Technical Specification

CoGDEM 001

April 2019

Electrochemical Gas Sensor Life Test protocol: Test Procedures and Performance Requirements

Contents

Foreword

This Technical Specification has been prepared by CoGDEM, the UK trade body representing the Gas Detection industry.

This test specification defines test procedures for estimating the lifetimes of amperometric electrochemical gas sensors used in domestic, commercial, environmental and industrial gas detection applications.

These are accelerated test procedures, designed to stress the sensors beyond the conditions normally encountered in use, so that sensor lifetimes may be estimated in reasonable timeframes, based on an understanding of the electrochemistry and kinetics of amperometric electrochemical gas sensors.

This technical specification will help manufacturers, test laboratories and users of apparatus to adopt a consistent approach to, and provide a framework for, the assessment of electrochemical gas sensor lifetimes. Manufacturers can self-certify, using their in-house testing laboratory.

Introduction

Electrochemical sensors have now been developed with expectations of lifetimes in some applications in excess of 10 years. To allow a consistent approach to verifying this performance, it is necessary to develop accelerated test procedures that can demonstrate such performance in reasonable timeframes. This document defines tests that accelerate the degradation of the sensor, defining a reliable lifetime beyond the testing regime, allowing a consistent lifetime prediction from different manufacturers of amperometric electrochemical gas sensors.

The tests provide an estimate of the mean time to failure (MTTF) from which the total capacity of the sensor can be estimated. Sensor lifetime can then be calculated from the sensor capacity and expected use.

The tests are divided into critical (required in all circumstances) and optional, which may be appropriate for particular applications.

The choice of accelerated tests is based on a Failure Mode and Effects Analysis (FMEA) of commercially available electrochemical sensors. See informative Annex A. Expected lifetime is then predicted from an understanding of the way the sensor electrochemistry and kinetics modifies the test results. See Informative Annex C.

1 Scope

This Technical Specification defines the general requirements and test methods for the determination of the lifetime of electrochemical sensors used for the direct concentration measurement of toxic gases, oxygen and vapours in domestic, commercial, environmental and workplace atmospheres.

This Technical Specification is not applicable to sensors:

- based on technology other than electrochemistry
- used only in laboratories for analysis
- used only for process control purposes
- used for the measurement of volatile organic compounds
- used for the measurement of combustible gases and vapours related to the risk of explosion.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC 17025, General requirements for the competence of testing and calibration laboratories

3 Definitions

For the purposes of this document, the following terms and definitions apply:

3.1 adjustment

procedure carried out to minimize the deviation of the measured value from the test gas volume fraction

3.2 ambient air

normal atmosphere surrounding the apparatus

3.3 calibration

procedure which establishes the relationship between a measured value and the volume fraction of a test gas

3.4 clean air

that is free of gases or vapours which the sensor is sensitive to or which influence the performance of the sensor air

3.5 interferent

any substance that leads to a false signal from the sensor

NOTE: this does not include poisons which modify the sensor sensitivity, either temporarily or permanently

3.6 mask for calibration and test

device that can attach to the sensor to present a test gas in a reproducible manner

3.7 measuring principle

type of physical, optical or physico-chemical detection principle and the measurement procedure to determine the measured value

3.8 output

current generated by the sensor when exposed to the test gas. Normally expressed as nA/ppm

3.9 sensor

assembly in which the sensing element is housed, and which can also contain associated circuit components

3.10 standard test gas

test gas with a composition specified for each apparatus to be used for all tests, unless otherwise stated

3.11 time of recovery (t10)

time interval, with the apparatus in a stabilised condition, between the time when an instantaneous decrease in volume fraction is produced at the apparatus inlet and the time when the response reaches a stated indication of 10 % of the initial indication

3.12 time of response (t90)

time interval, with the apparatus in a stabilised condition between the time when an instantaneous increase in volume fraction is produced at the apparatus inlet and the time when the response reaches a stated indication of 90 % of the final indication

3.13 toxic gas

general term for any gas that can be harmful to human health

3.14 VOC

Volatile Organic Compound: an organic chemical with a detectable vapor pressure at room temperature

3.15 volume fraction (V/V)

quotient of the volume of a specified component and the sum of the volumes of all components of a gas mixture before mixing. The volume fraction is dependent on the temperature and pressure of the resultant gas mixture and must be stated

NOTE: The volume fraction and volume concentration take the same value if, at the same state conditions, the sum of the component volumes before mixing and the volume of the mixture are equal. However, because the mixing of two or more gases at the same state conditions is usually accompanied by a slight contraction or, less frequently, a slight expansion (gas non-ideality), this is not generally the case.

