

Effluent sampling and catch up sampling periods are detailed in the table below:

<b>Number of Samples per Year</b>	<b>Representative Frequency per month</b>	<b>Ideal Period <u>during</u> which a catch up sample should be taken from pre-planned date</b>	<b>Deadline date that catch up sample must be taken from pre-planned date</b>
4	1 every 3 months	Within 30 days	Within 60 days
12	1	Within 14days	Within 30 days
24	2	Within 7 days	Within 14 days
48	4	Within 5 days	Within 10 days

A non-conformance log of failed sampling events, reasons for failure and rescheduling of the event, should be maintained. Failures must be reported to us within 24 hours of the failed event. Samples taken outside of the agreed sampling schedule cannot be used for compliance purposes unless the rescheduling has been agreed with us.

It is recognised that the above may not be practicable at all sites, that operational and travelling constraints, for example, may restrict sampling windows. In these cases we will give guidance and may agree a proposal for individual discharges.

## Operator Self Monitoring (OSM)

### WRA91 discharges

With the introduction of OSM for WRA discharges, there will be an opportunity for sampling frequencies of individual discharges to be reduced, if an operators that can demonstrate sustained compliance with the consent conditions. It is estimated that this could reduce the number of samples required by as much as 20%, thus reducing operators costs.

The first year's sampling frequency has been set to continue in line with our current sampling frequencies (see above). The normal monitoring frequency after year 1 will be 24 samples per year. If a discharge is fully compliant with its numeric limits over 12 consecutive months its sampling frequency will reduce to 12 samples per calendar year. Where a discharge fails any consented numeric water quality limit, it will return to the normal sampling frequency of 24 samples over a 12 month period as soon as reasonably possible and continue at the normal frequency until 12 consecutive months of numeric compliance have been reported when it can return to 12 samples a year or 12 month period.

The tables below relate to spot samples which must be collected at approximately equal intervals during the year, but should include samples from different days of the week and different times. Approximately 10% of samples should be outside of the normal sampling window which is 9am - 3pm, Monday to Friday.

### OPRA Tier 3 Sampling Frequency

Determinand	Number of samples from 01 April 2009 to 31 December 2009 (pro rata from the annual frequency below)	Normal frequency of samples per year from January 2010	Reduced Sampling regime after 12 consecutive months of numeric consent compliance	On consent failure return to Normal sampling frequency as soon as reasonably practicable	Out of hours samples
Sanitary	Same as current EA but no less than 12	24	than 12	24/12 months	For 24 samples 2 out of hours samples per annum
Non sanitary	12	12	12	12	For 12 samples 1 out of hours sample per annum

**OPRA Tier 2 Sampling Frequency**

<b>Tier 2 Category</b>	<b>Determinand</b>	<b>Normal frequency of samples per year from January 2010</b>	<b>Reduced Sampling regime after 12 consecutive months of numeric consent compliance</b>	<b>On consent failure return to Normal sampling frequency as soon as reasonably practicable</b>	<b>Out of hours samples</b>
>5 m <sup>3</sup> /d (not in tier 3) sewage or trade with numeric ammonia or nutrients or numeric dangerous substances or UWWTD self monitoring	Sanitary	12	6	12/12 months	For 12 samples 1 out of hours samples per annum, for 6, 1 every 2 years on average
	Non sanitary	6	6	6	For 12 samples 1 out of hours sample per annum
>20 m <sup>3</sup> /d (not in tier 3) sewage and trade	Sanitary	12	4	12/12 months	For 12 samples 1 out of hours samples per annum, for 4, 1 every 3 years on average

**Urban Wastewater Treatment Regulations**

For UWWTR the minimum frequency of sampling is specified in Part II of Schedule 3 of the Regulations and is detailed in the table below. UWWTR requires the use of 24 hour time proportional samples, aliquots to be taken at a minimum of hourly intervals. The rules for catch-up sampling defined for WRA91 compliance should also be applied to UWWTR sampling.

<b>Population equivalent</b>	<b>number of samples per year</b>	<b>number of weekend samples</b>
2,000 to 9,999	12 samples in first year 12 samples if any failures 4 samples then if no failures in 1st or subsequent years	1 sample / year when 12 samples / year taken occasional samples when 4 samples / year taken (1 sample / 3 years)
10,000 to 49,999	12 samples per year	1 sample per year
50,000 and greater	24 samples per year	2 - 3 samples per year

**Requirements of EPR**

EPR requires that best practice is used to assess the risks that the emissions from a particular installation pose to the environment. An appropriate level of monitoring should then be applied that is proportionate to the complexity of the operations of the installation and the perceived environmental effects.

