

# Performance Standards and Test Procedures for Portable Water Monitoring Equipment

Ammonia; Chlorophyll *a*; COD; Conductivity; Dissolved Oxygen; Free Cyanide; Nitrate; Nitrite; Orthophosphate; pH; Temperature; Total Arsenic; Total Cadmium; Total Chlorine; Total Copper; Total Lead; Total Mercury; Total Nickel; Turbidity

> Environment Agency Version 2.1

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# Foreword

The Environment Agency established its Monitoring Certification Scheme (MCERTS) to deliver quality environmental measurements. The scheme is based on international standards and provides for the type-testing and subsequent product certification of instruments, the competency certification of personnel and the accreditation of laboratories.

This document contains the performance standards and test procedures for certain types of portable water monitors (PWMs) used for the monitoring of:

- Water treatment and distribution
- Waste water treatment
- Natural rivers, lakes and estuarine environments
- Water storage reservoirs
- Boreholes
- Trade effluents.

# MCERTS for PWMs:

- makes available a certification scheme that is formally recognised within the UK and is acceptable internationally
- gives confidence to regulatory authorities that instrumentation, once certified, is fit for purpose and capable of producing results of the required quality and reliability
- gives confidence to users that the instrumentation selected is robust and conforms to performance standards that are accepted by UK regulatory authorities
- supports the supply of accurate and reliable data to the public
- provides instrument manufacturing companies with an independent authoritative endorsement of their products, which will facilitate their access to international markets and increase the take-up of their products in the UK.

The MCERTS performance standards for PWMs described in this document are based on relevant sections of a number of international ISO or CEN standards, as well as taking into account other relevant national standards.

The determinands covered by this standard are some of the most important parameters when monitoring discharges from both waste water treatment works and other industrial processes as well as the monitoring of natural receiving waters. As MCERTS develops, the performance standards may be expanded to cover other determinands and industrial processes.

MCERTS provides a formal scheme for the product certification of PWM's conforming to these standards. We have appointed Sira Certification Service (the Certification Body) to operate MCERTS on our behalf.

Product certification comprises three phases. These are:

• Laboratory testing – used to determine performance characteristics, where such testing

requires a highly controlled environment

- Field testing carried out on waters representative of the intended applications
- **Surveillance initial and continuing** which comprises an audit of the manufacturing process to confirm that the manufacturer has provisions to ensure manufacturing reproducibility and to control any design changes to ensure that they do not degrade performance below the MCERTS standards.

Test organisations shall demonstrate to the satisfaction of the Certification Body that they comply with the relevant requirements of ISO/IEC 17025 for the testing of PWMs under MCERTS.

The results of previous performance tests may be acceptable to the Certification Body, if equivalent to MCERTS and carried out independently. Manufacturers' own test data may also be considered. This is applicable to both laboratory and field tests.

# **Certification Committee**

- The role of the Certification Body is to assess and certify compliance with the MCERTS standard for defined applications and/or conditions.
- In performing this role the MCERTS scheme requires the Certification Body to consider the relevance of the procedures defined in the MCERTS standard to the specific product to be certified. The technology or defined application of a specific product may make certain of the documented tests inappropriate. The Certification Body is required by the MCERTS scheme to exercise its technical judgement when considering these matters.
- Any certification decision based on technical judgement of the standard shall be taken by an appropriately independent, competent person or group of persons, who in this MCERTS standard are referred to as the "Certification Committee".
- When the Certification Committee exercises its technical judgement the rationale supporting any such decision shall be appropriately documented.
- Any certificate issued by the Certification Body shall identify any variations from the normative MCERTS standard.

On request the Certification Body shall provide the MCERTS scheme owner with the rationale for any decision based on technical judgement, within the relevant confidentiality constraints.

If you have any questions regarding the certification process, or would like further information on how to make an application, please contact:

Sira Certification Service 12 Acorn Industrial Park Crayford Road Crayford Dartford, Kent DA1 4AL Tel: +44 (0)1322 520500 email: mcerts@siraenvironmental.com

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If you have any general questions about MCERTS, please contact:

Environment Agency National Monitoring Services PO Box 519 Preston PR5 8GD

or visit the MCERTS website at www.mcerts.net

# **Record of amendments**

Version	Date	Amendment				
number						
1.1	March 2008	Cover – Total chlorine and free cyanide added to list of determinands. Forward – Section on Certification Committee added. Section 1.1 – Clauses 1.1.3, 1.1.6 and 1.1.7 added. Section 1.2 – Section on repairs, maintenance and modifications to certified PWMs added. Section 1.3 – Clause 1.3.1 amended, clauses 1.3.2, 1.3.3 and 1.3.4 added. Table 1 updated. Section 3.2 – Clauses 3.2.1, 3.2.5 and 3.2.6 added. Section 4 – Table 3 changed to 3A and 3B and updated. Notes amended. Section 5 – Clauses 5.1.1 amended. Clause 5.2.2 and 5.2.6 added. Table 5 amended. Section 6 – Text for 6.3.1 Response Time and 6.3.2 Mean Error amended. Interference effects renamed as Sample Matrix Effects 6.3.3 and split into two sections with generic procedure. Warm up Drift test 6.3.4, Length of Battery Operation 6.3.5 and Ambient Temperature and Relative Humidity 6.3.7 all with minor amendments to text. Note added to Incident Light test 6.3.8. Robustness 6.3.10 amended to reflect there is no longer a requirement for drop or vibration testing. Section 7 – Clauses covered by Annex C and I removed and replaced with clauses 7.1.1, 7.1.2 and 7.1.3. Requirement for 200 hours field use replaced with 120 measurements in clause 7.2.2. Annex order changed to reflect new document. Annex A, B, C, D and F – updated Annex E – New. Guidance on test methods for interference effects. Annex I – New. Examples of evidence. Whole document: Reference to technical committee removed and replaced by Certification				
1.2	November 2008	Committee. COD added to determinands. Table 3A updated accordingly with COD performance requirements. Table 3 Note 2, 6.3.3.1 and Annex D. Clarification of use of interference test results in combined performance characteristic Annex H – Interference test example of colour on turbidity revised and effect of chlorides on COD added				
2	June 2009	Cover – Total Arsenic, Total Copper, Total Mercury, Total Cadmium, Total Lead and Total Nickel added to list of determinands. Section 1 – Table 1 amended with additional determinands Section 3 – Tables 3C added to give performance requirements for heavy metals. Presentation of lower limit values in tables 3A, 3B and 3C updated. Section 4 – Table 4 added and subsequent table numbers amended. 4.1.3 updated and replaces 4.1.3 and 4.1.4				

		Section 5 – 5.2.6 and 5.2.8 added					
		Section 6 – Amendment to 6.3.1, 6.3.5 and 6.3.4					
		Section 7 – Note added					
		Annexes B and F – updated for heavy metals.					
		Annex G Format of MCERTS test report – updated					
2.1	August	Forward – List of determinands removed page i.					
	2010	Section 1 – Table 1 typical ranges moved to Annex G, all subsequent					
		tables renumbered.					
		Section 3 – Reporting of the limit of detection and range added as					
		general requirements.					
		Section 4 – Table 2 Performance requirements for temperature updated.					
		Linearity requirements changed to be the same as for CWMs. Note 3					
		moved to 7.4. Resolution of the display for PWMs 4.1.4 changed from					
		better than 0.1 pH units to better than 0.01 pH units.					
		Section 5 - 5.3.1 updated, 5.4.1 refers to model test report.					
		Section 6 – Wording of the response time test 6.3.1 updated.					
		Section 7 – New note added in 7.4.1 field test response time.					
		Annex B – definition for limit of detection added.					
		Annex G Format of test report removed and replaced with typical ranges					
		for measurement.					

# Status of this document

This document may be subject to review and amendment following publication. The latest version of this document is available on our website at:

www.mcerts.net

# Contents

1.	Introduction	1
1.1	Background	1
1.2	Repairs, maintenance and modifications to certified PWMs	2
1.3	Performance tests	3
2.	Scope of the MCERTS scheme	3
3.	General PWM requirements	3
3.1	General requirements for all PWMs	3
3.2	Manufacturer's published documentation	4
4.	Performance requirements	5
4.1	Performance characteristics	5
4.2	Environmental requirements	10
4.3	Robustness	11
4.4	Field test characteristics	11
5.	Provisions for test organisations	11
5.1	General requirements for test-houses	11
5.2	General requirements for testing	11
5.3	Test conditions	12
5.4	Reporting	13
6.	Laboratory test procedures	14
6.1	Initial checks	14
6.2	Manufacturer's published documentation	14
6.3	Performance tests	14
7.	Guidance on field tests	20
7.1	Objective of field test	20
7.2	Requirements of field test	21

7.3	Error under field conditions	22
7.4	Response time	22
7.5	Maintenance	23
7.6	Reporting of field test	23
ANNE	X A - Bibliography	24
ANNE	X B – Definitions	27
ANNE	X C - Certification process	31
ANNE	X D - Determination of performance characteristics	35
ANNE	X E – Guidance on usage groups	43
ANNE	X F - Standard reference methods	44
ANNE	X G – Typical ranges for measurement	48
ANNE	X H – Test methods for interference effects	49
ANNE	X I – Examples of evidence	51

# Performance Standards and Test Procedures for Portable Water Monitoring Equipment

# 1. Introduction

# 1.1 Background

- 1.1.1 This document describes the performance standards, test procedures and general requirements for the testing of portable water monitors (PWMs) for compliance with the MCERTS performance standards.
- 1.1.2 The certification process is explained in Annex C.
- 1.1.3 The Environment Agency requires operators of regulated processes to utilise MCERTS certified equipment unless otherwise agreed in writing.
- 1.1.4 It is the responsibility of the user to ensure that the selection and operation of a PWM is appropriate to the application.
- 1.1.5 Portable water monitors (PWMs) are instruments used for the determination of the value of specified parameters of water quality. They may be easily carried by one person and require no external power.
- 1.1.6 A PWM comprises all components required to make the measurement.
- 1.1.7 A PWM should provide a direct read out of the determinand, in appropriate units of measurement and not require reference to a calibration chart or table.
- 1.1.8 The determinands currently covered are:
  - ammonia
  - Chemical Oxygen Demand
  - chlorophyll *a*
  - conductivity
  - dissolved oxygen
  - free cyanide
  - nitrate
  - nitrite
  - orthophosphate
  - рH

- temperature
- total arsenic
- total chlorine
- total copper
- total mercury
- total cadmium
- total lead
- total nickel
- turbidity
- 1.1.9 The requirements in this document are intended to be technology transparent to allow the certification of any technical solution that meets the requirements.
- 1.1.10 Multi-parameter instruments which measure more than one of the above determinands, or one of the above determinands and additional parameters may also be certified under this standard for one or more of the determinands listed, see Annex C.

- 1.1.11 The overall ranges for measurements of each of the determinands covered by this standard that may be encountered in typical applications are given in Table G1, Annex G. It is recognised that the actual ranges required will be application specific including any regulatory and process needs. The MCERTS tests are designed to take these conditions into account. The certification range for a specific instrument will be agreed between the manufacturer and the Certification Body, see Annex C.
- 1.1.12 The data in Table G1 Annex G gives an indication of the water quality conditions with which a PWM might have to contend, and the other components that may coexist with the determinand.
- 1.1.13 The performance standards cover a range of pollutant levels for waste water discharges from treatment works and industrial processes regulated under EPR and other legislation. The standards also cover receiving waters and natural waters.

### **1.2** Repairs, maintenance and modifications to certified PWMs

- 1.2.1 Any spares or replacement parts for certified PWMs must meet the same performance standards as the original parts. Operators and equipment suppliers may be required to provide evidence that the replacement parts meet the required performance standards of the original equipment as specified by the PWM manufacturer.
- 1.2.2 Modifications to certified PWMs are allowable so long as manufacturers can demonstrate that these design changes do not degrade the performance of the PWM below the MCERTS performance standards.
- 1.2.3 Manufacturers must keep detailed records and drawings of all design changes to PWMs, and have provisions for design verification, inspection and testing to ensure that the PWMs still meet the required performance standards.
- 1.2.4 The Certification Body will conduct audits of the design changes to PWMs to meet the requirements of product certification. Manufacturers must notify the Certification Body of any modifications to equipment that may have a significant effect on PWM performance.
- 1.2.5 Design modifications or extensions to the range of application of a PWM may require renewed testing. The extent of this renewed testing will depend upon the nature of the modifications to the PWM.
- 1.2.6 If there is evidence that a modification has only limited effects on the performance of the PWM, then it would not be necessary to retest a PWM completely. In such cases, only a supplementary test would be required to the applicable MCERTS performance standards.
- 1.2.7 In the case of modifications to software particularly in measuring instruments documentation must be presented to the Certification Body indicating the nature of the modification as well as resultant effects on operation and functionality. The Certification Body will then decide if further testing is required.