4 General Requirements

Amperometric electrochemical sensors require control and amplification circuitry for correct operation and to allow small currents from the exposure to test gas to be measured. Manufacturers' recommended circuitry must be used, or alternative circuitry must be agreed with the sensor manufacturer.

A suitable calibration mask may be provided, together with details of suggested pressure and flow rate for application of calibration gases to the sensor. When a mask is used for calibration or for the application of test gas to the sensor, the design and operation of the mask, specifically the pressure and velocity inside the mask, shall not influence the response of the apparatus or the results obtained.

Gas detection apparatus or parts thereof specifically intended for use in the presence of corrosive vapours or gases, or which can produce corrosive by-products as a result of the detection process (e.g. catalytic oxidation or other chemical process) shall be constructed of materials known to be resistant to corrosion by such substances.

5 Test methods

5.1 Normal conditions for test

5.1.1 General

The test conditions specified in 5.1.2 to 5.1.6 shall be used for all tests, unless otherwise stated in the particular test.

5.1.2 Test gases

The test gases shall be mixtures of the gas or vapour with a balance gas of clean air for which the sensor is intended to be used. If clean air cannot be used because of instability of the test gas, then nitrogen shall be used as the balance gas.

The tolerance on the nominal volume fraction of all test gases shall not exceed ±5%. The volume fractions of all test gases shall be known with a relative expanded uncertainty of ±5%.

5.1.3 Flow rate for test gases

When the sensor is exposed to the test gases, the test gas flow rate shall be in accordance with the manufacturer’s instructions.

5.1.4 Temperature

The ambient air and test gas shall be held at a constant temperature ± 2 °C within the range of 15 °C to 25 °C, throughout the duration of each test unless otherwise required by the test procedure.

5.1.5 Humidity

The relative humidity (RH) of the ambient air shall be within the range stated in the manufacturer's instruction manual throughout each test. Test gas RH shall be between 30 % to 70 % RH unless otherwise required by the test procedure or by the manufacturer. If RH is outside of this range, then this must be stated in the report.

For short applications of test gases, the use of dry gases is permitted if agreed between the manufacturer and the test laboratory. The performance of the sensor in dry gas shall be taken into account and reported by the test laboratory.

NOTE: Sensor drying can be a problem for an electrochemical gas sensor, especially in long term tests. Also, atmospheric reactions between nitrogen gases and water vapour can modify measurements; correction for this chemistry is the responsibility of the test laboratory.

5.1.6 Stabilization

In each instance where the sensor is subjected to a different test condition, the sensor shall be allowed to stabilize under these new conditions before measurements are taken. Stabilization time will be agreed between the manufacturer and test laboratory.

5.2 Tests

5.2.1 Overview

The tests are defined as two types:

- Mandatory tests which all sensors must complete
- Optional tests which may be appropriate for particular applications, or may be used to understand the characteristics of the sensor

5.2.2 Mandatory tests

5.2.2.1 Temperature Cycling – Durability Test

5.2.2.1.1 General

This test stresses the sensor design and internal seals which prevent liquid electrolyte from escaping and damaging the electronics or the detector.

5.2.2.1.2 Temperature Cycling Test

A sample of at least 30 sensors shall be selected randomly and placed in an environmental chamber. Sensors are exposed to a cyclical temperature profile as shown in Fig 1 below. This cycle is repeated until the number of failures is greater than 60%, or the manufacturer and test house agree when to finish the test and set a minimum durability period.

Minimum and maximum temperatures are defined as the minimum and maximum usage temperatures specified by the manufacturer. Temperature ramp rate is at least -2K/minute during cooling and at least +3K/min during heating, with a dwell time of 30 minutes at both the minimum and maximum temperatures.

