

Exemption Request Form

Date of submission: 19/01/2023

1. Name and contact details

1) Name and contact details of applicant:

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2) Name and contact details of responsible person for this application (if different from above):

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2. Reason for application:

Please indicate where relevant:

- Request for new exemption in:
- Request for amendment of existing exemption in
- Request for extension of existing exemption in Annex IV
- Request for deletion of existing exemption in:
- Provision of information referring to an existing specific exemption in:
 - Annex III
 - Annex IV

No. of exemption in Annex III or IV where applicable: 1b

Proposed or existing wording: Lead anodes in electrochemical oxygen sensors.

Duration where applicable: Maximum validity period of 7 years

Other: _____

3. Summary of the exemption request / revocation request

Honeywell is submitting this exemption renewal request for lead in oxygen sensors because the recent Pack 21 review did not consider the types of sensor and end-uses that are described here.

Oxygen concentrations in gases can be measured using a variety of methods but each has advantages and disadvantages. For some end-uses, such as small portable gas monitors and instruments that can operate in ATEX environments, only instruments with galvanic sensors are suitable and usually only lead anode sensors can be used.

One of the advantages of lead anode sensors are that they do not consume electricity so small battery powered portable instruments can be used for whole working shifts. Also, the electrical characteristics of lead anode sensors are different to all other types of oxygen sensors, so alternative types cannot be used as drop-in replacements in existing instrument designs. Research has been carried out with potential substitute anode materials, but all have been found to have disadvantages, the main one being that lead is the only suitable anode metal that does not self-corrode or passivate under any conditions inside the sensor.

Research into substitute sensor/instrument options is being carried out by Honeywell, but due to the need for approvals for many of the end-uses, this will take many years to complete.

4. Technical description of the exemption request / revocation request

(A) Description of the concerned application:

1. To which EEE is the exemption request/information relevant?

Name of applications or products: **Oxygen gas concentration analysers in industrial monitoring and control devices**

a. List of relevant categories: (mark more than one where applicable)

- | | |
|----------------------------|---------------------------------------|
| <input type="checkbox"/> 1 | <input type="checkbox"/> 7 |
| <input type="checkbox"/> 2 | <input type="checkbox"/> 8 |
| <input type="checkbox"/> 3 | <input checked="" type="checkbox"/> 9 |
| <input type="checkbox"/> 4 | <input type="checkbox"/> 10 |
| <input type="checkbox"/> 5 | <input type="checkbox"/> 11 |
| <input type="checkbox"/> 6 | |

b. Please specify if application is in use in other categories to which the exemption request does not refer: **8**

c. Please specify for equipment of category 8 and 9:

The requested exemption will be applied in

- monitoring and control instruments in industry
 in-vitro diagnostics

other medical devices or other monitoring and control instruments than those in industry

2. Which of the six substances is in use in the application/product?

(Indicate more than one where applicable)

Pb Cd Hg Cr-VI PBB PBDE

3. Function of the substance: [Anode in cells that are used to measure oxygen concentrations in gases](#)

4. Content of substance in homogeneous material (%weight): [ca. 99.5%](#)

5. Amount of substance entering the EU market annually through application for which the exemption is requested: [5 tonnes](#)

Please supply information and calculations to support stated figure.

[The Council of Gas Detection and Environmental Monitoring \(COGDEM\) trade association has estimated that about 5 tonnes of lead per annum is placed on the EU market in lead-anode electrochemical sensors that are used for RoHS category 9 applications, and which are used mostly in the industrial safety and emissions monitoring markets.](#)

[This estimate is based on the assumption that 10 g of lead is used per sensor which was deemed to be an average amount.](#)

6. Name of material/component: [Lead metal in electrochemical oxygen sensor and the associated analysing equipment](#)

7. Environmental Assessment: _____

LCA: Yes

No

(B) In which material and/or component is the RoHS-regulated substance used, for which you request the exemption or its revocation? What is the function of this material or component?

[Lead metal is used as the anode in electrochemical cells that are used to measure the concentration of oxygen in gases. These cells contain a lead anode and an inert cathode which](#)

are immersed in an aqueous electrolyte. There is also an electrical connection between the anode and cathode as shown in Figure 1 below.

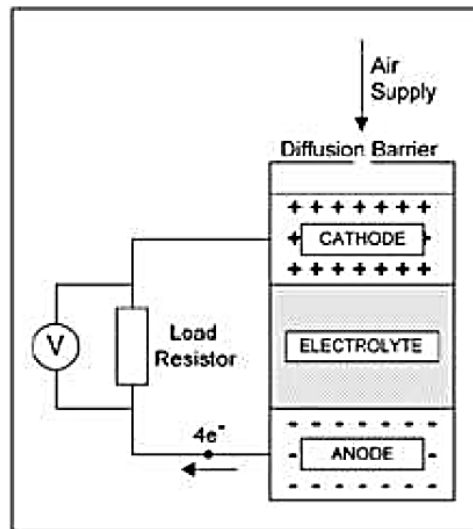


Figure 1. Schematic diagram of electrochemical oxygen sensor

When oxygen gas enters the cell, it dissolves in the electrolyte and undergoes an electrochemical reaction as follows:



One molecule of oxygen generates four electrons which pass along the electrical conductor that connects anode and cathode and so the quantity of oxygen is directly proportional to the electron flow. The current passing along the external circuit's electrical connection is measured, usually by measurement of the voltage across a load resistor in the circuit, to determine the oxygen concentration, according to Faraday's Law. In this way, oxygen gas concentrations can be measured without the need for a power supply to the cell. Lead metal is converted into lead oxide which remains inside the sensor.