## Appendix 3: Index of monitoring methods

### General determinands

Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Ammonia</b>	Water quality. Determination of ammonium nitrogen by flow analysis (CFA and FIA) and spectrometric detection	BS EN ISO 11732:2005	Several suitable BS ISO standards also available that cover other methodologies. LOD and range can be varied by different instrument configuration	0.1 – 1 mg/l	0.1 – 10 mg/l
	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 – 40 mg/l
	Method for the determination of ammonium: manual spectrometric method	BS 6068-2.11:1984 ISO 7150-1 1984	Many laboratories use an acceptable automated version of this method employing a discrete analyser.	0.01 mg/l 0.03 mg/l	0 to 0.5 mg/l 0 to 50 mg/l
<b>BOD</b>	Determination of biochemical oxygen demand after n days (BOD <sub>n</sub> ) –Part 1: Dilution and seeding method with allylthiourea addition.	BS EN 1899-1 (1998)	Procedures for 5 and 7 day incubation periods are presented. In the United Kingdom the 5 day test is normal, the 7 day test may give higher results.	3 mg/l O	0 – 6000 mg/l O
	Determination of biochemical oxygen demand after n days (BOD <sub>n</sub> ) –Part 2: Method for undiluted samples.	BS EN 1899-2 (1998)	Procedures for 5 and 7 day incubation periods are presented. In the United Kingdom the 5 day test is normal, the 7 day test may give higher results.	0.5 mg/l O	0.5 – 6 mg/l O
	5 Day Biochemical Oxygen Demand (BOD <sub>5</sub> ) 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 atu.		0-6 mg/l O extended by dilution

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Chemical disinfecting agents including chlorine</b>	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.		
<b>Chloride</b>	Chloride in Waters, Sewage and Effluents 1981  Water quality: Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection	SCA blue book 51 ISBN 0117516260  BS EN ISO 15682:2001	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
<b>COD</b>	Water quality. Physical, chemical and biochemical methods. Method for the determination of the chemical oxygen demand  Water quality. Determination of the chemical oxygen demand index (ST-COD). Small-scale sealed-tube method  Determination of Chemical Oxygen Demand in waters and effluents (2207)	BS 6068-2.34:1988 Same as ISO 6060  BS ISO 15705:2002  SCA blue book 215	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.  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.  Contains 5 methods 3 of which do not use mercury compounds,	30 mg/l O  6–15 mg/l O  10 mg/l O	30 – 700 mg/l O, extended by dilution  0 –1000 mg/l O extended by dilution  Up to 400 mg/l O, extendable by dilution
<b>Conductivity</b>	Water quality. Method for the determination of electrical conductivity	BS EN 27888:1993, ISO 7888:1985			

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Conductivity and pH</b>	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			
<b>Cyanide</b>	Water quality. Physical, chemical and biochemical methods. Methods for the determination of easily liberatable cyanide	BS 6068-2.18:1986	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 6068-2.17:1986	Three methods presented		Up to 100 mg/l
	Water quality. Determination of total cyanide and free cyanide by continuous flow analysis	BS EN ISO 14403:2002, BS 6068-2.75:2002			10-100 µg/l as CN can be extended.
	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 employed.	Up to 10 mg/l
<b>Nitrite and TON</b>	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 13395:1996		TON 0.2mg/l NO2 0.01mg/l	0 – 20 mg/l 0 – 1 mg/l can be varied
	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

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Nitrogen (Total)</b>	Water quality. Determination of nitrogen. Method using oxidative digestion with peroxodisulfate	BS EN ISO 11905-1:1998, BS 6068-2.62:1998	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 ml/l, extended by dilution.
	Water quality - Determination of nitrogen - Determination of bound nitrogen (TNb), following oxidation to nitrogen oxides	BS EN12260:2003 BS 6068-2.83:2003	As above	typically 0.5mg/l	1-200mg/l
<b>Orthophosphate and total phosphorus</b>	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 ISO15681-1:2004 BS 6068-2.86:2003	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 to 1.0 mg/l Total P 0.1 to 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 ISO15681-2:2004 BS 6068-2.87:2004	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 to 1.0 mg/l Total P 0.1 to 10 mg/l.
<b>Phosphorus and Silicon</b>	Phosphorus and Silicon in Waters, Effluents and Sludges 1992	SCA blue book 147 ISBN 0117523771	Compendium of methods for both P and Si.		
<b>pH</b>	Water quality. Physical, chemical and biochemical methods. Determination of pH	BS 6068-2.50:1995, ISO 10523:1994			
<b>Suspended Solids</b>	Water quality. Determination of suspended solids. Method by filtration through glass fibre filters	BS EN 872:2005	Method does not specify filter size and filter manufacturer, UK practice is to use a Whatman GF/C paper or equivalent.	2 mg/l	
	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	