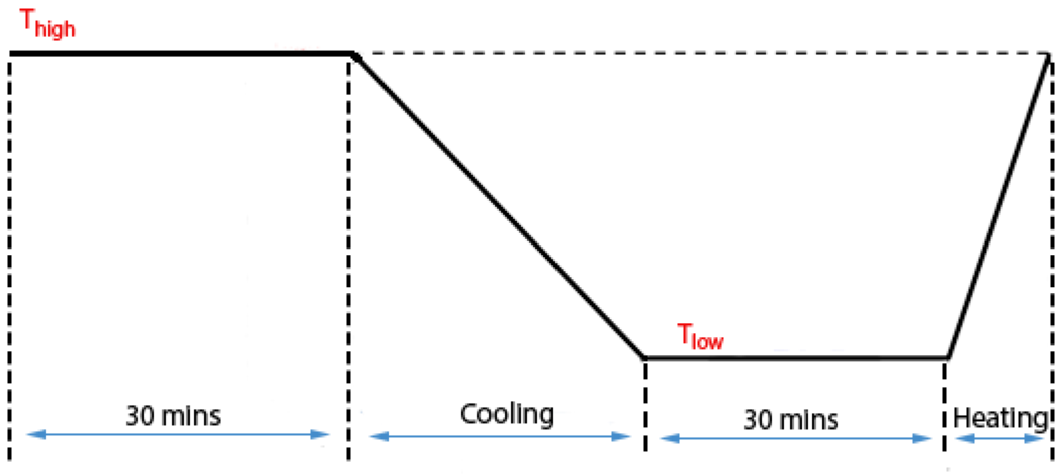


Figure 1. Temperature cycle for durability testing.

Sensors are checked at least twice weekly for signs of electrolyte leakage using appropriate pH indicator paper for aqueous-based electrolytes or visible leakage for organic/gel/polymer-based electrolytes. Sensors are also checked for electrical continuity. The time when an indicator colour change and/ or visual leakage or loss of electrical continuity is first detected is recorded for each sensor. Sensors which survive the total test cycles without any visible electrolyte leakage or loss of continuity are marked. The time that sensors are outside the environmental chamber for inspection and indicator testing is minimised. The remaining operating sensors are tested, and the response time and sensitivity are reported.

5.2.2.2 High Gas Concentration Exposure – Catalyst Degradation

5.2.2.2.1 General

This test stresses the electrocatalytic system by exposing the sensor to a raised temperature and increased test gas concentration at the working electrode, generating a larger than normal current.

Sensors built specifically for this test shall be produced with higher output currents. The degree of accelerated lifetime testing depends on both the temperature and increased output current.

NOTE: The increased output sensors should be the same in all aspects of construction to the standard sensors except that the means to control the signal should be increased e.g. by increasing the hole diameter in a sensor using a capillary hole as a gas diffusion barrier

5.2.2.2.2 Gas Exposure Test

At least 30 sensors with specially increased outputs shall be tested for their initial t_{90} and output at 20ºC and -20ºC, measured with standard test gas using potentiostats and calibration masks agreed between the test house and the manufacturer.

The sensors shall then be placed in a controlled environment at between 40ºC and 60ºC, depending on the required degree of lifetime acceleration and the limitations of the sensor. Sensors shall be powered continuously in their normal operating mode. RH shall be controlled between 40% and 60% RH. The sensors shall be exposed continuously to standard test gas at a flow rate agreed between the test laboratory and the manufacturer, selected to conserve gas usage while maximising sensor output current. Gas concentration shall be the maximum gas concentration that is in the linear concentration range, as determined in a stepwise linearity test, detailed in section 6.2. Linearity is defined as the maximum concentration where the response time remains within specification and output is stable after increased concentration.

Continuous gassing at high concentrations may be considered too severe for the test sensor. Manufacturer and test laboratory may decide to allow a periodic pulsed high concentration, then ambient air. The integrated coulombs will integrate only during gassing periods. This will extend the testing period and this test profile must be reported.

Sensors shall be withdrawn at agreed intervals (typically one or two week intervals) from the high temperature continuous gas test and allowed to cool to ambient temperature. Measurements will include t_{90} and output at ambient temperature and -20ºC. The sensors are then returned to the high temperature soak as soon as possible. The time to stabilise to ambient conditions and return to the test environment shall be as short as possible, as agreed between the manufacturer and test laboratory.

Sensors shall be deemed to have failed when the t_{90} response time has doubled or the ratio of the ambient signal to the -20C signal has halved. Sensor output and response time are plotted vs. time and the point where output loss and response time increase non-linearly is defined as the sensor time to failure - see Annex B.

The time to failure shall be recorded for each sensor and the test will continue until all sensors have failed or the anticipated lifetime for the accelerated test is reached.

Data is recorded as both total Coulombs to failure and as ppm.months, based on the mean nA/ppm specification from the manufacturer. See section 6.3 for the format for data presentation.

5.2.3 Optional tests

5.2.3.1 Filter Capacity Test

5.2.3.1.1 General

Where a filter is used to either avoid the influence of other gases or VOCs on sensor performance or to protect the sensor from damaging gases or vapours, then a filter capacity test shall be performed. The manufacturer will specify the interfering gases and concentrations. This will be recorded in the test report.

5.2.3.1.2 Filter Test

A random sample of at least eight sensors shall be tested. The interfering gas or vapour shall be applied continuously at ambient temperature to the sensor with balance clean air. The gas or vapour concentration shall be agreed between the manufacturer and test laboratory, with the assumption that concentrations up to 50x the expected level may be used to reduce testing time. This is consistent with the observation that the calculated ppm.hrs filter capacity is constant over a wide range of test concentrations and times.