Cells are designed so that they measure oxygen gas concentrations accurately and have a reasonably long lifetime before the anode is consumed, typically of 1 – 2 years, but this can be longer. This is achieved by allowing only a small proportion of the gas being analysed to enter the electrochemical cell. Honeywell achieve this using two methods, with each design of sensor having different end-uses:

1. Capillary cells have a very narrow hole in the external wall of the cell that allows a small amount of gas that is being analysed to enter the cell. These types of sensors are widely used including in medical applications, which are not covered by this exemption renewal

request¹, as well as in many industrial and commercial uses. Although Honeywell also produce such sensors for industrial applications these applications are described in the Alphasense exemption 1b exemption renewal request.

2. Membrane diffusion cells use a semi-porous membrane to allow a small amount of analysis gas to enter the electrochemical cell. These are also called “partial pressure oxygen cells.”

The following simplified schematic diagram shows the basic design of lead electrochemical oxygen sensors with a diffusion barrier.

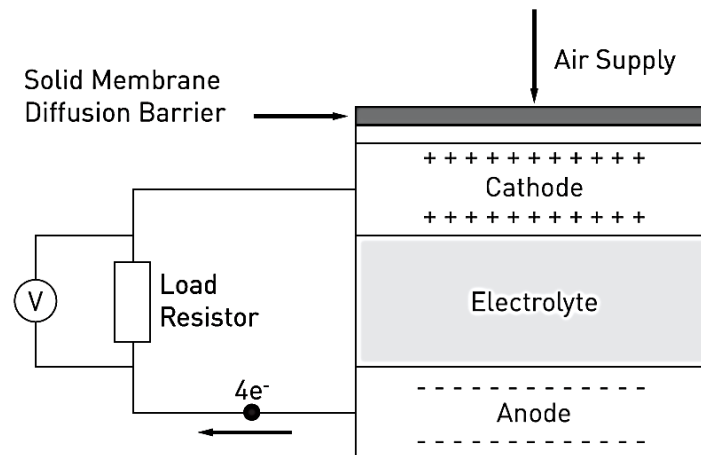


Figure 2. Simplified schematic diagram of a lead-electrochemical oxygen sensor cell with diffusion barrier

One limitation of capillary sensors is that if the concentration of acidic gases such as SO₂ or CO₂ concentrations in the gases being analysed are high, they can affect the accuracy of measurements (it increases the oxygen signal by about 0.3% per 1% CO₂). CO₂ however does not pass easily through the diffusion membrane and so membrane cells are much less affected by high CO₂ (or SO₂) concentrations.

The lead electrochemical sensors are designed as small components that plug into sockets in gas analyser equipment. The sensors are intended to be easily replaced when the lead has been consumed and converted into oxide. New analyser instruments are sold with oxygen sensors already installed and many designs of instrument also analyse other gases. Each gas is analysed using a specific type of sensor. When the lead-anode in an oxygen sensor is consumed in an analyser instrument, the analyser will no longer function. The sensor therefore needs to be replaced by a new but identical oxygen sensor as a replacement spare part. These replacements will need to be readily available throughout the lifetime of the analysers which can be more than 10 years.

¹ An exemption renewal request was submitted by COCIR in January 2020 and is available from https://www.cocir.org/fileadmin/5.5_Policies_Environment/RoHS/Exemption_renewals/COCIR_-_Renewal_Form_exemption_1b_Annex_IV_-_15012020.pdf

There are many types of analyser instruments on the market, each being designed for a different end-use. Some measure oxygen concentration only, others measure the concentrations of multiple gases and these instruments contain different types of sensor with one type for each gas being analysed.

Honeywell and other oxygen sensor manufacturers produce a wide variety of designs of oxygen gas sensor and gas analyser instruments in which they are used. Each model of instrument is designed to use only one specific type of oxygen sensor.

Differences in oxygen sensor design include:

- The layout of the connecting pins is different for each design of sensor which is used to prevent the use of the wrong type of sensor in an analyser instrument. Three examples (showing dimensions in millimetres) are shown below.