### **1.3 Performance tests**

- 1.3.1 Performance tests for certification of a PWM against the MCERTS requirements should normally be carried out in accordance with the procedures defined in this document.
- 1.3.2 The results of previous performance tests may be acceptable to the Certification Body, if equivalent to MCERTS and carried out independently. Manufacturers' own test data may also be considered. This is applicable to both laboratory and field tests.
- 1.3.3 Variations to the performance tests described in this standard may be acceptable provided that they demonstrate to the satisfaction of the Certification Body the PWM's performance against the requirements. Any such variations shall be agreed with the Certification Body.
- 1.3.4 The decision of the MCERTS Certification Committee on matters of data is final.

# 2. Scope of the MCERTS scheme

- 2.1.1 MCERTS is designed to support the requirements of EU Directives and the standards cited within these Directives.
- 2.1.2 MCERTS for PWMs covers:
  - Processes falling under Environmental Permitting Regulations
  - Processes that used to fall under the Integrated Pollution Prevention and Control Directive (1996/61/EC) and PPC regulations
  - Consented discharges for processes that used to be regulated through provisions of the Water Resources Act,1991
  - Sites falling under the Urban Wastewater Treatment Directive (UWWTD) (91/271/EEC and 98/15/EEC)
  - Sites falling under the Groundwater Directive (80/68/EEC)
  - Monitoring undertaken as part of other relevant directives e.g. Water Framework Directive.

# **3.** General PWM requirements

#### **3.1** General requirements for all PWMs

The following requirements will be assessed by inspection or manufacturer's statement for all PWMs.

3.1.1 The manufacturer shall state the measurement range for the PWM. The range (or ranges) over which the certification will be applied shall be agreed with the Certification Committee.

- 3.1.2 All MCERTS certified PWMs shall have a unique designation that unambiguously identifies the PWM as a certified model.
- 3.1.3 The instrument shall display a direct electronic readout of the determinand, in appropriate units of measurement and not require reference to a calibration chart or table or visual comparison.
- 3.1.4 Multi parameter instruments shall clearly identify the measurement currently being displayed.
- 3.1.5 The PWM shall have a means of displaying its operating status, for example, standby, maintenance mode or malfunction.
- 3.1.6 The PWM shall operate from a self contained power supply which consists of primary cells, rechargeable cells or any other power source which is capable of providing the required power under all operating conditions. A secondary mains power source may be used for recharging and/or operating the PWM in a laboratory.
- 3.1.7 A PWM shall incorporate a method of indicating when the power supply voltage is below its normal operating limit.
- 3.1.8 A PWM which is connected to a remote sensor intended to be lowered into a watercourse, chamber or tank etc shall be provided with a suitable means of supporting the sensor unit.
- 3.1.9 The facility to log a number of readings within the instrument, or to attach an external logging device, would be of use in many applications.
- 3.1.10 The PWM shall be designed such that calibration can be easily carried out in the field, or where this is impractical functionality checks can be carried out in the field to verify the correct operation of the instrument.

#### **3.2** Manufacturer's published documentation

The following guidance or statements shall be incorporated into the manufacturer's published literature.

- 3.2.1 The manufacturer shall provide operating instructions which cover the full functionality of the instrument.
- 3.2.2 The manufacturer shall state the storage life and requirements of all scheduled spares and reagents.
- 3.2.3 The manufacturer shall identify any special equipment required for the storage of spares and reagents and a source of such equipment.
- 3.2.4 The manufacturer shall state the typical time period over which the PWM shall operate without requiring maintenance with appropriate handling, storage and use.
- 3.2.5 The manufacturer shall supply documentation with replacement chemical reagents

stating the determinand, measurement range(s), and known interferences.

- 3.2.6 The manufacturer shall state any chemical, biological and physical interferents to the measurement method.
- 3.2.7 The manufacturer shall state the Limit of Detection for the PWM.

# 4. **Performance requirements**

# 4.1 **Performance characteristics**

4.1.1 Performance characteristics have been defined in such a way that they can be calculated from test data in accordance with the principles contained within the ISO Guide to the Expression of Uncertainty in Measurement (GUM).

Specific characteristics are expressed as error (x), change in error (X), standard deviation (u) or expanded uncertainty (U) as shown in Table 1.

Annex D describes in detail how the values are calculated for each characteristic.

Characteristic	Symbol	Expression of requirement
Mean error	$\overline{x}$	The mean of the errors measured at each test
		point (See Annex D)
Repeatability	<i>U</i> <sub>R</sub>	The standard deviation of the errors measured
		at each test point (See Annex D)
Linearity	$X_L$	The maximum deviation from a straight line
_		fitted to the measured values across the
		certification range (See Annex D)
Interferents	X <sub>IN</sub>	For any influence quantity the performance
Supply voltage	$X_V$	requirement is half the range of any change in
Ambient temperature	$X_T$	error measured as the influence condition is
Relative humidity	$X_{RH}$	varied from its minimum to its maximum
Incident light	$X_{LX}$	values. (See Annex D)
Sample temperature	$X_{ST}$	
Combined performance	$U_C$	An expanded uncertainty obtained by
characteristic		combining individual performance
		characteristics. (see Annex D)

 Table 1 Expression of performance characteristics

4.1.2 Tables 2A, 2B and 2C show the maximum value permitted for each performance characteristic. In order to achieve certification, an instrument must comply with all appropriate performance requirements. The values for individual determinands are expressed as a percentage of reading, except pH which is in pH units; temperature which is in °C; turbidity and conductivity which are expressed as percentage span. This is to reflect the ways in which instrument performance is typically specified by manufacturers for each parameter.

	Symbol	Test	Temperature	pH	Conductivity	COD	Turbidity	Dissolved oxygen
			°C	pH units	% of span	% of reading	% of span	% of reading
Mean error (see 4.1.3)	$\overline{x}$	6.3.2	0.3	0.2	1	10	2	5
						(or 10 mg/l)	(or 0.2 FTU)	(or 0.2 mg/l or 2% sat)
Linearity	$X_L$	6.3.2	0.2	0.1	0.2	5	1	2.5
Repeatability (see 4.1.3)	u <sub>R</sub>	6.3.2	0.2	0.1	0.5	5	1	2.5
						(or 5 mg/l)	(or 0.1 FTU)	(or 0.1 mg/l or 1% sat)
Sample matrix effects (notes 1,2)	$X_{IN}$	6.3.3	-	-	-	5	1	2.5
Supply voltage (battery)	X <sub>V</sub>	6.3.6	0.2	0.05	0.25	2.5	0.5	1
Ambient temperature	$X_{T}$	6.3.7	0.2	0.1	0.5	5	1	2.5
Relative humidity	$X_{RH}$	6.3.7	0.2	0.1	0.5	5	1	2.5
Incident light	$X_{LX}$	6.3.8	0.2	0.05	0.25	2.5	1	1
Sample temperature	X <sub>ST</sub>	6.3.9	-	0.1	0.5	5	0.5	2.5
Combined performance characteristic	U <sub>C</sub>	Annex D	0.5	0.3	1.5	12	2.5	6
Response time		6.3.1	Value achieved in tests shall be reported (note 3)					
Warm up drift test		6.3.4	The time necessary for stabilising the output signal shall not be greater than 2 minutes (note 3)					
Length of battery operation		6.3.5	The length of operation without requiring recharging or battery replacement shall be greater than 12 hours or 50 independent measurements (note 4)					

# Table 2A Performance characteristics for PWMs

Not all tests may be necessary. The certification committee, in consultation with the manufacturer, will make the decision as to which tests are required for an individual instrument.

	Symbol	Test	Ammonia as N	NO <sub>3</sub> and NO <sub>2</sub> as N	Ortho-phosphate	Chlorophyll a	Total chlorine	Free cyanide
			% of reading	% of reading	% of reading	% of reading	% of reading	% of reading
Mean error (see 4.1.3)	$\overline{x}$	6.3.2	10	5	10	15	10	10
			(or 0.03 mg/l – as N)	(or 0.2 mg/l - as N)	(or 0.05 mg/l - as P)	(or 0.3 µg/l)	(or 0.05mg/l)	(or 0.05mg/l)
Linearity	X <sub>L</sub>	6.3.2	5	2.5	5	5	2	2
Repeatability (see 4.1.3)	u <sub>R</sub>	6.3.2	5	2.5	5	10	5	5
			(or 0.015 mg/l – as N)	(or 0.1 mg/l - as N)	(or 0.025 mg/l - as P)	(or 0.2 µg/l)	(or 0.025mg/l)	(or 0.025mg/l)
Sample matrix effects (note 2)	X <sub>IN</sub>	6.3.3	5	2.5	5	5	5	5
Supply voltage (battery)	X <sub>V</sub>	6.3.6	2.5	1	2.5	5	2.5	2.5
Ambient temperature	X <sub>T</sub>	6.3.7	5	2.5	5	10	2.5	2.5
Relative humidity	X <sub>RH</sub>	6.3.7	5	2.5	5	5	5	5
Incident light	X <sub>LX</sub>	6.3.8	2.5	1	2.5	5	2.5	5
Sample temperature	X <sub>ST</sub>	6.3.9	5	2.5	5	5	5	5
Combined performance characteristic	U <sub>C</sub>	Annex D	12	6	12	18	12	12
Response time		6.3.1	Value achieved in test	s shall be reported (no	ote 3)			
Warm up drift test		6.3.4	The time necessary for stabilising the output signal shall not be greater than 2 minutes (note 3)					
Length of battery operation		6.3.5	The length of operation without requiring recharging or battery replacement shall be greater than 12 hours or 50 independent measurements (note 4)					

# Table 3B Performance characteristics for PWMs

Not all tests may be necessary. The certification committee, in consultation with the manufacturer, will make the decision as to which tests are required for an individual instrument.

	Symbol	Test	Total Arsenic	Total Copper	Total Mercury	Total Cadmium	Total Lead	Total Nickel
			% of reading	% of reading	% of reading	% of reading	% of reading	% of reading
Mean error (see 4.1.3)	$\overline{x}$	6.3.2	10	10	10	10	10	10
			(or 7.5 µg/l)	(or 1.0 µg/l)	(or 0.01 µg/l)	(or 0.01 µg/l)	(or 1.0 µg/l)	(or 3.0 µg/l)
Linearity	X <sub>L</sub>	6.3.2	5	5	5	5	5	5
Repeatability (see 4.1.3)	u <sub>R</sub>	6.3.2	5	5	5	5	5	5
			(or 3.75 µg/l)	(or 0.5 µg/l)	(or 0.005 µg/l)	(or 0.005 µg/l)	(or 0.5 µg/l)	(or 1.5 µg/l)
Sample matrix effects (note 2)	X <sub>IN</sub>	6.3.3	-	-	-	-	-	-
Supply voltage (battery)	X <sub>V</sub>	6.3.6	2.5	2.5	2.5	2.5	2.5	2.5
Ambient temperature	X <sub>T</sub>	6.3.7	5	5	5	5	5	5
Relative humidity	X <sub>RH</sub>	6.3.7	5	5	5	5	5	5
Incident light	X <sub>LX</sub>	6.3.8	2.5	2.5	2.5	2.5	2.5	2.5
Sample temperature	X <sub>ST</sub>	6.3.9	5	5	5	5	5	5
Combined performance characteristic	U <sub>C</sub>	Annex D	12	12	12	12	12	12
Response time		6.3.1	Value achieved in	tests shall be repor	rted (note 3)			
Warm up drift test		6.3.4	The time necessary for stabilising the output signal shall not be greater than 2 minutes (note 3)					)
Length of battery operation		6.3.5	The length of operation without requiring recharging or battery replacement shall be greater than 12 hours or 50 independent measurements (note 4)					

# Table 3C Performance characteristics for PWMs

Not all tests may be necessary. The certification committee, in consultation with the manufacturer, will make the decision as to which tests are required for an individual instrument.