Sensors shall be powered continuously during the test, with continuous monitoring of the sensors' output. When plotted as sensor response vs time, the intersection of the baseline current with the increase in sensor output, projected as a linear fit shall be the time to breakthrough. This time multiplied by the gas or vapour concentration will define the ppm.hr filter capacity.

5.2.3.2 Long Term Particle Exposure

5.2.3.2.1 General

Particles interfere with gas sensors in three ways: physical blocking of gas access to the sensor, blocking gas access to the electrode when the particles are very small, or transporting large organic molecules such as SVOCs and PAHs to the catalyst, coating the catalyst and blocking gas access to the catalyst.

5.2.3.2.2 Particle Exposure Test

A random sample of at least eight sensors are tested. This test will be agreed between the manufacturer and test laboratory. The particle type, concentration, flow rate and composition will depend on the required typical application for the sensor. Similar to the filter capacity test, the sensor will be monitored continuously while being exposed to test gas plus particles. A reduction in the output will be noted as the time when sensor performance changes non-linearly as explained in 5.2.3.1. The µg/m3.hrs will be reported, along with a clear statement of the particle size distribution, particle composition and concentration.

5.2.3.3 Cyclic exposure to Flue Gas

Sensors that are designed for use in measuring the composition of combustion gas should be tested to confirm they are stable when used in these applications. EN 50379:2012 details performance tests for such equipment and this CoGDEM specification recommends that the tests in section 5.6 be used to confirm these sensors have an adequate life.

5.2.3.4 High/Low RH long term testing

5.2.3.4.1 General

Electrochemical sensors contain various types of electrolyte which may be affected by absorbing or desorbing water when exposed to atmospheres of varying Relative Humidities (RH). This test exposes sensors to the maximum and minimum recommended RH exposure limit to confirm they still meet the specifications in their data sheets for the impact of RH variation.

5.2.3.4.2 Humidity Test

A minimum of 8 sensors are placed in a suitable container which maintains a RH at the maximum or minimum limit recommended by the manufacturer for continuous exposure. The sensors are weighed periodically until the weight has stabilised as water is gained or lost. Once the sensor weight has stabilised the sensitivity and response time are measured and compared to the values measured prior to the test and those stated in the manufacturer’s specification.

NOTE: It is permissible to run this test at elevated temperatures to reduce the time taken to reach a stable weight provided the RH is kept at the required level. In this case sensors should be allowed to return to room temperature prior to gas testing

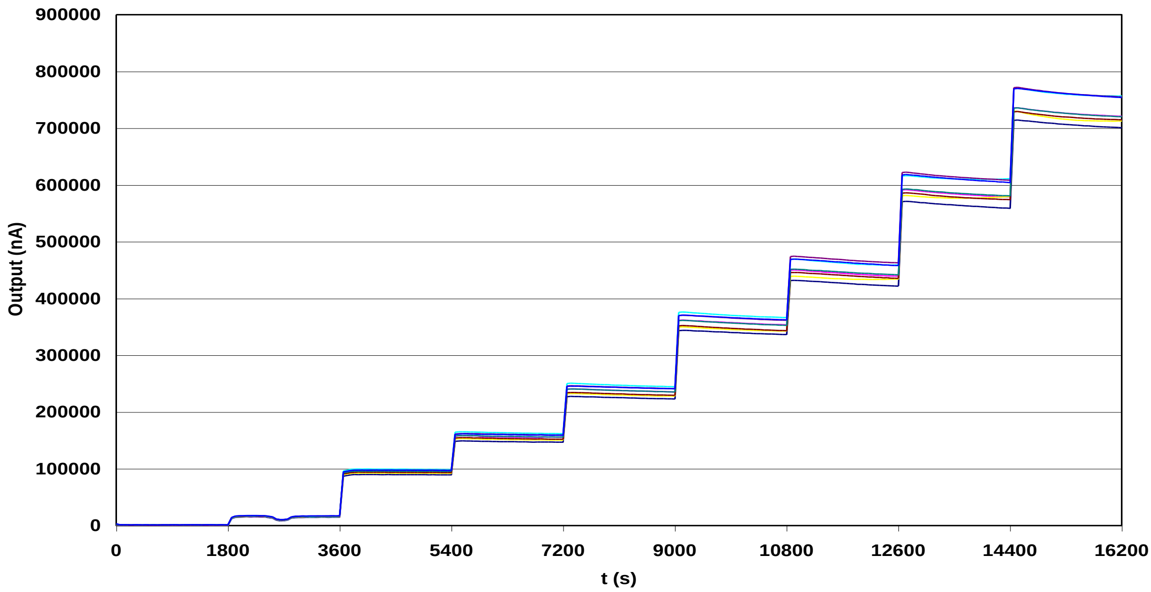
6 Data Processing

6.1 General

Testing conditions of temperature, humidity and pressure are reported by the test laboratory for each test.