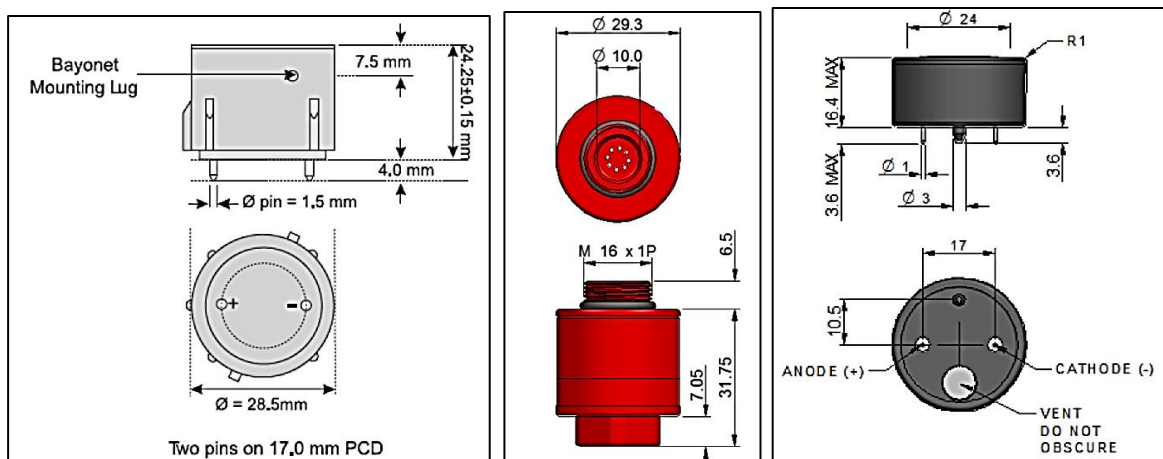


Figure 3. Examples of Honeywell lead-anode oxygen sensors (copied from datasheets). Left - 5FO capillary cell, middle –AO2 membrane cell, right-7OX membrane cell

In the above examples of lead anode sensors, the 5FO cell is intended for SCUBA diving applications, AO2 for analysis of vehicle exhausts and 7OX is a compact type used for analysis of oxygen in the 0 to 25% range.

- Connecting electronics. This is required to compensate for temperature, atmospheric pressure, etc. Some sensors have integral temperature compensation whereas others rely on compensation circuits in the analyser instrument.
- Sensors are designed for specific oxygen concentration ranges and use outside of these can damage them and severely shorten their lifetime. For example, Honeywell sensors are designed for: 0 to 2ppm, for 0% to 25% and others for 0% to 100%.
- Sensors are designed for specific end-uses such as SCUBA diving and vehicle exhaust analysers. Each design takes into account the environment in which they will be used and the presence of other gases that will be present, CO₂, CO, etc in vehicle exhausts and diving gases can contain helium. These analyser instruments are certified by approval bodies for these specific uses. For example, vehicle exhaust gas analysers

must be approved by New European Driving Cycle (NEDC) and the Bureau of Automotive Inspection (BAR).

- Most sensors have plastic cases, but types with metal cases are available where there is a risk that the end-use conditions may damage the plastic case.
- The amount of lead inside the sensor is variable. Usually, enough lead is used to ensure a lifetime of two years during normal use (although some types are intended for shorter periods). Small-size sensors with less lead are used when weight is important such as in analysers that are worn by users to alert them when hazardous conditions occur.

Examples of locations where oxygen analysers are used include, many of which are safety critical applications:

- Water treatment works
- Food packaging
- Refining
- Bio-gas monitoring
- Boiler flue/Emissions analysis
- In ships
- Military such as in submarines and for inspection of fuel storage tanks
- Paper mills
- Semiconductor and photocell manufacture
- For working in confined spaces, such as tunnels, sewers, tanks, etc.
- Building and construction sites, such as in tunnels and trenches
- In mines
- Commercial buildings, medical and laboratories, such as boiler rooms, cryogenic zones such as liquid nitrogen storage.
- Farming
- SCUBA diving gas analysis

Many of the sensor and analysers are designed to be used in industrial areas where potentially explosive gases or liquids may occur such as in fuel tanks, mines, etc., and so only ATEX approved equipment is permitted.

The sensors are also used both in fixed positions as well as in some applications as mobile sensors. Sensors that are used for mobile applications need to be very small and lightweight as they are used in small-size lightweight portable oxygen analysers that are worn by users. These analysers alert users if oxygen levels in the air in which they are working drop to unsafe levels.

(C) What are the particular characteristics and functions of the RoHS-regulated substance that require its use in this material or component?

The required characteristics for lead-anode electrochemical oxygen sensors are:

- Capable of continuous analysis of oxygen in the concentration range 0% to 100% oxygen
- Lifetime of two years when used for recommended applications
- Must not passivate or self-corrode
- Capillary sensors are close to linear response for sensor's output signal versus oxygen concentration. Response is $S = K \log_e 1/(1-C)$ (S = output signal, C = concentration and K = constant). Partial pressure membrane sensors are inherently linear
- Sensor output must be stable throughout its lifetime
- A warmup time of <2 mins for portable and fixed instruments
- Can operate in the range -20°C to +45°C
- Effects of temperature and pressure of lead anode sensors are predictable so that these can be compensated for (see section 6)
- Sensor must give a sudden and large drop in output signal when the lead anode has been consumed
- The sensor needs to be small, especially for portable air monitoring applications, typically less than 30mm wide and 25mm high. Honeywell's 4-series sensors are typically about 20 mm diameter, 17 mm high and weigh <16 grams
- Power consumption of sensors for use in portable monitoring instruments needs to be sufficiently low (ideally zero) so that the analyser can be powered by small lightweight batteries, ideally rechargeable types, for at least one working shift of 8 – 10 hours.
- Effects of other gases on output readings should be as follows:
 - Methane (100%) 0%
 - Hydrocarbons (100%) 0%
 - Hydrogen 100% <-2%
 - Carbon monoxide 20% <-0.5%
 - Carbon dioxide (1%) 0.3%
- Mechanical stability of the device such that it can be dropped and still function as intended