#### Notes to Tables 2A, 2B and 2C

- 1 A dissolved oxygen PWM shall be tested to check for the effect of chlorides present in the sample. For dissolved oxygen instruments intended solely for freshwater use with no built in salinity compensation, this test may be omitted.
- 2 The scope of interference testing shall be agreed, on a case by case basis, between the manufacturer and the Certification Body. Interferents may be physical (e.g. colour) or chemical. When interference effects are not included in the combined uncertainty, this shall be stated on the certificate.
- 3 Where an instrument operates in a batch mode, based on the development of a chemical reaction to the sample over a fixed period of time, the response time and warm up drift test may be omitted. Under these circumstances the normal time required to perform a measurement (i.e. sample preparation, addition of chemicals, reaction time for development and measurement) shall be reported.
- 4 Where an instrument can be configured to operate either continuously or in a power-save/batch mode the power-save/batch mode shall be used and requirement for 50 measurements must be met.
- 4.1.3 The error requirements for the majority of parameters are expressed as a percentage of reading. As the value of the determinand becomes small it is increasingly difficult to determine the error of a measurement, expressed as a percentage of reading, in any meaningful way. This is caused by limitations on the resolution or accuracy of reference methods.

Where two values are given (e.g. Mean error for ammonia is shown as 10 (or 0.03 mg/l – as N), then the greater value apples to the test.

Example – If the test point for an ammonia instrument is 0.1 mg/l, then 10% of reading = 0.01 mg/l which is below 0.03 mg/l, therefore the mean error test requirement will be 0.03 mg/l and the repeatability requirement will be 0.015 mg/l.

- 4.1.4 The resolution of the reading displayed by a PWM shall be 0.1°C or better for temperature probes and 0.01 pH units or better for pH probes. Any different resolution shall be agreed with the Certification Committee.
- 4.1.5 All pre-set data, including calibration and alarm set points and adjustments, shall be retained for a minimum period of 1 hour to allow for battery changes.

# 4.2 Environmental requirements

- 4.2.1 Guidance on the operating conditions to which PWMs are likely to be subjected is given in Annex E. The rated operating conditions have been divided into two usage groups for typical operating environments.
- 4.2.2 The extent of the environmental testing shall be agreed between the manufacturer and the Certification Body, taking into account the intended usage class of the instrument, see Annex E.

4.2.3 For usage group II, the minimum rated operating conditions for ambient temperature shall be  $-5^{\circ}$ C to  $+35^{\circ}$ C. See Annex E for more detail.

### 4.3 Robustness

4.3.1 The instrument shall be designed to withstand the knocks and jolts likely to occur in routine use.

### 4.4 Field test characteristics

Table 3 provides a summary of the field test characteristics as detailed in Section 7.

Requirement	Reference	Note
Period of operation	7.2	Shall consist of at least 120 measurements taken over a period of at least 3 months.
Error	7.3	A minimum of 24 reference measurements shall be taken. In at least 90% of these reference measurements the error shall be less than or equal to the combined performance characteristic as given in Table 2.
Response time	7.4	Measured at the beginning and end of the trial. Values achieved shall be reported.
Maintenance	7.5	Reported as detailed in 7.5.1 to 7.5.6

### Table 3 Summary of field trial

# 5. **Provisions for test organisations**

#### 5.1 General requirements for test-houses

5.1.1 Test organisations shall demonstrate to the satisfaction of the Certification Body that they comply with the relevant requirements of ISO/IEC 17025 for the testing of PWMs under MCERTS.

# 5.2 General requirements for testing

5.2.1 Standard reference methods for each determinand are described in Annex F. Where agreed by the Certification Body, simulated inputs or secondary standards may be used.

Note: Ideally, the uncertainty of the reference system should be no more than  $1/5^{th}$  of the performance requirement being tested.

- 5.2.2 With prior agreement of the Certification Committee fewer measurements than required by the individual test may be made if this can be justified e.g. where a pattern of low variability is supported by statistical analysis. This shall be shown in the test report.
- 5.2.3 The PWM shall be maintained, cleaned or recalibrated in line with manufacturer's instructions prior to any test, but adjustments shall not be carried out during the course of the test.
- 5.2.4 For dip sensors, during all tests which use more than one reference solution, the following sensor treatment shall be followed, unless stated in the test procedure and agreed with the Certification Committee.

The sensor shall be rinsed with demineralised water prior to the test, then rinsed with the new solution and finally immersed in fresh reference solution. The sensor will then be rinsed with the next value of wash and then immersed in the next value of the reference solution. In every case, measurements shall be made in continuously stirred solutions.

- 5.2.5 The manufacturer's operating instructions shall be followed, specifically in relation to sample preparation and instrument cleaning.
- 5.2.6 Testing should be undertaken using the manufacturer's supplied reagents or, where the manufacturer allows, reagents prepared to the manufacturer's specification.
- 5.2.7 Data from tests shall be processed in accordance with the calculation methods summarised in Annex D.
- 5.2.8 Any self-cleaning mechanisms or other automatic maintenance functions shall be disabled during any laboratory test unless these are part of the normal measurement cycle or the test procedure states otherwise.

# 5.3 Test conditions

5.3.1 Table 4 shows the standard test points that should be used as required by each individual test. In situations where the following test points are not practical, alternative test points shall be agreed with the certification committee.

Test point	Limits of determinand value
1	$(5\% \pm 2.5\%)$ of the certification range
2	$(25\% \pm 5\%)$ of the certification range
3	$(50\% \pm 5\%)$ of the certification range
4	$(75\% \pm 5\%)$ of the certification range
5	$(95\% \pm 5\%)$ of the certification range

#### Table 4Test point values

*NOTE:* Where it is not possible to produce standards to the test points identified in Table 4, secondary standards may be used as an alternative. Secondary standards

may be provided by the instrument manufacturer as specific to the instrument but should be identified to a specific concentration and referenced to a primary standard. This may be particularly relevant to chlorophyll measurements where the preparation of a range of standards from a single stock algal culture presents measurement issues relating to the chlorophyll behaviour when diluted. For chlorophyll a measuring instruments the use of secondary standards for interference and performance tests is recommended with the exception of the mean error test, linearity and repeatability which must be performed with a prepared algal sample at the test points specified. See Annex F for recommendations on producing algal samples and suitable standards.

5.3.2 Table 5 gives the reference conditions for possible influence quantities. Tests shall be carried out with all influence quantities at their reference values, including tolerances, unless where specifically varied in any one test.

Influence quantity	<b>Reference value</b>	Tolerance
Ambient temperature	20°C	±2°C
Ambient humidity at 20°C	<60%	-
Incident light	Existing local light level	-
Sample temperature	20°C	±5°C
Sample flow-rate	To be stated by the	$\pm 5\%$ of reference
	manufacturer	value
Supply voltage (battery)	To be stated by the	±2%
	manufacturer	
Presence of know interferents	Below minimum	-
	detectable value	
Conductivity (pH and	>200 µS/cm	-
instruments with ion selective		
electrodes)		

#### **Table 5 Reference conditions**

- 5.3.3 Tests for the effect of ambient temperature and relative humidity shall be carried out using a climatic chamber, which can vary the temperature and humidity over the range for which the PWM is to be certified.
- 5.3.4 Where an instrument incorporates battery saving routines, such as automatic switch off after a pre-set interval, this shall be disabled during laboratory testing. Alternatively the instrument may be powered from a DC power supply (except during test 6.3.5).
- 5.3.5 Where an instrument is only activated to give a reading whilst a button or switch is being held down by the user, the reading taken shall be that displayed after 10 seconds or the manufacturer's recommended interval, whichever is shorter.

# 5.4 Reporting

5.4.1 The test-house shall produce a report using the model test report provided by the

Certification Body.

# 6. Laboratory test procedures

# 6.1 Initial checks

6.1.1 The test-house shall ensure that the PWM is set up calibrated and adjusted in accordance with the manufacturer's instructions.

*NOTE: The manufacturer may set up and demonstrate the PWM before the testing begins.* 

- 6.1.2 The test-house shall verify by inspection or by a statement from the manufacturer that the general requirements listed in Section 3.1 are fulfilled, as appropriate to the PWM under test. The means by which each requirement is fulfilled shall be reported.
- 6.1.3 The test-house shall verify and report that the displayed operational status is correct.
- 6.1.4 The test-house shall report the resolution of the displayed reading.

# 6.2 Manufacturer's published documentation

6.2.1 The test-house shall verify and report that the manufacturer's published documentation includes the relevant statements required in Section 3.2, as appropriate to the PWM under test.

# 6.3 **Performance tests**

#### 6.3.1 Response time

Where an instrument operates in a batch mode, based on the development of a chemical reaction to the sample over a fixed period of time, the response time test may be omitted. Under these circumstances the normal time required to perform a measurement (i.e. sample preparation, addition of chemicals, reaction time for development and measurement) shall be reported.

For other instruments provide means to apply a step change in the determinand to be applied to the sensor. For dip sensors, two continuously stirred solutions of known determinand value contained in beakers may be used. When transferring the sensor unit from one beaker to the other, shake off the test solution from the sensor unit but do not wipe or rinse. This action should be competed as quickly as possible in order to provide a single step change in determinand value.

Provide the means of recording the measurement during the test, either by activating an internal memory or attaching a recording device to the instrument output. If these options are not available, e.g. hand held meters, the reading with the time step can be recorded manually but must be sufficiently frequent to reproduce the instrument response curve. Provide the PWM with a solution having a determinand value of 5 - 25% of the certification range until a constant output reading is obtained.

Apply a step change by switching to a solution having a determinand value of 75 - 95% of the certification range. Record the time of switching.

Record the instrument output and continue to supply this solution until the measurement is stable.

Apply a decreasing step change by reverting to the lower value solution, recording a second event marker at the instant of switching. Record the instrument output and continue to supply this solution until the measurement is stable.

From the instrument record, calculate the size of step change and the response time.

The response time is the time required for the instrument output to reach and remain within a band between the initial value *plus* (for an increased step) or *minus* (decreased step) 90% and 110% of the step change.

Repeat the procedure twice more and report the mean response times for an increasing and a decreasing step change.

NOTE: The solutions used for the response time test need not be certified standard so long as the solutions are of known values and stable over the period of the test. Should the reading fail to maintain a value within the 90% to 110% band for the increasing or decreasing changes, report the value which it does reach. In such cases, it will not be possible to calculate the response time.

# 6.3.2 Mean error, linearity and repeatability

Expose the sensor unit, in turn, to five reference solutions at test points 1 to 5 (see Table 4) in ascending order. Allow sufficient time for each reading to stabilise and record the readings from the local display. Repeat the series of test points in descending order. Repeat the sequence of ascending and descending points twice more to give six discrete readings at each test point.

Where the PWM operates in a batch type mode each repeat measurement shall be made as independent measurement using the same reference solution.

Calculate and report the mean error,  $\bar{x}$ , and repeatability,  $u_R$ , for each test point and the linearity error,  $X_L$ .

# 6.3.3 Sample matrix effects

# 6.3.3.1 General interference tests

The scope of the interference testing shall be agreed between the manufacturer and the Certification Body based on knowledge and experience relevant to the nature of the water, the instrument, the operating method and the determinand. If several potential interferents are identified the instrument shall be tested for the effect of at least two interferents. Testing is based on the method described in BS EN ISO 15839:2006 and involves spiking calibration solutions at 50% and 100% of the expected interference level at test point 2 and 4.

A generic procedure is described below.

Expose the sensor to a blank calibration solution (where a blank is not possible the level of determinand in the solution should be below the limit of detection of the instrument) and record the PWM response,  $y_0$ . Prepare two further blank calibration solutions spiked with the selected interferent at 50% and 100% of the expected interference level. Record the PWM response as  $y_1$  and  $y_2$  respectively.

Prepare three calibration solutions at test point 2, the first unspiked the second spiked with the selected interferent at 50% of the expected interference level and the third at 100% of the expected interference level. Record the PWM responses as  $y_{3,}$   $y_{4,}$   $y_{5}$  respectively.

Prepare three calibration solutions at test point 4, the first unspiked, the second spiked with the selected interferent at 50% of the expected interference level and the third at 100% of the expected interference level. Record the PMW responses as  $y_{6}$ ,  $y_7$ ,  $y_8$  respectively.

Calculate and report the change in the reading at zero determinand and interferent at 50% ( $y_1$ - $y_0$ ) and interferent at 100% ( $y_2$ - $y_0$ ). Calculate and report the change in the reading at determinant test point 2 with the interferent at 50% ( $y_4$ - $y_3$ ) and with the interferent at 100% ( $y_5$ - $y_3$ ). Also calculate and report the change in the reading at determined test point 4 with the interferent at 50% ( $y_7$ - $y_6$ ) and with the interferent at 100% ( $y_8$ - $y_6$ ).