6.2 Determining maximum accelerated ageing gas concentration

The maximum accelerated gas test concentration is defined by testing the sensor for performance at high gas concentrations. This test performed by the sensor manufacturer at ambient temperature is a stepwise increase of gas concentration beyond the maximum gas concentration as specified by the sensor manufacturer. Output is monitored continuously, with typically up to ten times the specified maximum continuous usage gas concentration. The sensor manufacturer reviews the output trace, looking for slower t_{90} and drifting output as the concentration is increased. Figure 2a shows a typical overgas test plot. When t_{90} is slowing significantly and/or the output is not stable, then the gas concentration below this value is used for accelerated lifetime testing. Each stepwise concentration is held for 30



minutes.

Figure 2a. Typical overgas output trace. Sensor output is not stable after 9000 seconds, 250,000 nA.

This procedure may be considered too severe for the test sensor. The manufacturer and test laboratory may decide to allow an ambient air exposure in between each increasing gas exposure. Figure 2b shows a typical example.

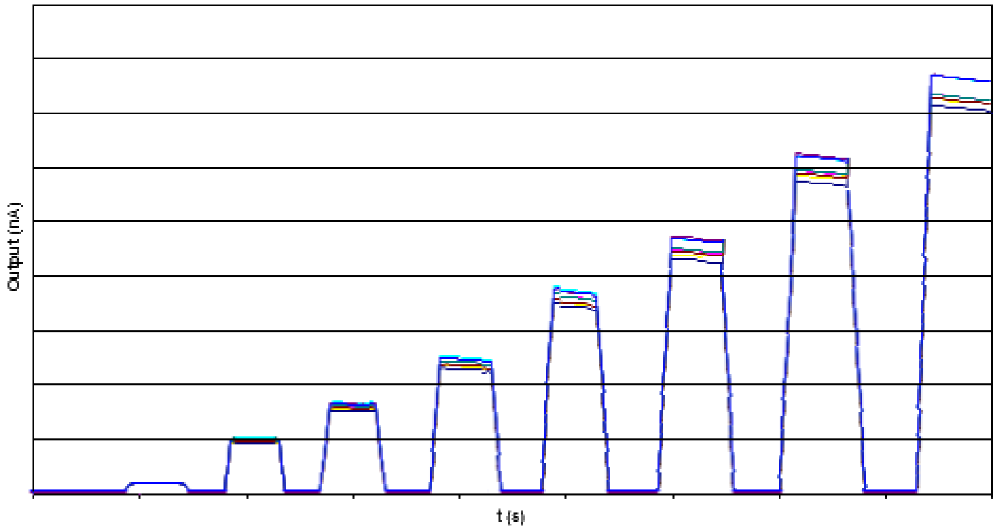


Figure 2b Alternative over-gas output trace

6.3 Data Overview

Data from these reliability tests is unlikely to contain exact failure times because sensors will only be checked periodically. Therefore, in order to process this data, we must first understand the three different types of data. These may be classified as:

Left Censored – sensor(s) that failed before the first observation point

Interval Censored – sensors known to be working at time t but seen to have failed at time t + Δt

Right censored – sensors still working at the completion of the test.

Statistical packages, such as Minitab, can be used to identify the frequency distribution that best fits such data, allowing the Mean and Variance of the population the items are drawn from to be predicted.

Annex C shows an example of how such data may be analysed.

7 Test report

The test report shall be in accordance with ISO IEC 17025 and in addition shall contain at least the following information:

a) the specification, uncertainty and validation of the test gas mixtures;

b) the test parameters and conditions used (e.g. t_{90}, t_{10}) together with justification of any change from the standard test method;

c) the tests in which dry gases were used;

d) Durability cycling test results reported as mean number of cycles to failure, presented as a histogram or as the uncertainty about the mean.

e) Lifetime based on results in the High Gas Concentration Exposure test, expressed as Coulombs; ppm-month is also reported as typical lifetime, based on expected exposure limits. If the expected lifetime based on this calculation is excessive then the manufacturer must consider other failure modes which can then be the dominant failure mode.

f) All optional tests are detailed, including test parameters and results.