Users will choose an oxygen analyser instrument on the basis of the following characteristics²:

- Accuracy within the range of concentrations required
- Resolution by the readout of the instrument
- Limited interference with other gases also experienced in the products operating environment. This is mainly affected by the type of sensor chosen
- Size and weight. Important for portable analysers
- Short warm-up time after being switched off for 24 hours.
- Response time is the time taken to give an accurate reading (usually 90 or 95% of the actual concentration). In safety critical applications, this must be short.
- Limited drift which is a measure of instrument stability over time. Drift can be caused by changes in the sensor or to the instrument's electronics.

- Operating time for battery powered instruments (this is maximised as lead sensors do not consume power)
- Certification is required for several end-uses including diving, vehicle exhaust emissions analysis and ATEX environments
- If used as a personal monitor, it must be small and unobtrusive and not impair the wearer's work function. They are usually worn continuously for the working shift of 8 hours or more so batteries must last much longer than this.

Analysers with lead in electrochemical sensors are ideal as the lead metal does not self-corrode in the absence of oxygen, so does not produce a current without oxygen being present. However, lead reacts rapidly when in contact with oxygen, giving a fast response time to the sensor.

The sensors based on lead do not require power to operate, unlike other sensor types. The sensor is a consumable part of the analyser with a relatively long lifetime, typically for 1 to 2 years. This is important for sensors which are in hard-to-reach areas where replacement opportunities are limited.

5. Information on Possible preparation for reuse or recycling of waste from EEE and on provisions for appropriate treatment of waste

- 1) Please indicate if a closed loop system exist for EEE waste of application exists and provide information of its characteristics (method of collection to ensure closed loop, method of treatment, etc.)

No. Customer dispose of used sensors according to local waste requirements and they are not returned to Honeywell.

2) Please indicate where relevant:

- Article is collected and sent without dismantling for recycling (this refers to oxygen sensors and analyser instruments)
- Article is collected and completely refurbished for reuse
- Article is collected and dismantled:
- The following parts are refurbished for use as spare parts: _____
 - The following parts are subsequently recycled: _____
- Article cannot be recycled and is therefore:
- Sent for energy return
 - Landfilled

3) Please provide information concerning the amount (weight) of RoHS substance present in EEE waste accumulates per annum:

- In articles which are refurbished _____

² More details available from <http://www.cogdem.org.uk/Publications/DisplayDocument.php?documentid=19>

- In articles which are recycled 5 tonnes (same as annual EU sales)
 In articles which are sent for energy return _____
 In articles which are landfilled _____
-

6. Analysis of possible alternative substances

- (A) Please provide information if possible alternative applications or alternatives for use of RoHS substances in application exist. Please elaborate analysis on a life-cycle basis, including where available information about independent research, peer-review studies development activities undertaken**

Honeywell and other manufacturers produce a wide variety of types of oxygen sensors and analysers, several of which are lead-free types, but each sensor type has its own advantages and disadvantages making each type suitable for only certain specific end-uses. For some applications, currently only lead electrochemical sensors are technically suitable and have proven reliability and accuracy under all of the end-use conditions for which these sensors are intended to be used.

The following describes recent research into potential substitutes for lead in electrochemical sensors and the status of alternative sensor designs.

Substitution of lead

The currently used lead anode electrochemical sensors have the advantage that the sensor does not require a power supply, which is important in small-size portable applications as this avoids the need for large batteries. The sensors need only two electrical connections so that the measured voltage is proportional to oxygen concentration. The simplest option for substitution that might allow a similar analyser design to be used would be to replace lead with an alternative metal, however to date, this has not been possible (with a few exceptions outlined below) as no drop-in replacements have been found and all alternative anodes appear to have disadvantages.

Substitute metals must not react with the electrolyte unless oxygen is present but should provide a galvanic voltage with oxygen, without passivation and this severely limits which elements of the periodic table can be considered. Clearly metals that are inert such as gold and platinum are unsuitable as anodes, but also metals that passivate, such as niobium, forming inert oxide coatings will also be unsuitable. Too reactive metals that self-corrode in the absence of oxygen (they generate hydrogen and induce a current within the cell) are also unsuitable such as zinc and aluminium which react in both acid and alkali electrolytes (aluminium can also passivate in near neutral pH solutions). The reason lead is ideal for this application is that it does not passivate or self-corrode at any pH. Radioactive and toxic metals are also rejected.

Selection of an alternative anode material is complicated. Suitable anode metals will generate a potential difference with a suitable cathode in a suitable electrolyte such it does not passivate

or self-corrode and generate hydrogen gas. It is possible to identify suitable anodes from plots of anode-voltage versus pH, known as Pourbaix diagrams, but the actual anode voltage inside the cell at any specific pH and current flow is also dependent on the choice of cathode metal. The electrode potentials of metals in aqueous solution are an important characteristic for galvanic oxygen sensors, but avoiding passivation and self-corrosion are essential criteria. The standard electrode potentials of lead and other metals are listed below in Table 1 for comparison.