Identify the maximum change as the error due to interferents,  $X_{IN}$ .

*NOTE:* Example test methods are given in Annex H for specifically identified interferences. For some determinands the above approach may not be appropriate. Annex H contains examples of how an alternative simplified testing approach may be adopted for these determinands.

# 6.3.3.2 Salinity compensation for dissolved oxygen instruments

For instruments intended solely for freshwater use with no salinity compensation this test may be omitted. This shall be reported on the MCERTS certificate.

Prepare two solutions using distilled water, the first containing chloride at an approximate concentration of 25-30 g  $l^{-1}$  NaCl using sea salts, and the second unmodified. Aerate both to ensure they are at 100% saturation. This should be confirmed using a calibrated reference dissolved oxygen meter with in built salinity compensation.

Expose the sensor firstly to the un-modified solution at 100% saturation. Once stabilised, record the instrument response as percentage saturation and as mg/l  $O_2$ . Move the sensor to the 'sea water' reference solution at 100% saturation and once stabilised record the instrument response as percentage saturation and as mg/l  $O_2$ .

Repeat a further two times, carefully washing the sensor with distilled water between measurements. The manufacturer's instructions should be followed with regard to positioning and movement of the sensors during measurement.

Calculate and report the change in error,  $X_{sc}$ , for both percent saturation and mg/l ranges. Confirm change using Table A.1 in ISO 5814: 1990.

# 6.3.4 Warm up drift test

*NOTE:* Where an instrument operates in a batch mode, based on the development of a chemical reaction to the sample over a fixed period of time, the warm up drift test may be omitted.

The instrument will be switched off overnight. Expose the sensor to a stirred reference solution at test point 4 (or 100% saturation for dissolved oxygen instruments), see Table 4. The temperature of the reference solution should be maintained within  $\pm$  2°C during the test. The instrument will be switched on and readings will be taken every 10 seconds for the first 2 minutes. Continue to take readings every 30 seconds up to a maximum of 10 minutes, then every 5 minutes up to 30 minutes, then every 30 minutes for at least 2 hours.

If the instrument has an internal logger available this will be enabled at the earliest opportunity. Also, if an analogue output is available this will be attached to a logging system. When a logging device is active, manual measurement may be unnecessary.

For PWMs which are only activated whilst a switch is held down by the user; incorporate a power save function or operate in a batch type mode, repeated measurements shall be made at a frequency appropriate to the instrument up to a period of at least 2 hours.

If the instrument has an automatic shutdown, which can be disabled by the user, then it shall be disabled for the period of the test. Where it is not possible to over-ride the shutdown then the test will be carried out for a total period of at least 30 minutes during which the instrument shall be switched back on immediately each time it switches off.

The warm up drift shall be reported in the following manner. A graph should be produced showing the measurements as a time series. The final stable value (V<sub>s</sub>), the value after 1 minute and the difference between them shall be calculated and reported. Also, the time required for the measurement to reach and remain within a band defined by  $V_s \pm u_R$  shall be calculated and reported. (Where  $u_R$  is the repeatability value shown in table 2 for the instrument determinand).

The mechanism used to record instrument readings and any other deviation from this test requirement shall be agreed with the certification committee who will make a decision based on the instrument under test.

# 6.3.5 Length of battery operation

This test is intended to ensure that the instrument can operate for a suitable period and determine whether it is energy efficient. It may not be practical to determine the full life of the batteries, so this test has been devised. In the laboratory, the PWM shall be supplied with new batteries or alternatively where rechargeable batteries are used these will be fully charged.

For a PWM which is continuously powered, (i.e. the instrument does not have a power save function which shuts the instrument down after a measurement or a period of inactivity), the PWM shall be switched on and set with the sensor exposed to a reference solution having a determinand value at test point 4.

The instrument shall be run at the highest practical measurement frequency, agreed with the manufacturer, for a period of 24 hours.

The instrument shall be left making continuous measurements until the low battery warning is activated. The length of operation shall be recorded. If after 24 hours continuous operation the instrument is still operating correctly then the test shall be ended.

For PWMs which are only activated whilst a switch is held down by the user, incorporate a power save function or operate in a batch type mode, repeated measurements shall be made on a reference solution at test point 4 and the number of readings recorded before:

- the low battery warning is activated
- The instrument fails to activate.

If after 50 complete measurements the instrument is functioning correctly then the test shall be ended.

Variations from this test requirement shall be agreed with the certification committee who will make a decision based on the instrument under test.

#### 6.3.6 Low voltage test

The batteries shall be removed and power supplied from a variable DC power supply, initially set to the nominal battery voltage. Expose the sensor unit to a reference solution having a determinand value at test point 4. Reduce the supply voltage in 0.5V steps. Record and report:

- the voltage at which the low battery alarm occurs
- the voltage at which the reading changes by more than 10% (if this occurs before the PWM switches off)
- the voltage at which the PWM switches off or fails to switch on.

Identify and report the maximum change in error due to supply voltage,  $X_V$ , prior to activation of the low battery alarm.

#### 6.3.7 Ambient temperature and relative humidity

During environmental testing, where practicable, the PWM shall be continuously

supplied with a reference solution of known value at sample reference conditions.

Where an instrument operates in a batch mode, based on the development of a chemical reaction to the sample over a fixed period of time the manufacturer's recommendations for storage of reagents shall be followed.

The PWM is placed in a climatic chamber (both sensor and controller if separate), the temperature of which is set to 20°C. The PWM must be allowed to warm up and be calibrated, if required.

The following conditions shall be set in the climatic chamber in the order given in Table 6, where Tmin and Tmax are the minimum and maximum values for ambient temperature over which the PWM is to be certified. The transitional temperatures (steps 2 and 5) may be omitted.

	Temperature °C	Humidity	Minimum exposure time
1. Reference	20	Reference	2 hours
2. Transition	(Tmax+ref)/2	Reference	2 hours
3. High T dry	Tmax	Dry	2 hours
4. Reference	20	Reference	2 hours
5. Transition	(20+Tmin)/2	Reference	2 hours
6. Low T	Tmin	Reference	2 hours
7. Reference	20	Reference	2 hours
8. High T humid	Tmax	≥95% RH	6 hours
9. Reference	20	Reference	2 hours

 Table 6 Test cycle for environmental conditions

At each step, after a sufficient stabilisation period, the PWM shall be provided with a reference solution having a determinand value at test point 4 and the output recorded. For dissolved oxygen instruments expose the sensor to a reference solution of 100% saturation. The measurement shall be repeated three times to give three discrete readings.

Calculate and report the change in error due to ambient temperature,  $X_T$ , from steps 3, 4 and 6.

Calculate and report the change in error due to high humidity and temperature,  $X_{RH}$ , from steps 7 and 8.

# 6.3.8 Incident light test

NOTE: This test shall be applied to all PWMs using optical measurements methods. The need to test PWMs utilising other measurement methods will be considered by the Certification Committee on a case by case basis.

The light source shall be chosen to simulate the spectrum of natural sunlight, for example a high pressure xenon arc lamp. Illuminate the sensor from above.

Expose the sensor to a reference solution having a determinand value at test point 4 (see Table 4). For dissolved oxygen instruments expose the sensor to a reference solution of 100% saturation.

Position the sensor in the orientation expected during normal operation.

Cover the instrument to prevent any ambient light reaching the sensor. Record the measurement value given by the PWM.

Illuminate the sensor from above with an intensity of  $1.120 \text{ kW/m}^2$  and record the measurement value given by the PWM.

Repeat the procedure a further two times.

Calculate and report the change in error  $X_{LX}$ , due to incident light.

*NOTE:* Further guidance on testing for solar radiation testing can be found in BS EN 60068-2-9:2000 and BS EN 60068-2-5:2000.

### 6.3.9 Sample temperature

Expose the sensor unit to a reference solution having a determinand value at test point 4 (see Table 4). For dissolved oxygen instruments expose the sensor to a reference solution of 100% saturation. Record the value of the output with the sample temperature at the lower limit of the rated operating conditions, the reference value and at the upper limit of the rated operating conditions. Take three discrete measurements at each value of sample temperature.

Calculate and report the change in error due to sample temperature,  $X_{ST}$ .

*NOTE:* Stability of reference standards with temperature variations should be considered. Care should be taken in selecting suitable standards for this test.

#### 6.3.10 Robustness

There are no specifications for drop tests or vibration tests. However, if a PWM has undergone such tests for other purposes, then this will be reported on the certificate.

# 7. Guidance on field tests

NOTE: Table 3 (section 4.4) summarises field trial requirements.

# 7.1 Objective of field test

7.1.1 The objectives of the field test are to demonstrate that the performance of a PWM is maintained under representative operational conditions and to allow an assessment of the reliability over an extended period of normal operation.

It is recognised that no two field trials will be identical and the nature of the trial

will depend on many factors such as:

- The PWM being tested
- The intended applications for the PWM
- The presence of existing manufacturer and / or customer data.

Annex I gives guidance in the form of examples of different approaches used to meet the requirement of the field trial.

- 7.1.2 A test plan detailing the proposed field trial shall be submitted to the Certification Body for consideration by the Certification Committee. This shall include:
  - Nature of site and specific application
  - Typical range of determinand
  - Reference method
  - Traceability
  - Installation environment.

NOTE: A check sheet is available from the Certification Body to assist in collecting the information the Certification Committee will need to establish whether data from an existing installation would be acceptable as a basis for certification.

7.1.3 The decision of the Certification Committee on matters of the test plan and data is final.

# 7.2 **Requirements of field test**

- 7.2.1 The PWM under test shall be the same model as for the laboratory testing. Any differences between to the instrument shall be justified and agreed with the Certification Body.
- 7.2.2 The field test for a PWM shall consist of at least 120 measurements. It is expected that the PWM under test will be in regular and frequent use and the field test shall take at least 3 months. Only in exceptional cases, which must be fully justified (for example, in the case of operation-related interruptions or process breakdown), will it be possible to count shorter testing periods towards the test period.
- 7.2.3 Details of ambient conditions pertaining during the field test facilitate the understanding of field test data. Where possible, field test data should be supported by any such relevant data on ambient conditions.
- 7.2.4 During the field test, the performance characteristics of the PWM shall be determined under representative operational conditions. This means that the reference measurements (see 7.3.3) shall only be taken when all parameters are within the rated operating conditions of the PWM.

7.2.7 Data obtained when conditions are outside the rated operating conditions can be reported to demonstrate performance in excess of the MCERTS requirements.

### 7.3 Error under field conditions

- 7.3.1 The error of a PWM is determined by comparing the measurement obtained by the PWM with that from a standard reference method (SRM). SRMs for the determinands covered by this Standard are listed in Annex F.
- 7.3.2 If a second PWM is being used for the reference measurement then this should be a certified measurement technique suitable for the application. If appropriate, both the PWM under test and the reference instrument should be calibrated with the same calibration materials.
- 7.3.3 A minimum of 24 pairs of reference measurements (simultaneous determinations from the PWM and the SRM) shall be taken over the duration of the field test. The timing of readings shall be chosen such that:
  - they are spread throughout the field test period
  - the determinand value is stable (i.e. does not change by more than  $\pm 5\%$  whilst each pair of readings is being taken)
  - they are carried out at a number of different times during the normal operating cycle(s) for the site whether these be diurnal, weekly or monthly
  - they are spread across as wide a range of determinand values as possible
  - they encompass as wide a range of the proposed applications for the instrument as possible (typical applications are given in Annex G)
  - they are carried out at a number of different points during the maintenance cycle of the PWM.
- 7.3.4 For each pair of reference measurements the error shall be determined, see Annex D, and reported.

#### 7.4 **Response time**

7.4.1 Two response time tests shall be carried out according to clause 6.3.1. The first shall be carried out at the start of the field test and the second at the end. For the test at the end of the field test, normal procedures to operate the instrument shall be followed but no additional maintenance shall be carried out.

Note: It should be noted that low conductivity in some upland raw waters can give rise to drift and slow response on pH meters.