Annex A Electrochemical Sensor FMEA

The table below lists failure modes and symptoms. Catalyst degradation and mechanical robustness are the two most critical failure modes, but other failure modes must be considered in specific applications.

Failure Mode Group	Design Decision	Failure Mode	Symptom(s)
Sensor design & manufacture	Pin/ body design Body welding/ sealing	Leakage (External)	High Zero current, Reduced output, External residue
	Electrolyte type and volume mineral acid, organic, RTIL, gel, water Electrode material/ sealing	Leakage (Internal), increased internal impedance, open circuit sensor	High Zero current, Reduced output, slow t90
	Catalyst/ electrode design/ manufacture Type of catalyst Bias voltage	Loss of catalytic activity,poor selectivity	Excessive thermal transient, Sensitivity drift outside specification, Zero Current too high, Unrepeatable response, Reduced sensitivity, Poor sensitivity tempco, Slow t90, incorrect cross-sensitivity
	Pin-conductor welding stack compression	Corrosion current, open circuit sensor; poor ionic transport	Sensitivity drift outside specification, Zero Current not in specification, slow t90, Sensitivity out of specification
Gas detector design & manufacture	Gas access to sensors	slow gas diffusion, limited sticky gas access	Slow t90, low and variable gas reading
	Bias voltage	catalyst damage	Loss of sensitivity,poor x-sensitivities, poor tempco
	Water ingress protection	high RH during storage	Sensor leakage (internal or external)
	poor circuit design/ layout	noise pickup	Poor S/N, EMC interference
Application	Extreme ambient conditions	High RH, Low RH, Extreme temperatures (fixed systems or T/RH transients (portable detectors) or low Oxygen	External Residue, Slow t90, leakage, Unrepeatable response, Reduced sensitivity
	Contaminants	Capillary or filter blockage	Sensitivity drift outside specification, Reduced sensitivity
		Filter consumption causing cross-sensitivity and electrode poisoning	Sensitivity drift outside specification, Reduced sensitivity, High cross-sensitivity, Unstable sensor output

Annex B Expected lifetime

Electrochemical gas sensors generally have three periods in their lifetime:

1 Initial stabilisation, which can be from days to months, depending on the catalyst, application and required resolution. Sensor manufacturers stabilise electrochemical gas sensors before shipping; required stabilisation in the gas detector should be discussed with the sensor manufacturer.

2 After initial stabilisation, the sensor will perform reliably, showing a slow decrease in output- the rate of stability/ loss of output depends on the sensor catalyst and application. Generally, the sensor output will remain predictable for many years.

3 Eventually the sensor output will decrease rapidly and t_{90} will increase significantly. The catalyst is no longer operating to requirement and at this time the sensor is no longer reliable. The time when sensor performance decays rapidly is considered the end of life, although the sensor will continue to respond to test gas. Sensor manufacturers may quote % output as still adequate for use, but when the sensor activity is decreasing rapidly, this is defined as end of life. Figure 2 below diagrams the output vs. lifetime, with the slopes and timelines depending on sensor design.

The intercept of the stable plateau and decreasing performance is defined as MTTF: the time to failure for an individual item. MTTF is calculated from the aggregate of all tests by a distribution analysis.

This is reported as Coulombs by the test house and can be translated into ppm.month by the sensor manufacturer. Converting these measurements into lifetime requires knowledge of the intended applications and should be agreed between the test laboratory and manufacturer.