Table 1. Standard electrode potentials in water at 25°C³

Metal	Electrode potential (volts)
Lead ($\text{Pb}^{2+} = \text{Pb} + 2\text{e}^-$)	-0.126
Tin ($\text{Sn}^{2+} = \text{Sn} + 2\text{e}^-$)	-0.136
Tin ($\text{Sn}^{4+} + 2\text{e}^- = \text{Sn}^{2+}$)	+0.15
Germanium ($\text{GeO}_2 + 4\text{H}^+ + 4\text{e}^- = \text{Ge} + 2\text{H}_2\text{O}$)	-0.15
Zinc ($\text{Zn}^{2+} = \text{Zn} + 2\text{e}^-$)	-0.76
Aluminium ($\text{Al}^{3+} = \text{Al} + 3\text{e}^-$)	-1.66
Bismuth ($\text{Bi}^{3+} = \text{Bi} + 3\text{e}^-$)	+0.317
Antimony ($\text{SbO}^+ + 2\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Sb} + \text{H}_2\text{O}$)	+0.212
Copper ($\text{Cu}^{2+} = \text{Cu} + 2\text{e}^-$)	+0.337

Actual electrode potentials will be different in non-standard conditions, such as high and low pH and with metal alloys, where the alloying additives will shift electrode potential values. The only metals in the periodic table that have standard electrode potentials that are similar to lead are tin and germanium. Germanium is unsuitable as it forms an inert oxide that will passivate the metal (germanium is also very uncommon). Tin has a similar standard electrode potential for divalent ion formation, but the divalent tin ion can be further oxidised to the tetravalent tin ion with a vastly different electrode potential whereas, the divalent lead ion is stable and cannot easily be oxidised. Tin also self-corrodes, generating hydrogen in acid and strongly alkali electrolytes, especially at higher temperatures, so for substitution, the choice of electrolyte is important. Lead however does not self-corrode or passivate at any pH value.

³ Data from <http://hyperphysics.phy-astr.gsu.edu/hbase/Tables/electpot.html#c1>, https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Electrochemistry_Tables/P1%3A_Standard_Reduction_Potentials_by_Element and Handbook of Chemistry and Physics, pub The Chemical Rubber Company

Research has been carried out by Honeywell and other oxygen sensor manufacturers to investigate alternative electrodes with tin, zinc, aluminium, copper, bismuth and antimony⁴. The work published in reference 4 showed that tin, zinc, and aluminium can self-corrode in the absence of oxygen, whereas while copper, bismuth and antimony are good candidates based on their Pourbaix diagrams and so were worthwhile investigating. Research results, however showed that passivation does occur with all three metals. There have also been several patents published describing lead-free galvanic sensors as summarised in Table 2.

Table 2. Patents published describing lead-free galvanic sensors

Patent number, application company and publication year	Summary
US 0231253 A1 Life Safety Distribution AG, 2014	Sb, Bi and Cu anodes. Prior art in EP 159362 A1 states that it is difficult to control the rate of anode consumption and a two-year lifetime cannot be achieved, but modifications described in this patent are claimed to achieve two years.
EP 2813844 A1, Honeywell, 2014	Sb, Bi and Cu anodes uses anodes with larger surface area (sintered particles) to increase lifetime as passivation of large mass anodes can occur. This also proposed addition of fluoride to alkali electrolytes.
EP 3495810 B1 Maxell, 2019	Tin-5%antimony anode membrane cells, electrolyte contains a chelating agent (citric acid).
US 772736882, ITG, 2010⁵ (also US11,243183B1, ITG, 2022	Tin anode in caesium carbonate solution electrolyte. 2022 patent is for a sensor which is not affected by N ₂ O.

It needs to be noted that patents, such as those listed above, are intended to give a favourable impression of these devices and limitations and problems are not usually divulged. Where a patent has been published but no commercialised sensors exist, this suggests that technical issues have not yet been resolved and have prevented commercialisation.

Only a small number of lead-free galvanic sensors have been commercialised⁶. These commercial products are not drop-in replacements because they are larger size than the smaller lead anode sensors and they also have different characteristics, Differences include:

⁴ For example, see <https://ieeexplore.ieee.org/document/6400667> also, abstract available from <https://www.semanticscholar.org/paper/Lead-free-galvanic-oxygen-sensors-%E2%80%94A-conceptual-Cobianu-%C8%98erban/e4cfb461b42eba465ee2410d5637bf7453079bf6>

⁵ Patent <https://patents.google.com/patent/DE102006024022B4/en>

⁶ One manufacturer (ITG) produces many types of industrial oxygen sensors with lead anodes, but only a few which are lead-free.

Temperature capability: No lead-free galvanic sensors are recommended for use below 0°C (lead anode sensors are rated down to -20°C). Also, accuracy (static temperature error) of lead-free galvanic sensors at temperatures below 10°C is reported to be only $\pm 10\%$ ⁷, which is inferior to lead anode sensors.

Pressure and temperature response: The temperature and pressure behaviour of tin anode galvanic sensors is different to that of lead anode sensors, which prevents their use as drop-in replacements.