Note: The results from the laboratory response time test may be used as the start response time value but this may increase the likelihood of failing to meet this

#### performance requirement.

#### 7.5 Maintenance

- 7.5.1 Any maintenance activities, scheduled or otherwise, required during the field test shall be recorded.
- 7.5.2 Settings and frequency of any maintenance or calibration routines shall be recorded.
- 7.5.3 Any changes to the frequency of any automatic or scheduled manual maintenance activities during the field test period shall be reported.
- 7.5.4 If one or more major components (for example, the entire sensor) of the PWM are replaced during the field test period, the matter shall be referred to the Certification Body who shall consider whether additional data is required.
- 7.5.5 The following shall be reported with regards to each unscheduled maintenance event:
  - nature of the fault
  - actions required to remedy fault
  - time taken in man-hours to remedy the fault
  - any problems or difficulties experienced in following the manufacturer's recommendations for fault diagnosis and repair
  - requirement for manufacturer's attendance on site
  - any components replaced
  - total time while the PWM was not operational, i.e. from point of failure to time the PWM was back available for use.
- 7.5.6 If the total time while the PWM is not operational due to failure is more than two weeks, the Certification Body may require an extension of the test to ensure that sufficient operational data are collected.

#### 7.6 **Reporting of field test**

7.6.1 The field test shall be summarised in the MCERTS test report. This should be forwarded to the certification committee for consideration.

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# **Annex B – Definitions**

Note: Underlined terms within a definition are themselves defined in this Annex.

**Arsenic:** A highly toxic metal released naturally into the aquatic environment as a result of weathering of arsenic-containing rocks or from industrial and agricultural pollution. Total arsenic includes dissolved arsenic and arsenic attached to matter.

**Cadmium:** A heavy metal that accumulates in the environment. Cadmium and several cadmium-containing compounds are known carcinogens and can induce many types of cancer. Total cadmium includes dissolved cadmium and cadmium attached to matter.

Certification range: Range over which the <u>PWM</u> is certified.

**Chemical Oxygen Demand (COD):** The COD of a water or wastewater is a measure of the quantity of oxygen required to completely oxidise all the organic and inorganic material in the water under standard empirical conditions. The COD value, also known as the Dichromate Value, is determined by measuring the quantity of acidic dichromate consumed by a sample of the water under standard conditions.

**Chlorine:** A powerful oxidant used for disinfection of water and wastewaters. Free chlorine is defined as the concentration of residual chlorine in water present as dissolved gas (Cl2), hypochlorous acid (HOCl), and/or hypochlorite ion (OCl-). Combined chlorine is defined as the residual chlorine existing in water in chemical combination with ammonia or organic amines which can be found in natural or polluted waters. Total chlorine is the sum of free and combined chlorine.

**Chlorophyll** *a***:** A cyclic tetrapyrrol compound with a magnesium atom chelated at the centre of the porphyrin ring system. Green in colour, all algae contain Chlorophyll *a* as a large fraction of their photosynthetic pigments.

**Combined performance characteristic:** Combination of individual <u>performance</u> <u>characteristics</u>, see Annex E.

**Conductivity:** The ability of a material to conduct electrical current. For aqueous samples conductivity is measured in  $\mu$ Siemens and mSiemens. Temperature compensation is required to remove the effect of liquid temperature. Commonly used as a surrogate for TDS.

**Copper:** A metal released into the environment by both natural sources and human activities. Soluble copper compounds form the largest threat to human health. High uptakes of copper may cause liver and kidney damage. Total copper includes soluble copper and insoluble copper (attached to matter).

**Cyanide:** A highly toxic chemical which is characterised by the presence of a cyano functional group, CN-. Inorganic compounds include simple salts of cyanide with various metals such as sodium cyanide NaCN(s) and potassium cyanide KCN(s). These simple salts are highly soluble in water.

**Determinand:** The property that is required to be measured.

Dip sensor: Sensor designed to be located directly in a channel or tank and in contact with

the process fluid.

Drift: Measure of the <u>PWM</u>'s response to a defined <u>reference material</u> over a period of time.

**Error** (x):. Difference between the value given by the <u>PWM</u> and the conventional true value, see Annex E.

**Expanded uncertainty (U):** Quantity defining a level of confidence about the result of a measurement that may be expected to encompass a specific fraction of the distribution of values that could reasonably be attributed to a measurement.

NOTE: The level of confidence would typically be 95%.

Flow cell: <u>Sensor</u> housing designed to be mounted directly in series with a process line or sample line.

Insertion sensor: Sensor unit designed to be inserted directly into a process pipe.

**Influence quantity:** Any quantity, generally external to the equipment, which may affect the performance of the equipment.

**Interferent:** Property of the fluid, other than the <u>determinand</u>, which influences the measurement.

**Lead:** A highly dangerous metal which is found in the environment as a result of human activities. It is one metal with the most damaging effects on human health, entering human body through uptake of food, water and air. Unwanted effects include brain damage or behavioural disruptions of children. Lead has poisoning effects for humans but also on shellfish even at low concentration. Total lead includes dissolved lead (PbCO<sub>3</sub> or Pb(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>) and lead attached to matter.

**Linearity:** Measure of fit of the <u>PWM</u>'s response to a straight line using a number of values of a <u>determinand</u>.

**Limit of detection (Instrument detection limit):** is the lowest quantity of the determinand that the PWM can be distinguished from the absence of that substance (a *blank value*) within a stated confidence limit (generally 1%). Detection limits are affected by the sample matrix and may therefore be application specific.

**Lower limit value:** Limit value for errors as the measurement approaches zero and expression as percentage of value becomes meaningless.

**Mercury:** Mercury occurs in deposits throughout the world and it is harmless in an insoluble form, such as mercuric sulfide, but it is poisonous in soluble forms such as mercuric chloride. Total mercury includes dissolved mercury and mercury attached to matter.

**Nickel:** A metal which organic matter has a strong ability to absorb. Uptake in large quantities increases the risk of many types of cancer. Total nickel includes dissolved nickel and nickel attached to matter.

Nitrate: An oxidized ion of nitrogen which contains a nitrogen atom, three oxygen atoms and

a lone pair of electrons. It is the last stage of the aquarium nitrogen cycle and is converted from nitrites. It is harmful to aquatic animals in high concentrations.

**Nitrite:** A form of nitrogen with the chemical formula NO<sub>2</sub>. Intermediate nitrogen compound in the biological conversion of ammonia to nitrate in the nitrogen cycle. Nitrite is toxic to fish, but less so than ammonia.

**Output:** A reading, or a digital or analogue electrical signal, generated by an instrument in response to a <u>determinand</u>.

**Performance characteristic:** One of the quantities (described by values, tolerances, range) assigned to <u>PWM</u> in order to define its performance.

Portable analyser: <u>PWM</u> which makes discrete measurement of the determinand.

**PWM:** Acronym for a portable water monitor

**Rated operating conditions:** The minimum to maximum values of any environmental, fluid or electrical parameter within which the <u>PWM</u> is designed to operate without adjustment, with errors within the required <u>uncertainty</u>.

**Reference conditions:** A specified set of values (including tolerances) of influence variables, delivering representative values of performance characteristics.

**Reference material:** A substance or mixture of substances, with a known composition within specified limits. One or more of the properties of the reference material are sufficiently well established over a stated period of time to be used for the calibration of an apparatus, for the assessment of a measuring method, or for assigning values to materials. Reference materials appropriate to the determinands covered by this standard are given in Annex F.

**Reference method:** Method to be used to obtain the <u>determinand</u> value of the test fluid to a stated <u>uncertainty</u>, against which the readings from the <u>PWM</u> under test can be compared. Reference methods appropriate to the <u>determinands</u> covered by this standard are given in Annex F.

**Repeatability:** The ability of a <u>PWM</u> to provide closely similar indications for repeated applications of the same <u>determinand</u> under the same conditions of measurement.

**Response time:** The time interval between the instant when a <u>sensor</u> is subjected to an abrupt change in <u>determinand</u> value and the instant when the readings cross the limits of (and remain inside) a band defined by the 90% and the 110% of the difference between the initial and final value of the abrupt change.

**Secondary turbidity standard:** Material having a fixed value for <u>turbidity</u> based on a substance other than formazine. Such standards are often specific to an individual instrument and are provided by manufacturers for calibration purposes.

**Sensor:** Transducer consisting of one or more components from which is derived an electrical output related to the value of the <u>determinand</u> in the sample.

**Standard uncertainty (u):** <u>Uncertainty</u> of the result of a measurement expressed as a standard deviation, see Annex E.

**Total ammonia:** The total ammonia concentration is the sum of ammonia in the forms of unionised (free) ammonia and ammonium ions present in a sample. Total ammonia concentration may be expressed in terms of the nitrogen (NH<sub>3</sub>-N), ammonium ion (NH<sub>4</sub><sup>+</sup>) or ammonia (NH<sub>3</sub>) concentration of a sample in units of milligrams per litre (mg  $I^{-1}$ ). Unless otherwise stated, all references to total ammonia in this document are expressed in terms of milligrams per litre of nitrogen (mg  $I^{-1}$  NH<sub>3</sub>-N), often referred to as ammoniacal nitrogen.

**Transmitter:** Device which takes the signal from the <u>sensor</u> and converts it into a visual or electrical output proportional to the value of the <u>determinand</u>. The transmitter may include a user interface with the <u>PWM</u>.

**Turbidity:** The optical property of particles suspended in a fluid that causes light to be scattered and absorbed rather than transmitted through the fluid without change. For the purpose of this specification all measurements of turbidity shall be expressed in formazine turbidity units (FTU). One formazine turbidity unit (FTU) equals 1/400th of the Stock Turbidity of the suspension prepared by the method as set out in 'Methods for the Examination of Waters and Associated Materials - Colour and Turbidity of Waters 1981.

Informative note: Other systems of units are in common use for turbidity measurement. The nephelometric turbidity unit (NTU) is the turbidity of the sample measured by a detector at 90° from the source light. BS EN ISO 7027:2000 Water Quality – Determination of turbidity, uses formazine nephelometric units (FNU) and formazine attenuation units (FAU). There is no direct relationship between any of these units.

**Uncertainty:** The parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurement.

**Warming-up period:** The interval between the energizing of the auxiliary circuit and the instant when the instrument may be used, as specified in the manufacturer's instructions.

# **Annex C - Certification Process**

#### C1 Certification process

Product certification comprises three phases. These are:

- **Laboratory testing** used to determine performance characteristics, where such testing requires a highly controlled environment
- **Field testing** carried out on processes representative of the intended industrial sectors and applications
- Surveillance initial and continuing which comprises an audit of the manufacturing process to confirm that the manufacturer has provisions to ensure manufacturing reproducibility and to control any design changes to ensure that they do not degrade performance below the MCERTS standards.

Manufacturers seeking certification should contact the Certification Body who will advise on any specific requirements for the PWM under consideration.

Only a complete PWM shall be certified. Where a PWM can be supplied with a number of options, for example where more than one sensor or sensor configuration can be used to cover different ranges, one complete PWM shall undergo the full conformity tests. In selecting the options to be tested, consideration should be given to the options likely to be used in the identified applications. For additional sensors or sensor configurations, it may be possible to extend certification by carrying out a subset of the full test programme. Similarly, where different electronics units having different facilities may be used with a single sensor, one complete example of the PWM shall undergo the full conformity tests. For additional variants, it may be possible to extend certification by carrying out a subset of the full conformity tests. For additional variants, it may be possible to extend certification by carrying out a subset of the full conformity tests.

When the performance of a certified product is likely to be invalidated by use of alternative equipment, e.g. non-certified sensors, an appropriate reminder to users of the product may be included on the certificate.

Multi-parameter instruments may be certified for one or more of the determinands covered by this standard. The test certificate shall make clear for which determinands the instrument is certified. Any reference by the manufacturer to certification shall make clear for precisely which determinands the instrument is certified.

# **Certification Committee**

- The role of the Certification Body is to assess and certify compliance with the MCERTS standard for defined applications and or conditions.
- In performing this role the MCERTS scheme requires the Certification Body to consider the relevance of the procedures defined in the MCERTS standard to the specific product to be certified. The technology or defined application of a specific product may make certain of the documented tests inappropriate. The Certification Body is required by the MCERTS scheme to exercise its technical judgement when considering these matters.

- Any certification decision based on technical judgement of the standard shall be taken by an appropriately independent, competent person or group of persons, who in this MCERTS standard are referred to as the "Certification Committee".
- When the Certification Committee exercises its technical judgement the rationale supporting any such decision shall be appropriately documented.
- Any certificate issued by the Certification Body shall identify any variations from the normative MCERTS standard.
- On request the Certification Body shall provide the MCERTS scheme owner with the rationale for any decision based on technical judgement, within the relevant confidentiality constraints.