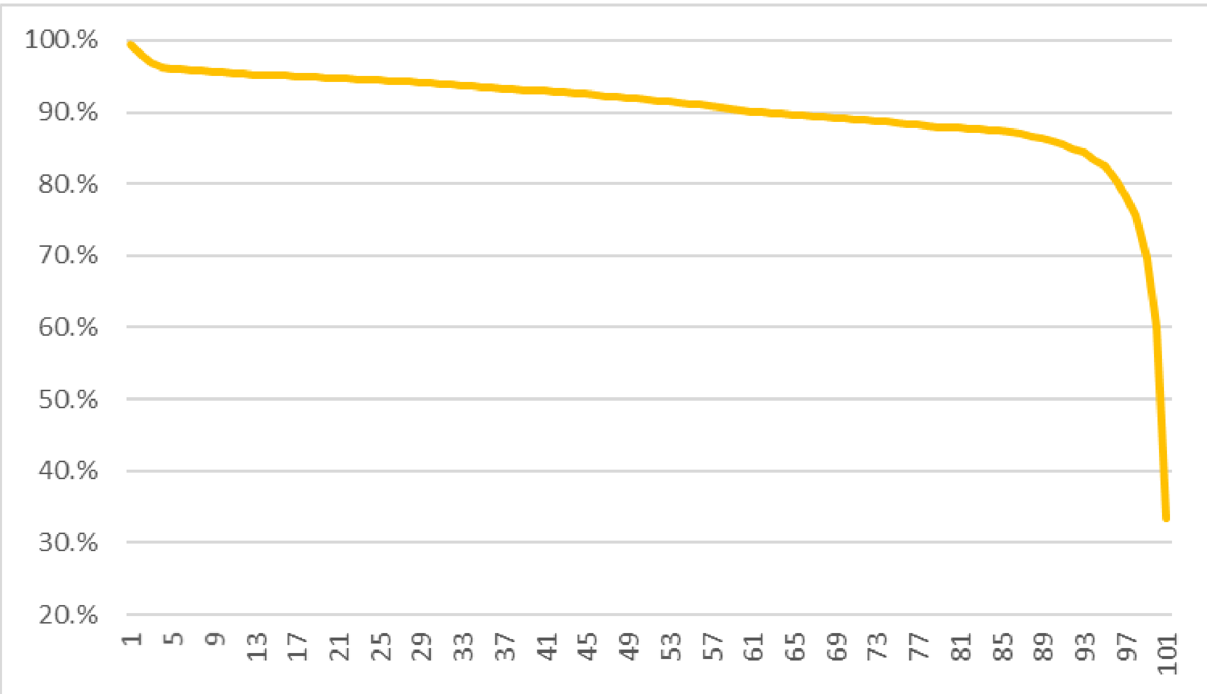


Figure 2. Output vs time for typical electrochemical gas sensors

Annex C Statistical data analysis

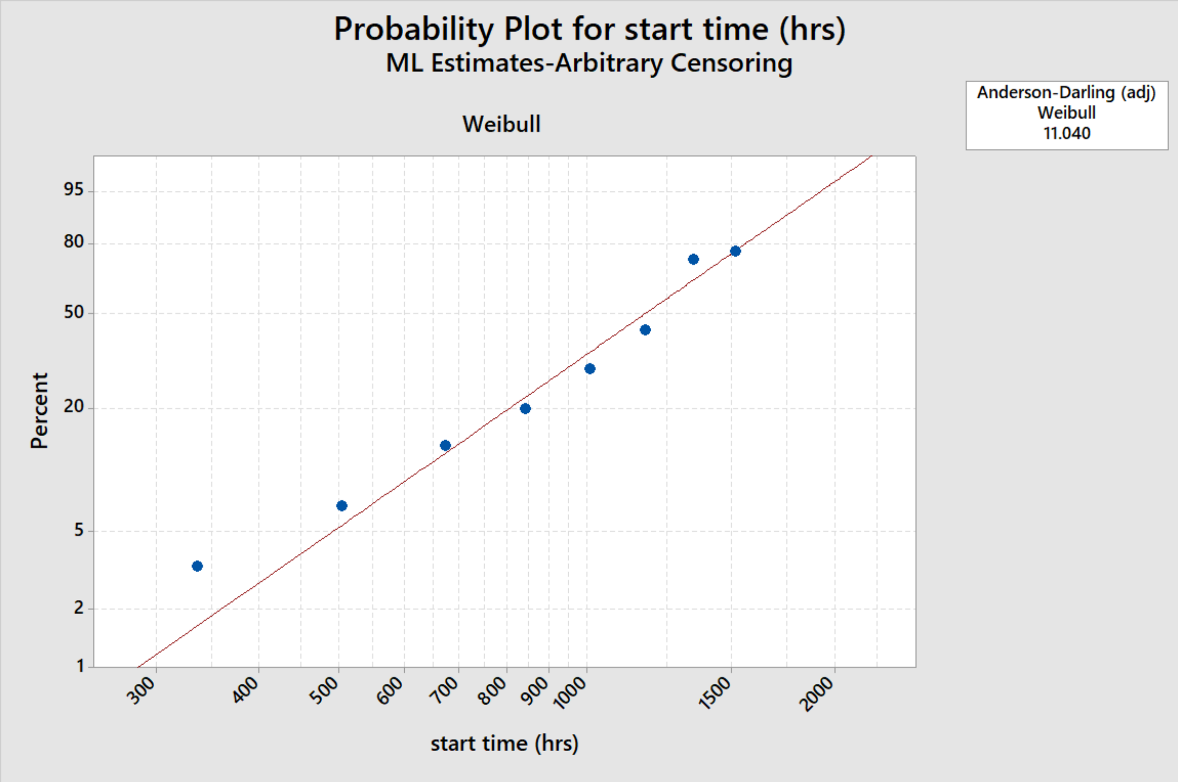
As an example, if 30 sensors are placed in a test and checked initially after 2 weeks stabilistion, then weekly. One sensor is found to have failed on the first check and then sensors are found to have failed at the weekly checks as per the table below. The test is stopped after 10 weeks with 7 sensors still working.