Electrical behaviour: Testing by a member of COCIR¹ found that the commercial tin anode sensors do not behave electrically in the same way as lead anode sensors, especially when the anode has been consumed as there is no sharp drop in output when the sensor is no longer accurate. Without this sudden change, anode consumption is not detectable by the analyser instrument. This is a severe problem in safety critical oxygen monitors that are used to warn workers of too low oxygen concentrations if they do not provide an immediate alarm.

Response time: For lead-free cells with tin anodes, this varies depending on the type of sensor and ranges from <5 seconds to 1 minute with many types being 25 to 40 seconds⁸. Response times for lead anode sensors can be as short as 2 seconds.

Size: Currently there are no lead-free galvanic oxygen sensors that can replace sensors of 20mm diameter and 17mm height. A typical commercial medical lead-free oxygen sensor has dimensions 80 x 48mm⁷ whereas an industrial lead-free sensor is 31.5mm wide and 40.5mm high (I-01 made by ITG). These are too large for wearable oxygen monitors.

Approvals: No lead-free galvanic sensors or their analyser instruments are available that are approved for use in automotive emissions monitoring, for diving applications or are ATEX approved. Instruments cannot be used in these applications without having the appropriate certification and approvals.

Low oxygen concentrations: Analysers in the 0 – 2ppm O₂ range with lead-free galvanic sensors are not available.

Honeywell believe that tin anodes will passivate and this is why larger size anodes are needed for a reasonable lifetime. Acidic compounds in the gases being analysed are an issue if they reach the electrolytes. CO₂ will react with carbonate ions if used in electrolytes to form bicarbonate which has a lower pH. Passivation of tin is more likely at near neutral pH (this explains why there are no capillary lead-free sensors which allows CO₂ to reach the electrolyte). Metals other than tin may be suitable, but to date, technical issues have not been resolved. Options include adding alloying metals to shift the electrode potential to prevent

⁷ <https://asatech.en.made-in-china.com/product/GCBngkiOXuVY/China-Itg-O2-Oxygen-Sensor-Leadfree-Medical-Sensor-0-100-Vol-O2-Mlf-16.html>

⁸ Reference 7 and Maxell website

passivation⁹ or self-corrosion, by the use of more unusual electrolytes (such as caesium carbonate used by ITG or addition of citrate ions as used by Maxell) and by alternative cathodes to adjust cell voltages. Research by Honeywell however has found that all lead-free anode galvanic cell designs have technical issues that prevent them from being drop-in replacements for lead-anode galvanic cells. These issues include:

- The energy density of metals depends on atomic weight, density, and valency of the most stable oxidation state. Honeywell's patent EP 2813844 A1 gives the equivalent weights of antimony, lead and copper that would be required at an output current of 100 μ A to last five years, for comparison. The volumes of these metals can be calculated from these equivalent weights and the density of these metals. This shows that the mass and volume of lead is larger than the equivalent weights of antimony and copper (this will also be true for bismuth and tin)¹⁰. Commercially available lead-free galvanic oxygen sensors⁷ are significantly larger than lead anode sensors (as explained above) and Honeywell have determined that sensors with tin, antimony, bismuth and copper would all have to be significantly larger than sensors with lead for the following reasons:
 - For antimony, bismuth, copper and tin, passivation can occur at least under some use conditions, so that only a proportion of the anode is consumed before the sensor ceases to function. One manufacturer uses a coil of tin⁵ and another has patented sintered particulate anodes to increase surface area¹¹ but this may only partially alleviate this issue.
 - Different methods of electrical connection may be needed as well as use of high surface area anodes to reduce the effects of passivation and both would result in a larger sensor size.
 - A larger volume of electrolyte may be required. This is necessary if an ingredient is consumed.
 - If the anode is an alloy, only the principal metal oxidises
- Optimum performance relies on a suitable cell voltage. If lead anodes are replaced by a different metal, especially one with a very different electrode potential, the choice of cathode may need to be changed to prevent anode passivation or self-corrosion. For alternative anode / cathode combinations, the cell voltage will be different to lead anode sensors and so these sensors cannot easily be used as drop-in replacements.
- Lead anode cells use mildly alkaline potassium acetate solution as the electrolyte. This is relatively non-hazardous, gives a fast response time with lead anodes and does not react with CO₂. Commercial tin anode cells contain caesium acetate solution electrolyte which will react with CO₂ to form the bicarbonate with a lowered pH. Trials by Honeywell found that the potassium acetate solutions that are used in lead anode cells gives

⁹ For example, mercury and indium alloyed to zinc prevent it from self-corroding in alkali batteries.

¹⁰ Equivalent weight of antimony is 6.5g, density is 6.683 so volume is 0.97cm³. Equivalent weight of lead is 16.9g, density is 11.34 so volume is 1.49cm³.

¹¹ US 772736882, ITG, 2010 and EP 2813844 A1, Honeywell, 2014

inferior performance (such as passivation) as an electrolyte for antimony, bismuth and copper and a Honeywell patent¹² describes the use of strongly alkali potassium hydroxide solutions and the addition of potassium fluoride to prevent passivation of antimony, bismuth or copper anodes. These solutions can be used at low temperatures (-20°C) as they do not freeze. Potassium hydroxide solutions are highly corrosive to human skin and potassium fluoride is classified as toxic, so although leaks are unlikely, they are possible if the sensor is damaged, so these electrolytes would be a disadvantage when compared with potassium acetate that is used with lead anodes.