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Selection of anions</b>	Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate	BS EN ISO 10304-1:2009			Up to 20 mg/l or up to 50 mg/l depending on anion.
<b>Sulfate</b>	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
<b>TOC</b>	Water analysis– Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)  The Instrumental Determination of Total Organic Carbon and Related Determinands 1995	BS EN 1484: 1997  SCA blue book 157 ISBN 0117529796	Results obtained will be influenced by instrument dependant considerations.  Results obtained will be influenced by instrument dependant considerations  Two methods presented.	Instrument dependant  Instrument dependant nominally 0.05 to 0.2 mg/l	Up to 1000 mg/l  Instrument dependant
<b>Turbidity</b>	Water quality—Determination of turbidity  Colour and Turbidity of Waters 1981	BS EN ISO 7027:2000  SCA blue book 103 ISBN 0117519533			

## Trace Metals

Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Arsenic</b>	Water quality. Determination of Arsenic. Atomic absorption spectrometric method (hydride technique)	BS EN ISO 11969:1996	Not tested on wastewater		1 – 10 µg/l
	Water quality. Determination of total arsenic. Silver diethyldithiocarbamate spectrophotometric method	BS EN 26595:1993, BS 6068-2.1:1983, ISO 6595-1985	Extra digestion step required if effluent likely to contain silicon fluoride or difficult to decompose organic arsenic compounds		1 - 100 µg/l
	Arsenic in potable waters by atomic Absorption Spectrophotometry (Semi Automatic method) 1982	SCA blue book 69. ISBN 0117516791	Not tested on wastewater		0.05 – 5 µg/l
<b>Cadmium</b>	Water quality. Determination of cadmium by atomic absorption spectrometry	BS EN ISO 5961:1995	Two methods given, flame atomic absorption spectrometry (FAAS) and electrothermal atomisation atomic absorption spectrometry (EAAAS)		
<b>Chromium</b>	Water quality. Determination of chromium. Atomic absorption spectrometric methods	BS EN 1233:1997	Two methods given, flame atomic absorption spectrometry (FAAS) and electrothermal atomisation atomic absorption spectrometry (EAAAS)		
<b>Chromium VI</b>	Water quality. Physical, chemical and biochemical methods. Determination of chromium (VI). Spectrometric method using 1,5-diphenylcarbazide	BS 6068-2.47:1995, ISO 11083:1994	Susceptible to interference, sample to be analysed as soon as possible after sampling.		

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Mercury</b>	Water quality. Determination of mercury.	BS EN 1483:2007	Two methods presented, choice depends on available equipment and interferences present.		0.1 – 10 µg/l
	Water quality. Determination of mercury. Enrichment methods by amalgamation	BS EN 12338:1998	Includes accounts of several pre-digestion methods that may be required for wastewater analysis		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 17852:2008	Highly sensitive method that may require an additional digestion step for wastewater samples	1-10 ng/l	0.01 – 10 µg/l
	Mercury in waters, effluents, and sludges by flameless atomic absorption spectrophotometry 1978	SCA blue book 10. ISBN 0117513261		0.1 – 0.2 µg/l	0 – 2 µg/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 to 2 ng/l	
<b>Selenium</b>	Water quality. Physical, chemical and biochemical methods. Determination of selenium by atomic absorption spectrometry	BS 6068-2.45:1993, ISO 9965:1993			1 – 10 µg/l
<b>Silver</b>	Silver in Waters, Sewages and Effluents by Atomic Absorption Spectrophotometry 1982	SCA blue book 68. ISBN 0117516783		0.03 mg/l	Up to 6 mg/l