### Certification range

A PWM will be certified over the measurement range for which it is tested. If a manufacturer wishes to demonstrate performance over one or more supplementary ranges some additional testing will be required over those ranges. This additional testing shall at least include evaluations of the accuracy, repeatability, linearity and response time.

The extent of the environmental testing will be agreed between the manufacturer and the Certification Body, taking into account the intended usage class of the instrument, and will be reported on the MCERTS certificate.

#### C2 Testing

Manufacturers may commission testing from any organisation, provided that the requirements for testing organisations can be met (see 5.1.1). Manufacturers own test data may also be acceptable. This applies to both laboratory and field tests.

#### Field test

The field test requirements take into account two scenarios:

- Established products that have a track record of use in a variety of applications
- Products that are new onto the market and as such do not have data to demonstrate use in a real environment.

In keeping with the European new approach directives, MCERTS sets out some essential requirements, (see Section 7) written in general terms which must be met before products can be certified as meeting MCERTS.

Emphasis will be placed upon the manufacturer setting out a case justifying, with appropriate evidence, why the product will meet the field test requirements.

Acceptable data might include:

• Field test reports from qualified laboratories

- Validated reports from users of the equipment
- Manufacturer's data validated by an independent third party.

This data will be augmented by a rigorous assessment of maintenance and service records carried out during the manufacturing audit. More emphasis will also be placed on continued compliance of the products to the general requirements and this will be carried out during the regular surveillance audits.

The field test requirements are intended to be sufficiently flexible to allow manufacturers to utilise existing applications, provided that there is some way of validating measurements by one of the reference methods described in Annex F. Alternative methods may also be acceptable but in such cases, the manufacturer is advised to discuss the matter with the Certification Body to ensure that the proposed method is acceptable.

Where data from an existing application is used in support of an MCERTS certification, it should be from a PWM of the same type for which certification is sought. Any options included in the field test device shall be reported, as shall any modifications or differences between it and the device used in the laboratory testing stage. The Certification Body may require the full history of the PWM, including details of any maintenance or repairs. Corroboration may be sought from the equipment owner via a confidential questionnaire.

# C3 Auditing and surveillance

An audit of the manufacturing process shall be conducted by the Certification Body to confirm that the manufacturer has provisions to ensure manufacturing reproducibility and to control any design changes that may affect product performance.

Subsequent surveillance audits are normally conducted annually until sufficient evidence of a well-proven, robust system has been collected. Once this has been established the Certification Body may extend the interval between audits or require submission of specific audit data for review off site.

# C4 Certificate validity

MCERTS certificates are valid for five years. After this time, the certification is reviewed and any necessary retesting will be identified to maintain the certification. Assessment for recertification shall be carried out against the MCERTS standards current at the time of recertification.

# C5 Modifications to certified PWMs

Modifications to a certified PWM are allowable so long as manufacturers can demonstrate to the Certification Body that these design changes do not degrade the performance of the PWM below the MCERTS performance standards.

Manufacturers must keep detailed records and drawings of all design changes to a PWM, and have provisions for design verification and inspection to ensure that the PWM still meets the required performance standards.

The Certification Body will conduct audits of the design and software changes to a PWM to

meet the requirements of product certification. Manufacturers must inform the Certification Body of any modification affecting any of the documents, drawings or other information referred to in the certificate.

# **Annex D - Determination of performance characteristics**

### D1 Introduction

The approach to specifying performance requirements and analysing data from product testing to be used in the certification of water monitoring equipment against the MCERTS performance requirements has been developed to be:

- Internationally acceptable, i.e. based on the principles of the ISO Guide to the Expression of Uncertainty in Measurement (GUM)
- Consistent with the approach taken across the MCERTS business
- Applicable across the range of different equipment types and technologies covered by MCERTS product certification
- Fit for purpose.

# D2 Errors

For any individual test point, the error, x, is the difference between the value given by the PWM and the conventional true value.

Note: In this standard, errors are expressed as a percentage of reading, a percentage of span, or absolute units. Reference shall be made to the column headings in Table 2 to ensure that the appropriate values are used.

The mean error,  $\overline{x}$ , from a series of *n* measurements is:

$$\overline{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$
 Equation D1

# D3 Repeatability

Repeatability is standard deviation of the measurements taken at reference conditions.

$$u_R = \sqrt{\frac{\sum_{i=1}^{n} (\bar{x} - x_i)^2}{n-1}}$$
Equation D2

As the MCERTS test for repeatability (see 6.3.2) requires the test point to be approached from both higher and lower values, the calculation of repeatability here includes any effect due to hysteresis.

#### D4 Linearity

Linearity is a measure of the deviation of the instrument response from a straight line over the measurement range. It is calculated by using the method of least squares to fit a straight line to the mean measurement values obtained at each test point over the range. The maximum deviation from the best fit line is taken as the linearity error,  $X_L$ , to be compared with the MCERTS performance characteristic for linearity.

Where an instrument would be expected to have a zero response to a determinand value of zero, a zero-based linearity should be calculated, i.e. the best fit line should be forced through the origin. Where this is not the case, e.g. for pH, a terminal based linearity should be used.

# D5 Effect of influence conditions

The performance requirement for the effect of an influence condition,  $X_I$ , is the half range of any change in error resulting from varying the influence condition from a low to a high value, including the reference value, expressed as a percentage of reading, i.e. referring to Figure D1:

$$X_{I} = \left(\frac{\left|\overline{X}high - \overline{X}ref\right| + \left|\overline{X}low - \overline{X}ref\right|}{2}\right)$$
Equation D3

Note 1: In tests 6.3.3 and 6.3.7, the reference conditions and the low influence conditions are the same, hence  $(\overline{X}low - \overline{X}ref)$  is zero. In test 6.3.6 there is no high value so  $(\overline{X}high - \overline{X}ref)$  is zero.

Note 2: In cases where the response is U shaped, see Figure D2, calculate  $X_I$  as half the maximum difference, i.e. in the example shown in Figure D2:

$$X_{I} = \left(\frac{\left|\overline{X}high - \overline{X}ref\right|}{2}\right)$$
 Equation D4



Figure D1 Effect of influence conditions – linear response



# Figure D2 Effect of influence conditions – U shaped response

# **D6 Combined performance characteristic**

It is frequently convenient to have a single value for an instrument's uncertainty under any circumstances. MCERTS therefore defines a combined performance characteristic by combining the components measured in the individual tests. To combine the characteristics in accordance with the GUM it is necessary to convert them to standard uncertainties (u) which take account of the probable distribution of errors.

For the purposes of this standard, all measured characteristics (except repeatability) are

assumed to have a rectangular probability distribution, i.e. there is an equal chance of any value of error occurring within the range that has been measured in any individual test. In the case of a rectangular distribution the standard uncertainty is calculated as:

$$u = \frac{X}{\sqrt{3}}$$
 Equation D5

Repeatability has been calculated as a standard deviation at each test point (Equation D2) and hence represents a normal distribution of errors. The value to be used in the calculation of the combined performance characteristic shall be the maximum value measured, excluding that taken at test point 1.

In the GUM, standard uncertainties are combined using a root square sum with due account taken of the contribution of each component through the use of sensitivity co-efficients. To determine sensitivity co-efficients, it is necessary to know the analytical functions by which each component contributes to the overall error. In the case of instrument testing this will rarely be known. Hence for the purposes of this standard, the sensitivity co-efficients are all taken as 1. However, in specific cases, the Certification Body may require particular weighting to be given to certain components and hence require other values of sensitivity co-efficients to be used.

The requirement for the combined performance characteristic is expressed as an expanded uncertainty. The expanded uncertainty, U, is obtained by multiplying the standard uncertainty by a coverage factor. The coverage factor is determined by the confidence level required. For MCERTS, a 95% confidence is used with a coverage factor assumed to be 2. Thus:

$$U_c = 2 \times u_c$$
 Equation D6

Table D1 shows the components which are to be combined when determining the combined performance characteristic,  $U_c$ . Specific components depend on the type of PWM, although some are common to all types of PWM.

Performance characteristic	Symbol	Test
(Mean error – see Note)	$u_A$	6.3.2
Repeatability	$u_R$	6.3.2
Linearity	$u_L$	6.3.2
Supply voltage	$u_V$	6.3.6
Ambient temperature	$u_T$	6.3.7
Incident light	$u_{LX}$	6.3.8
Sample temperature	$u_{ST}$	6.3.9

 Table D.1
 Components for the combined performance characteristic

# **Inclusion of Mean Error**

The Certification Committee shall decide on a case by case basis whether the mean error shall be included in the calculation of  $U_C$ . A net mean error in test 6.3.2 could indicate a number of things, for example:

- For a factory calibrated instrument a net mean error could be due to a systematic offset between the test-house facility and the manufacturer's calibration facility, both of which could have demonstrable traceability routes. In such cases it would be unfair to include in  $U_c$ .
- For a user calibrated instrument, a net mean error could be the result of deficiencies in the calibration routine or the calibration standards supplied by the manufacturer. In these cases the mean error should be included in  $U_c$ .

The Certification Committee shall take such factors into account and be able to justify the inclusion or otherwise of the mean error component in  $U_c$ .

Where a mean error component is included, it shall be as a standard uncertainty with an assumed rectangular distribution, i.e.:

$$u_A = \frac{(\max \bar{x})}{\sqrt{3}}$$
 Equation D7

The combined performance characteristic,  $U_c$ , is therefore calculated by summing the components as a root sum of their squares and multiplying by the coverage factor, 2, i.e.

 $U_{c} = 2 \times \sqrt{u_{A}^{2} + u_{R}^{2} + u_{L}^{2} + u_{V}^{2} + u_{T}^{2} + u_{LX}^{2} + u_{ST}^{2}}$ 

Equation D8

# D7 Worked example

A PWM is to be certified over the range 0-50 mg/l.

The instrument has a resolution of 0.01 mg/l. Resolution is specified as a % range, hence in this case it is 0.01/50 x 100% or 0.02%.

It is subjected to the test procedure in 6.3.2 and the readings in Table D2 are obtained (in mg/l).

Table D2	Example measurement results
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	L	-	-		-
Test point:	1	2	3	4	5
Ref. value	2.55	13.50	25.50	37.30	47.40
Run 1	2.52	12.98	25.02	37.10	48.20
Run 2	2.48	12.97	25.03	37.01	47.96
Run 3	2.48	12.95	25.00	36.90	47.80
Run 4	2.45	12.95	25.02	37.02	47.95
Run 5	2.48	12.97	25.01	36.85	47.96
Run 6	2.47	12.99	25.03	37.15	48.01

The errors (in mg/l) for each measurement are determined by subtracting the reference value from each reading, then converted to percentage of reading to obtain the values shown in Table D3. The mean error at each test point is calculated from Equation D1.

Test point	1	2	3	4	5
Run 1	-1.19%	-4.01%	-1.92%	-0.54%	1.66%
Run 2	-2.82%	-4.09%	-1.88%	-0.78%	1.17%
Run 3	-2.82%	-4.25%	-2.00%	-1.08%	0.84%
Run 4	-4.08%	-4.25%	-1.92%	-0.76%	1.15%
Run 5	-2.82%	-4.09%	-1.96%	-1.22%	1.17%
Run 6	-3.24%	-3.93%	-1.88%	-0.40%	1.27%
Mean error	-2.83%	-4.10%	-1.93%	-0.80%	1.21%

Table D3Errors from example measurement data

The mean errors at each test point are compared with the MCERTS requirement for mean error.

The Certification Body decides that as the instrument requires user calibration in the field against synthesised solutions provided by the manufacturer, a mean error component shall be incorporated into the combined performance characteristic.

This is calculated from Equation D7 as  $(-4.10)/\sqrt{3} = 2.37\%$ .

The repeatability at each test point is calculated from Equation D2 as shown in Table D4.

### Table D4Example repeatability values

Test point	1	2	3	4	5
Standard deviation	0.94%	0.13%	0.05%	0.31%	0.27%

The repeatability values at each test point are compared with the MCERTS requirement for repeatability.

The value for repeatability to be carried through to the calculation of the combined performance characteristic is the maximum, excluding test point 1, in this case 0.31%.

The mean measurement values at each test point are plotted against the reference values and a best fit line is calculated by method of least squares. In this case, it is assumed that the best fit line would pass through the origin. The equation of the best fit line is therefore y= 0.9993x. The deviation from the best fit line at each test point is calculated in engineering units and as a percentage of reading, see Table D5.