- As far as we know, all commercial lead-free two-electrode sensors have membrane diffusion barriers, there are no commercial lead-free sensors with capillaries.
- Lead-anode oxygen sensors use solid metal anodes to which reliable electrical connections are made. If anodes need to be made with sintered particles or coils of wire, then it is essential that the metals used to connect to the anode are not exposed to the electrolyte as this will generate a galvanic cell. This cell is likely to either affect the performance of the anode or to self-corrode. This issue is probably not insurmountable but is an added difficulty that does not occur with lead anodes.
- Honeywell's research with alternative anodes has found that at higher temperatures (above 20°C), self-corrosion becomes an issue so that a current is generated when no oxygen is present. The effect of temperature on output is also different to that of lead anode cells.
- Honeywell found that antimony, bismuth and copper will passivate when the sensor is exposed to high concentrations of oxygen. This is most pronounced with bismuth and copper but also occurs with antimony¹². Use of a high surface area and electrolytes that contain fluoride ions delays passivation, but it still occurs so that only by the use of much larger anodes can a reasonable lifetime be achieved. However, as explained above antimony self-corrodes at higher temperatures, even in the absence of oxygen, so its overall performance is inferior to lead.
- Zinc has been considered as an alternative anode. Zinc is used as an electrode in alkali batteries. These batteries use zinc alloys with a high surface area in an alkali electrolyte, Zinc anodes in alkali electrolytes have been considered for oxygen sensors but self-corrosion is an issue. This maybe because of the very significant differences between batteries and oxygen sensors. Batteries are intended to operate at or near to an open circuit voltage (they are not normally short-circuited in normal use), whereas oxygen sensors operate at as close to short-circuit as possible and so the electrode potentials of zinc in batteries and in oxygen sensors are very different. In an oxygen sensor the cathode's potential is pulled to the same potential as the anode (e.g. zinc) with the result that large amounts of hydrogen evolution occur on the cathode, much more than the self-discharge hydrogen evolution on the anode due to the high catalytic activity of the cathode. Further research is needed to overcome the limitations of zinc, such as the options described in a patent on "Potentiostatic Circuits for Electrochemical

¹² This is described in European patent EP2813844A1.

Sensors”¹³, however as this option requires a circuitry design change, these sensors would not be a drop-in replacement for lead-anode sensors.

Despite these difficulties and limitations, this is an option that warrants further research, but significant technical difficulties exist before two-electrode lead-free anode sensors can be developed that are suitable for all end-use applications. In practice, for some end-uses, 3-electrode pump cells can be used, but due to their different characteristics, these cannot be drop-in replacements and are not suitable for many end-uses, as described below.

3-electrode amperometric type electrochemical cells - Pump cells

A substitute design of oxygen sensor has been developed based on lead-free technology and is used commercially. Unlike the two-electrode lead-anode galvanic cell, these contain a “sensing” electrode, a “counter” electrode and a “reference” electrode. A power supply is required to control the electrode potentials of the anode and cathode so that the following reactions take place in the presence of oxygen.

Sensing electrode reaction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Counter electrode reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

A disadvantage of this sensor when compared to the lead-anode two electrode sensor is that it requires more complex electronics to control the sensor and measure its output as shown below in Figure 4

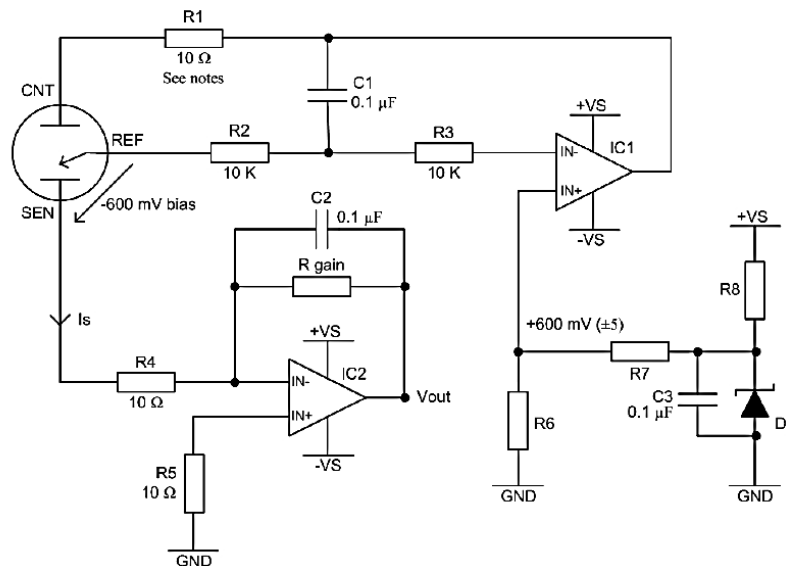
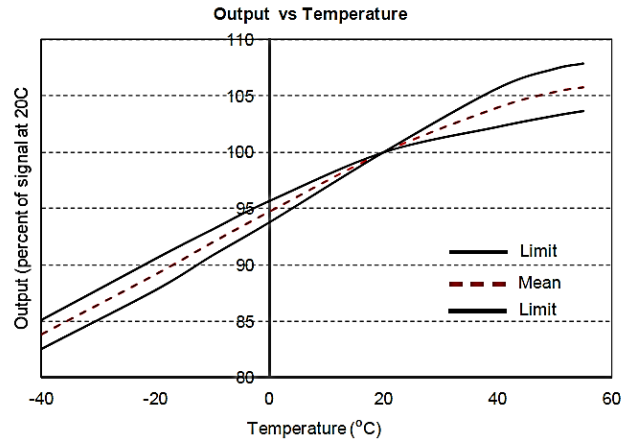