Frequency	week
1	2
1	3
2	4
2	5
3	6
4	7
9	8
1	9
7	10

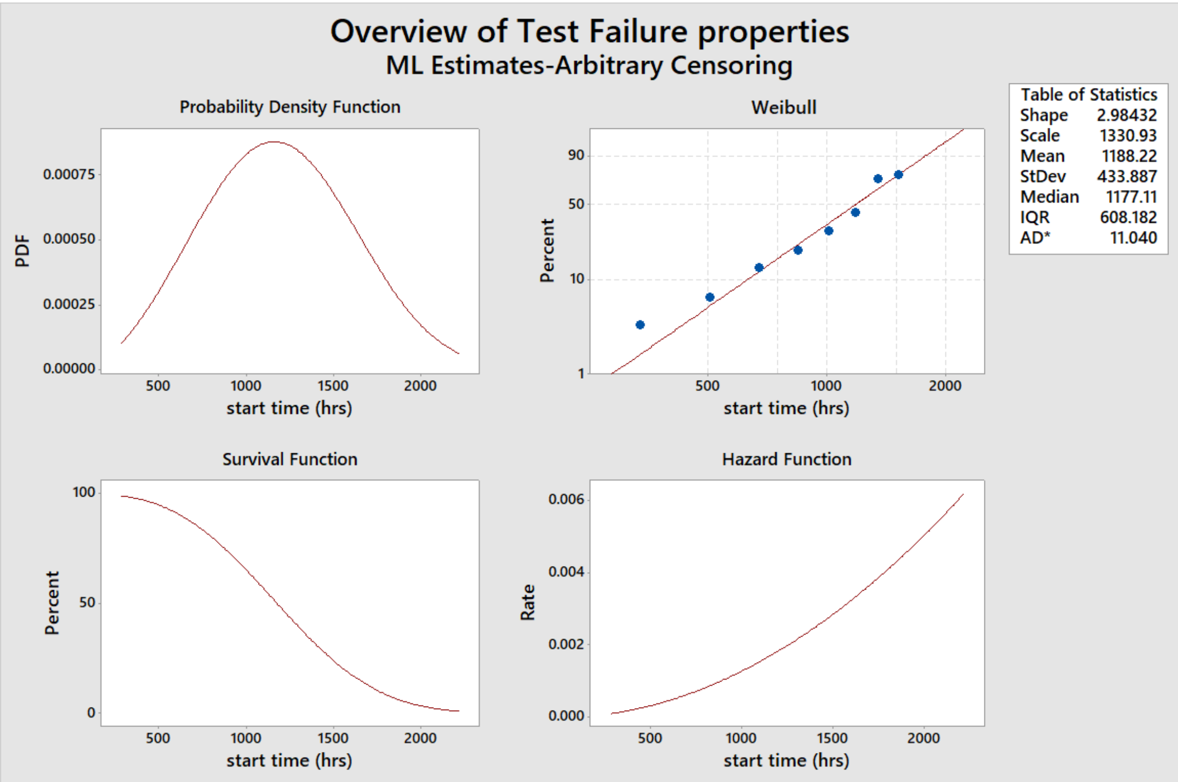
The first failure is Left censored, i.e. it failed before the first check at the end of week 2. The next 22 sensors are Interval censored i.e. they failed between two time periods and the remaining 7 sensors are Right censored having a failure time greater than 10 weeks. We can summarise this in a table thus where the * means unknown:

start time (hrs)	end time (hrs)	frequency
*	336	1
336	504	1
504	672	2
672	840	2
840	1008	3
1008	1176	4
1176	1344	9
1344	1512	1
1512	*	7

As this is a mixture of different sensor types, the ‘Arbitrary Sensor’ data type analysis in Minitab is used to process the data. Step 1 is to identify the frequency distribution that best fits the data. The Weibull distribution is a good fit, as shown below. This is often the case for time-bound reliability data.



The properties of the Weibull distribution can be used to review the failure rate in this test:



The Shape statistic (2.98) is greater than two, implying this is a ‘wear out’ failure mechanism and the Hazard Function graph indeed shows a rising failure rate with age. The MTTF of the distribution is 1188 hours. However, the 95% confidence interval for the MTTF is approximately 1000 hrs to 1400 hrs as a result of the uncertainty in exact failure time of the data. Observing the experiment more frequently will reduce this uncertainty.