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<p><b>Trace metals</b></p> <p><b>(Multi determinand methods)</b></p>	<p>Water quality. Physical, chemical and biochemical methods. Determination of cobalt, nickel, copper, zinc, cadmium and lead: flame atomic absorption spectrometric methods</p>	<p>BS 6068-2.29:1987, ISO 8288-1986</p>	<p>Three methods are given, one involving direct determination and two involving prior complex formation and extraction. The first is applicable when concentrations are relatively high whereas the last two are most applicable for waters of an unknown nature or high in dissolved solids. Performance data not given on all elements. No performance data on wastewater.</p>	<p>0.1 to 10µg/l in clean samples</p>	<p>linear over several orders of magnitude</p>
	<p>Water quality. Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy (ICPAES)</p>	<p>BS EN ISO 11885:1998</p>	<p>LOD may not be adequate for some elements, e.g. Cadmium, arsenic. Will be the method of choice at many laboratories.</p>		
	<p>Inductively Coupled Plasma Spectrometry 1996</p>	<p>SCA blue book 163. ISBN 0117532444</p>	<p>ICPAES and ICPMS both covered. ICPMS may be the most appropriate method for very low concentrations.</p>		
	<p>Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS)— Part 1: General guidelines and basic principles</p>	<p>BS ISO 17294-1:2006</p>			
	<p>Water quality —Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of 62 elements</p>	<p>BS EN ISO 17294-2:2004</p>			
<p>Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace</p>	<p>BS EN ISO 15586:2003</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>			

## Organics

Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Acid herbicides</b>	Water quality — Determination of selected phenoxyalkanoic herbicides, including bentazones and hydroxybenzotrioles by gas chromatography and mass spectrometry after solid phase extraction and derivatization.	BS EN ISO 15913:2003	Not tested on effluents		
<b>Chlorophenols</b>	Water quality – Gas chromatographic determination of some selected chlorophenols in water	BS EN12673:1999	Includes pentachlorophenol.		0.1 µg/l to 1 mg/l
<b>Dioxins/Furans</b>	Water quality —Determination of tetra to octa-chlorinated dioxins and furans — Method using isotope dilution HRGC/HRMS	BS ISO 18073:2004			
<b>Hydrocarbon Oils</b>	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 .	
<b>Hydrocarbon Oil index</b>	Water quality — Determination of hydrocarbon oil index — Part 2: Method using solvent extraction and gas chromatography	BS EN ISO 9377-2:2000	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.		concentrations above 0.1mg/l
<b>Steroid Oestrogens</b>	The determination of steroid oestrogens in waters using chromatography and mass spectrometry (2008)	SCA blue book 220	Several methods presented	typically to 25ng/l	typically 0.1ng/l

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Organochlorine compounds</b>	Water quality — Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes — Gas chromatographic method after liquid-liquid extraction	BS EN ISO6468:1997 BS 6068-2.57:1997	May not be suitable for samples with high suspended solids (>50 mg/l)	1 – 50 ng/l with waters of low organic content	
<b>Organotin compounds</b>	The Determination of Organic, Inorganic, Total and Specific Tin Compounds in Water, Sediments and Biota 1992  Water quality – Determination of selected organotin compounds. Gas chromatographic method	SCA blue book 142. ISBN0117523607  BS EN ISO 17353:2005	No performance data presented for effluents		
<b>Organo-phosphorus compounds</b>	Water quality – Determination of parathion, parathion-ethyl and some other organophosphorus compounds in water by dichloromethane extraction and gas chromatographic analysis	BS EN 12918:1999 BS 6068-2.67:1999			up to 1µg/l
<b>PAH</b>	Water quality. Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction  Water quality . Determination of polycyclic aromatic hydrocarbons (PAH) — Part 2: Determination of six PAH by high-performance liquid chromatography with fluorescence detection after liquid-liquid extraction	BS ISO 17993:2002, BS 6068-2.79:2002  BS ISO7981-2:2005 BS 6068-2.96:2005	No performance data presented for effluents		

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
<b>Phenol Index</b>	Water quality — Determination of phenol index by flow analysis (FIA and CFA)	BS EN ISO 14402:1999 BS 6068-2.68:1999	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 – 1 mg/l
<b>Phenol Index</b>	Water quality — Part 2: Physical, chemical and biochemical methods — Section 2.12 Determination of phenol index: 4-aminoantipyrine (4-aminophenazone) spectrometric methods after distillation	BS 6068-2.12: 1990 ISO 6439:1990	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 0.01 mg/l	
<b>Phenols and phenol Index</b>	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.		
<b>Volatile halogenated hydrocarbons</b>	Water quality. Determination of highly volatile halogenated hydrocarbons. Gas-chromatographic methods	BS EN ISO 10301:1997, BS 6068-2.58:1997	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		

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Determinand	Title	Standard/ method	Comments	Reported LOD	Reported Range
VOCs	<p>The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998</p> <p>Water quality —Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption</p>	<p>SCA blue book 170.</p> <p>BS EN ISO15680:2003 BS6068-2.85:2003</p>	<p>Covers many volatile compounds including halogenated hydrocarbons. applicable to (diluted)Wastewater, no performance data presented for wastewater</p>		

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