#### Table D5Linearity example

Test point	1	2	3	4	5
Deviation from best fit	-0.068	-0.522	-0.464	-0.269	0.613
As % reading	-2.75%	-4.03%	-1.85%	-0.73%	1.28%

The maximum non-linearity error is identified as that at test point 2, and compared with the MCERTS requirement for linearity.

The component for linearity to be included in the combined performance characteristic is calculated from Equation D5 as  $(-4.03)/\sqrt{3} = 2.33\%$ .

The instrument is then subjected to a test for the effect of sample temperature. Three measurements are taken at test point 3 with the sample temperature at its reference value, then 3 more with the sample temperature at its lower limit and 3 more with the sample temperature at its upper limit. The data points in Table D6, in mg/l, are obtained.

Reference value	Lower limit	<b>Reference</b>	Upper limit
25.00	24.95	25.05	25.10
25.10	25.00	25.17	25.18
24.80	24.88	25.00	25.00

Table D6Example influence condition results

The errors, as percentage of reading, are as shown in Table D7.

### Table D7Influence condition errors

	Lower limit	<b>Reference</b> conditions	Upper limit
1st measurement	-0.20%	0.20%	0.40%
2nd measurement	-0.40%	0.28%	0.32%
3rd measurement	0.32%	0.80%	0.80%
Average	-0.09%	0.43%	0.51%

The effect of sample temperature is calculated from Equation D3 as:

$$X_{V} = \frac{|0.51 - 0.43| + |(-0.09) - 0.43|}{2} = 0.3\%$$

 $X_V$  is compared with the MCERTS performance characteristic for the influence of sample temperature. From Equation D5, the component to be included in calculation of  $U_C$  is  $0.3/\sqrt{3} = 0.17\%$ .

The instrument undergoes all remaining MCERTS performance tests with the results as shown in Table D8.

Performance characteristic	Symbol	Value
Mean error	$u_A$	2.37%
Repeatability	$u_R$	0.31%
Linearity	$u_L$	2.33%
Supply voltage	$u_V$	0.17%
Ambient temperature	$u_T$	0.25%
Incident light	$u_{LX}$	N/A (not an optical sensor)
Sample temperature	UST	0.67%

### Table D8 Example performance characteristics

The combined performance characteristic is then calculated from Equation D5.

 $U_{\rm C} = 2 \ x \ (2.37^2 + 0.31^2 + 2.33^2 + 0.17^2 + 0.25^2 + 0.67^2)^{1/2}$ 

= 6.84%

This value is compared with the MCERTS requirement for the combined performance characteristic.

# Annex E – Guidance on usage groups

Table E1 gives guidance on the operating condition to which PWMs are likely to be subjected (see BS EN 60746-1 Expression of performance of electrochemical analysers: General.). The extent of environmental testing will be agreed between the manufacturer and the Certification Body, taking into account the intended usage group of the instrument.

Usage	Explanation	Recommended rated operating
group		conditions
Ι	For indoor use under conditions which	Ambient temperature: $\pm 5^{\circ}$ C to $\pm 40^{\circ}$ C
	factorias and where apparetus will be	+3 C to +40 C
	handled earofully. In this type of	Relative humidity.
	environment the ambient temperature	Up to 95% RH including
	will normally remain within fairly	condensation
	narrow limits. The PWM will not be	
	exposed to water sprays or drips, high	
	humidity or significant concentrations	
	of airborne dust.	
II	For outdoor use and in areas where the	Ambient temperature:
	apparatus may be subjected to rough	
	handling. PWMs in this category will	Storage -25°C to +70°C
	be exposed to the full range of outdoor	Operation $-10^{\circ}$ C to $+55^{\circ}$ C
	environmental conditions in use, and	
	may be carried and stored in vehicles	Relative humidity:
	where they may be subjected to	Up to 95% RH including
	temperatures significantly above	condensation
	normal ambient conditions and very	
	low temperatures. The equipment may	
	be exposed to heavy rainfall and high	
	power water jets from all directions	
	for long periods of time.	

Tabla F1	Ιωσο	groups	(for	anchiun	١
I able EI	Usage	groups	(10f	guiuance	)

# Annex F - Standard reference methods

GUIDANCE NOTE: Other methods may be accepted including a second PWM or a continuous water monitor (CWM) provided that they are of known and demonstrable uncertainty.

If samples are taken for laboratory analysis then appropriate sample preservation procedures must be observed to minimise any changes in sample composition between sampling and laboratory analysis.

### Temperature

Temperature probes of an appropriate type for the test being undertaken which have been maintained and calibrated to a known and demonstrable uncertainty shall be used in both laboratory and field tests.

### pН

A specific reference analytical technique has not been specified in this document for the determination of pH. For the field test the reference values for field test error measurements may be derived by having a second pH meter which is maintained and calibrated to a known and demonstrable uncertainty.

### Ammonia

The method is given in Methods for the Examination of Waters and Associated Materials Ammonia in Waters 1981 for analysis used to obtain the total ammonia concentration of the test fluid to a stated uncertainty, or producing a reference solution. For the field test, suitable reference methods are a second ammonia instrument of known and demonstrable uncertainty or laboratory analysis of samples.

# COD

The recommended reference technique for the determination of COD is method A in the publication Chemical Oxygen Demand (Dichromate Value) of Polluted Waters 1986 (Second Edition) Methods for the Examination of Waters and Associated Materials. HMSO, London. ISBN 011 7519154. Details are also given for the preparation of a solution with a known COD value. For the field test, the reference values for field test error measurements may be derived from samples taken and measured by a laboratory that is accredited for the determination of COD in the value range of interest under quality assured conditions to a known uncertainty, or alternatively, by use of a process COD analyser which is maintained and calibrated to a known and demonstrable uncertainty.

#### **Dissolved oxygen**

Details of the reference analytical method can be found in the following publication: Methods for the Examination of Waters and Associated Materials - Dissolved Oxygen in Natural and Waste Waters 1979. Method A - Winkler titration. A method is described for preparation of solutions of different dissolved oxygen concentrations. It should be noted that these solutions are not stable. The reference values for field test error measurements may be derived from samples taken and measured using the Winkler titration method, under quality assured

conditions to a known uncertainty (though the Winkler titration may have a higher uncertainty than an electrochemical DO sensor), or by having a second dissolved oxygen analyser in line which is maintained and calibrated to a known and demonstrable uncertainty. In high ionic strength samples, there is a disparity between Winkler titration and electrode methods. This needs to be taken into account if seawater or high salinity estuarine samples are of interest. Tables providing an indication of the effects of ionic strength and temperature on oxygen solubility are included in BS EN 25814.

Where a number of levels of saturation are required i.e. for linearity checks an alternative method involved using a mixture of nitrogen and oxygen (ACT TV04-01, 2004). A zero dissolved oxygen sample may be prepared either by sparging with 100% nitrogen or with the addition of 5 grams of Sodium Sulfite (Na2SO3) in 500 ml of water.

# Orthophosphate

The recommended reference method is method B in the publication Methods for the Examination of Waters and Associated Materials. Phosphorus and Silicon in Waters. Effluents and Sludges 1992.

A series of reference solutions may be prepared by serial dilution of a stock solution containing a known quantity of phosphorus. The formulation of the stock reference solution for total phosphorus consists of an aqueous solution of the following compounds in equal proportions as phosphorus:

- disodium hydrogen orthophosphate
- sodium beta-glycerophosphate
- sodium tetrametaphosphate
- sodium tripolyphosphate.

The reference values for field test error measurements may be derived from samples taken and measured in the laboratory under quality assured conditions to a known uncertainty, or by having a second total phosphorus analyser in line which is maintained and calibrated to a known and demonstrable uncertainty.

# Nitrate and Nitrite

There are several different recognised analytical methods for the determination of nitrogen compounds. A specific reference analytical technique has not been specified in this document for the determination of nitrate because the most suitable approach varies according to the concentration range and sample matrix of interest. However the laboratory undertaking the analysis should be accredited for the determination of nitrate and nitrite in the matrix of interest. A method for preparation of reference solutions is described in Methods for the Examination of Waters and Associated Materials - Oxidized Nitrogen in Waters 1981. HMSO. The reference values for field test error measurements may be derived from samples taken and measured in the laboratory under quality assured conditions to a known uncertainty, or by having a second nitrate or nitrite analyser in line which is maintained and calibrated to a known and demonstrable uncertainty.

# Turbidity

A specific reference analytical technique has not been specified in this document for the determination of turbidity. For the field test, the reference method shall be to expose the sensor to reference solutions. Formazine may be used, made up in accordance with BS EN ISO7027:2000 under quality assured conditions to a stated uncertainty. BS EN ISO7027:2000 also includes data on a synthetic polymer, made from Styrene Divinylbenzene beads, which shows good correlation to the formazine standard. This may be preferred as the production of formazine requires the use of chemicals which are known to be carcinogenic. Proprietary secondary standards may be used for routine calibration activities or determining the effect of various influence conditions, which are not sample dependent, in line with manufacturer's instructions but cannot be used to derive field test error values.

# Conductivity

A specific reference analytical technique has not been specified in this document for the determination of conductivity. For the field test the reference values for field test error measurements may be derived by having a second conductivity meter which is maintained and calibrated to a known and demonstrable uncertainty.

# Chlorophyll a

There are several different recognised analytical methods for the determination of Chlorophyll *a*. HPLC analysis of extractive Chlorophyll is the preferred technique for the analysis of Chlorophyll a. It is known that different HPLC methods may give slightly different results due to the different solvents and extraction procedures. For this reason it is recommended that a published and proven HPLC method and sample preparation techniques are followed, such as those in the Standard Methods for the Examination of Water and Wastewater (2006) APHA. It is strongly recommended that laboratories with experience in the analysis of algal pigments are used for this work.

Unlike all other MCERTS parameters chlorophyll, as a biologically active component of algae and bacteria, presents a difficulty when preparing standard suspensions for instrument performance testing. Many factors such as light, nutrient and dilution can have a significant impact on the sample and if not considered may be attributed to be instrument errors. In line with other recent published methods for assessing the performance of Chlorophyll monitoring instruments (Alliance for Coastal Technologies, Protocols for the Verifying the Performance of In Situ Chlorophyll Fluorometers, ACT PV05-01) it is recommended that an algal species be cultured specifically for use as a sample for instrument testing.

It is recommended that the unicellular algae *Chlorella vulgaris* (CCAP 211/11B) from the Chlorophyceae class be used, as this is easy to grow in batch culture. It is important that culture conditions follow standard methods (illumination, temperature and growth medium) to promote healthy algal growth without light or nutrient adaptation. Samples to be used for instrument performance tests should ideally be taken mid-log phase. A cyanobacterium such as Microcystis aeruginosa (CCAP 1450/10) may be used where there is a specific interest in the measurement of cyanobacteria.

Non algal standards – Basic Blue, C.I.51004, CAS33203-82-6, M.W. 359.9) is a stable water soluble dye which has been successfully used as a standard to test florescence based

chlorophyll a measuring instruments (ACT, PV05-01, 2005) and is recommended as a suitable standard solution for the interference, supply voltage, ambient temperature, relative humidity, incident light, response time, warm up drift and battery operation tests.

# Chlorine

Methods for the determination of Total available Chlorine by Iodometric Titration and chlorine, chloramines using the Diethyl-p-phenylendiamine (DPD) method are described in Methods for the Examination of Waters and Associated Materials - Chemical Disinfecting agents in water and effluents (2008).

# Cyanide

Methods for the Examination of Waters and Associated Materials. The determination of cyanide in waters and associated materials, (EA 2007) describes several analytical methods for the determination of cyanide, in various forms, in water.

An alternative method is the EPA Method 335.1, Cyanides Amenable to Chlorination is based on visible spectroscopy. This method incorporates two determinations of total cyanide. One determination is done after free cyanide in the sample has been chlorinated to CNCl, which degrades quickly, and a second is done without chlorination. The concentration of free cyanide is given by the difference of the two measurements of total cyanide.

# Arsenic, copper, cadmium, lead and nickel

Methods for the determination of arsenic, copper, cadmium, lead and nickel are given in the 21<sup>st</sup> edition of Standard Methods for the Examination of Water and Wastewater. Method 3120 B Inductively coupled plasma (ICP) emission spectroscopy and method 3125 Metals by Inductively coupled plasma / mass spectrometry are both suitable for arsenic, copper, cadmium, lead and nickel.

# Mercury

Methods for the determination of mercury are given in the 21<sup>st</sup> edition of Standard Methods for the Examination of Water and Wastewater. Method 3112 Metals by Cold-Vapor Atomic Absorption Spectrometry is the method to analyze mercury. Method 3125 Inductively coupled plasma/mass spectrometric method can also apply, even though mercury is not listed in the method.

# Annex G – Typical ranges for measurement

Table G1 Typical ranges for measurement (As guidance –certification range to be agreed with the certification body)

Determinand	Units	Untreated	Treated	Surface	Groundwater	Estuarine / Coastal
	1	wastewater	wastewater	waters	(Note 4)	Waters (Note 1)
Ammonia (Note 3)	mgl <sup>-1</sup> NH <sub>4</sub>	< 300	< 20	< 5	< 5	<0.2
Chlorine (total)	mgl <sup>-1</sup>	N/A	< 1	< 0.1	< 0.1	N/A
Chlorophyll a	$\mu$ gl <sup>-1</sup> Chl <i>a</i>	N/A	N/A	< 200	N/A	<100
COD	mgl <sup>-1</sup> Oxygen	< 4000	< 250	N/A	N/A	N/A
Conductivity (Note 2)	μS/cm	< 500	< 500	< 1000	< 1000	<0.1-40 mS/cm
Dissolved oxygen	% saturation	< 100	< 100	< 200	< 200	<200
Free cyanide	mgl <sup>-1</sup>	< 1	< 1	< 1	< 1	N/A
Nitrate	mgl <sup>-1</sup> N	< 350	< 50	< 50	< 25	<1
Nitrite	mgl <sup>-1</sup> N	< 10	< 10	< 2	< 2	< 0.05
Orthophosphate	mgl <sup>-1</sup> P	< 50	< 5	< 2	< 2	<0.1
pH	pH units	2-12	4-10	< 10	< 10	<10
Temperature	°C	< 50	< 30	< 30	< 20	<25
TOC	mgl <sup>-1</sup> C	< 1000	< 100	< 20	< 5	<20
Total Arsenic	μgl <sup>-1</sup>	< 100	< 10	< 5	< 200	<6
Total Cadmium	µgl <sup>-1</sup>	< 20	< 1	< 1	< 20	<1
Total Copper	µgl <sup>-1</sup>	< 120	< 50	< 40	< 200	< 40
Total Lead	μgl <sup>-1</sup>	< 60	< 5	< 5	< 500	<1
Total Mercury	µgl <sup>-1</sup>	< 1	< 1	< 1	< 1	<0.2
Total Nickel	μgl <sup>-1</sup>	< 100	< 50	< 20	< 50	<5
Total phosphorus	mgl <sup>-1</sup> P	< 50	< 5	< 2	< 2	<0.1
Turbidity	FTU	<2000	< 50	<500	N/A	<500

Note 1: Estuarine and coastal tidal environments can be physically and chemically demanding on water quality monitors. Instrumentation challenges in these waters include changes in salinity over the tidal cycle, high suspended sediment which creates an abrasive environment, highly variable water velocities due to tides and biological fouling.

*Note 2: Conductivity in the mS/cm range may be common in saline waters.* 

Note 3: Ammonia as total ammoniacal nitrogen.

Note 4: Mine water may contain significantly elevated levels of some determinands compared to other groundwaters.

# **Annex H – Test Methods for Interference Effects**

This section provides an example method suitable for determining interference effects. This example may be used to develop methods specific to other interferences.

The scope of interference testing shall be agreed, on a case by case basis, between the manufacturer and the Certification Committee. This should cover:

- *Nature of the interferent(s) to be tested;*
- *Level(s) of the interferent;*
- *Test point(s) at which test is to be carried out.*

Thus the nature and level of interferent tested can be made appropriate to each CWM, its method of operation and its intended range and application.

### Turbidity effect to chlorophyll *a* measurement

Turbidity effects may be assessed using either a secondary standard solution (dye) or a sample of algal cells. For both approaches expose the sensor to a blank solution and record the reading,  $y_0$ .

Prepare a reference sample of algal cells or use a secondary standard solution (Annex F). The concentration should adjusted to give a sample at test point 3. Divide the sample into 2 equal volumes.

To one half of the reference chlorophyll sample, add an equal volume of the blank solution to give a concentration of chlorophyll a at test point 2. Expose the sensor to this solution and record the chlorophyll a reading,  $y_3$ .

Prepare a suspension of Styrene Divinylbenzene beads (SDVB) with a turbidity of 20 FTU (50% of the expected interference level). Divide the sample into 2 equal volumes.

To one half of the SDVB sample, add an equal volume of blank solution to give a turbidity of 10 FTU. Record the chlorophyll a reading,  $y_1$ .

To the second half of the SDVB sample add an equal volume of the chlorophyll sample to give a reference chlorophyll a sample (test point 2) with an additional 10 FTU turbidity. Record the chlorophyll a reading, y<sub>4</sub>.

Calculate and report the change in the zero chlorophyll sample with 10 FTU turbidity  $(y_1-y_0)$  and the change in chlorophyll reading at test point 2 with 10 FTU additional turbidity  $(y_4-y_3)$ . Identify the maximum change as the error due to interferents,  $X_{IN}$ .

This method should be repeated at 100% of the expected level of interferent with a blank sample and a sample at test point 2. The interference effects should also be determined at test point 4 following the same method.

#### Colour effects to turbidity measurement

Colour effects shall be assessed at two colour levels which relate to 50% and 100% of the expected interference level. In this example these have been selected at 15 and 30 colour units.

Test samples  $y_0$  to  $y_5$  shall be prepared as given in table H1.

Potassium chloroplatinate shall be used to prepare the colour standards, as described in Method 2120 B Standard Methods for the Examination of Water and Wastewater, APAH. 20<sup>th</sup> edition. SDVB beads are recommended to provide the required turbidity.

 Test sample
 Colour
 Turbidity

 (Colour units)
 (Test point)

Table H1 Samples required for colour effects to turbidity testing.

Test sample	(Colour units)	(Test point)
<b>y</b> 0	0	0
<b>y</b> 1	15	0
<b>y</b> <sub>2</sub>	30	0
<b>y</b> <sub>3</sub>	0	Test point 2
<b>y</b> 4	15	Test point 2
<b>y</b> 5	30	Test point 2

Measure each of test samples  $y_0$  to  $y_5$  with the CWM under test and record the turbidity reading.

Calculate and report the change in the reading at zero turbidity and 15 colour units  $(y_1-y_0)$  and 30 colour units  $(y_2-y_0)$ . Also calculate and report the change in the reading at turbidity test point 2 with 15 colour units  $(y_4-y_3)$  and 30 colour units  $(y_5-y_3)$ .

Identify the maximum change as the error due to interferents,  $X_{IN}$ .

# Effect of chloride on COD measurements

Expose the sensor to reference solutions at test points 1 to 5 (see Table 4) in turn, to each of which 450 to 500 mgl<sup>-1</sup> chloride has been added (using sodium chloride as the source of chloride). At each point, allow sufficient time for the reading to stabilise and record the reading. Repeat the series of test points a further two times.

Identify the maximum change as the error due to interferents,  $X_{IN}$ .

# **Annex I – Examples of Evidence**

The MCERTS Certification Body can accept evidence from a variety of sources. The following examples may be used as guidance when determining an approach to meet the field trial requirements. The proposed approach shall be agreed with the Certification Body whose decision on the acceptability of the any approach is final.

#### Case study 1 – New instrument with a full field trial run by test house

#### Background

The instrument under test was a new model. Therefore only limited data existed from product development testing.

#### Available existing data

None which met the MCERTS requirements for field test data.

#### Approach

One new fully serviced instrument was supplied for the field trial. This was the same model, although not the same instrument, as that used for the laboratory testing. The trial was run in conjunction with a user known to the test house experienced in the operation of handheld water monitoring instruments. The test instrument was used by three different individuals over the period of the trial and each individual was trained in the correct operation of the instrument and made aware of the procedures to be followed for the trial. The trial consisted of three months use of the instruments in a typical application.

#### How the data requirements were met

Prior to delivery of the instrument to the user, the test house carried out a response time test. Each month, for three months, 40 measurements were made with 8 of these being paired measurements; the timing of these being reasonably even across the trial period. This met the requirement for a 120 measurements in total and 24 paired referenced measurements. The 24 paired measurement samples were analysed in a UKAS accredited laboratory within 12 hours of collection using a recommended standard method.

In addition to recording the values given by the instrument under test, for each of the 120 measurements, the operator undertaking the test also recorded their name, the location and time, the period of operation at that location, any recent calibration and any changes to the settings to the test instruments. In addition the operator recorded relevant data on ambient and water conditions e.g. pH and temperature. At the end of the test period, the instrument was returned to the test house for a final response time test. All the information collected was recorded in a log book which was made available to the Certification Body when the trial finished.

# Case study 2 – Existing instrument, field test run by manufacturer

#### Background

The instrument under test was an existing instrument in use with a number of customers.

#### Available data

Whilst users had records of readings taken over an extended period, no formal validation of any of those readings was available.

#### Approach

The manufacturer approached a customer with whom they had a good relationship. The customer used the instrument to take check measurement on a number of water flows on their site. The customer agreed to take 2 samples per week over a twelve week period during the course of their normal operations when they were using the instrument. The customer also agreed to release records of all readings taken during this period and respond to any questions raised by the Certification Body. It was made clear to the customer that the records would be used solely for the purpose of MCERTS certification. At the start of the test, the manufacturer serviced the instrument and checked response time.

#### How the data requirements were met

The samples taken by the customer were analysed in a UKAS accredited laboratory and compared with the readings recorded at the time they were taken. This provided 24 paired readings for assessment of field performance. The reading records provided in excess of the 120 measurements required. The Certification Body put some brief questions to the user to ensure that the trial, though run by the manufacturer, had been conducted in a fair and unbiased manner.

#### Case study 3 – Existing instrument using customer records

#### Background

The instrument under test was an existing model in use with a number of customers on different applications. One customer used the instrument as calibration check of an on-line analyser each day and as such checked the calibration and response time of the portable instrument each week in their laboratory against brought in standard solutions.

#### Available existing data

The customer had in excess of 6 months records of laboratory calibrations on the instrument, together with daily records of the readings from the portable and on-line instruments.

#### Approach

The user's laboratory was not UKAS accredited though had defined and rigorous procedures for their laboratory work and the standards used were traceable. The user agreed to release the records for the purpose of MCERTS certification. The data was shown to be robust and no further field trial was required.

#### How the data requirements were met

The calibration records provided the paired readings from which performance was assessed, and also the response time data. The daily records provided in excess of the required 120 measurements.

# Case study 4 –Existing instrument carried out by manufacturer using a second instrument

#### Background

The instrument under test was an existing model but with no field test data available. The instrument included a data logging facility.

#### Available existing data

None which met the requirements of MCERTS.

#### Approach

The manufacturer agreed with two customers that one of its technicians would visit their sites once a week each and take measurements over a period of twelve weeks. The two sites covered two typical applications for the instrument. At the time of each measurement, a second reading was taken with another instrument operating on a different principle. This second instrument was calibrated at the start of the trial against a recognised standard and checked weekly using secondary standards. At the end of the trial, the reference instrument was recalibrated against the primary standard. The data logger was downloaded to show all the measurements that had been made and would show the history of any adjustments.

#### How the data requirements were met

The performance was assessed by comparing the readings taken by the instrument with those from the reference instrument whose performance was known. The data logger provided assurance that no changes had been made to the instrument. Response time was not required for this instrument.

#### **Case study 5 – Instrument with multiple determinands**

#### Background

The instrument under test was a multi parameter device with different probes for each determinand and an in-built data logger.

#### Available existing data

None which met the requirements of MCERTS.

#### <u>Approach</u>

It was agreed that the field test could be conducted on all probes simultaneously. The instrument was suspended in a typical flow and left for a period of three months. The data logger was set to take a reading from each probe once an hour. At the start of the trial, a

series of 6 samples were collected over a day. This was repeated at the end of month 1, 2 and 3. The samples were sent for analysis against each determinand under evaluation. At the end of 3 months the data logger was downloaded. Response time was assessed at the start and end of the trial by setting the data logger to its minimum interval and immersing the probes first in a bucket of clean water, then transferring it to a bucket of sample water which had been spiked to raise the levels of each determinand under test.

#### How the data requirements were met

Performance was assessed from a comparison of the logged readings against the values obtained from the samples taken. The data logger readings provided in excess of the 120 measurements required. The response time was assessed from the rapidly logged values.