Figure 4. Circuit diagram required for 3-electrode oxygen cell

Other differences to lead anode sensors include:

¹³ European patent EP 2860517A1, Honeywell International Inc., published 2014

- Changes in temperature and pressure cause different responses so they cannot be used as a drop-in replacement in applications where accurate sensing of oxygen content is required when these occur. The graphs below shows that the temperature dependence of electrochemical sensors is not identical to lead-anode capillary and membrane sensors.



Baseline Offset Variation with Temperature

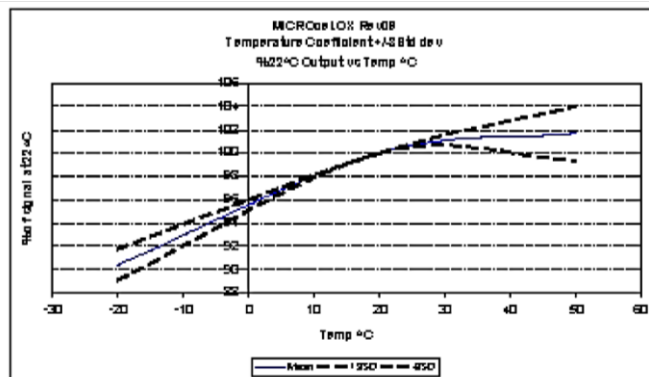


Figure 5. Dependence of oxygen sensors on temperature – above three-electrode pump-cell electrochemical sensor, below capillary lead anode galvanic sensor

The graph below shows the dependence of these sensors on atmospheric pressure which is not the same as that of lead-anode capillary and membrane sensors.

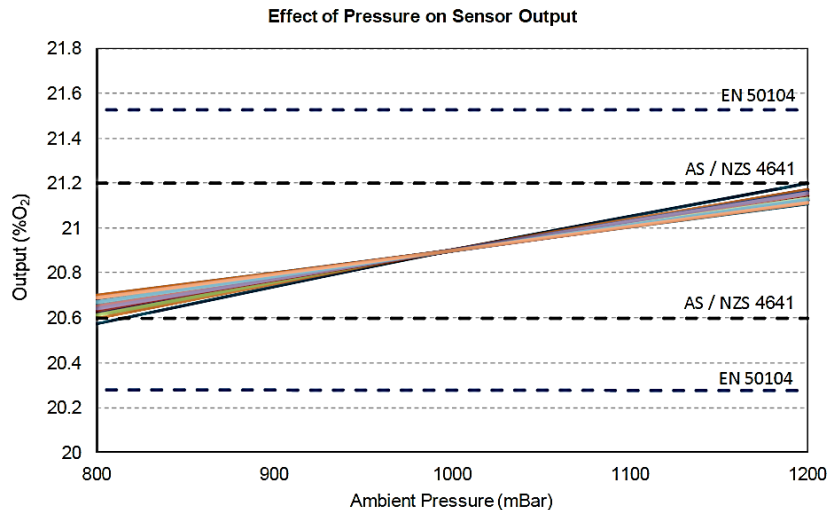


Figure 6. Dependence of three electrode electrochemical sensor output on atmospheric pressure

- A power supply of at least 2.5 volts is needed. Oxygen pump sensors need a larger positive supply rail than most toxic gas sensors as the counter electrode needs to be continuously driven to a sufficiently high positive voltage to maintain sensor operation over all conditions (especially at temperature extremes). Using a minimum positive rail of +2.5V ensures enough headroom for correct operation. The cell itself consumes 0.25mW, or more if the supply voltage is higher. Therefore, portable instruments will be larger and heavier due to the need for batteries to supply this voltage and power for the cell's operation
- Oxygen gas is generated at the counter electrode. This must not reach the sensing electrode as this would give false readings. This is a significant disadvantage in ATEX approved analysers as the evolved oxygen gas would usually be vented into the analyser's housing and this could cause a potentially explosive gas mixture when used in ATEX environments. Analyser instrument housings need to be vented to prevent pressure build up from internally vented generated oxygen but venting also allows flammable gases into the inside of the instrument's housing.
- Lead-anode oxygen sensors have very short start up times after power to the analysis instrument is disconnected (e.g. battery change or switching off when not in use), typically less than 2 minutes and some types are less than 10 seconds. Three electrode electrochemical cells take at least 15 minutes and up to several hours to reach stable and accurate measurement. The example below is a Honeywell three electrode electrochemical sensor's response when switched on after 24 hours without power.

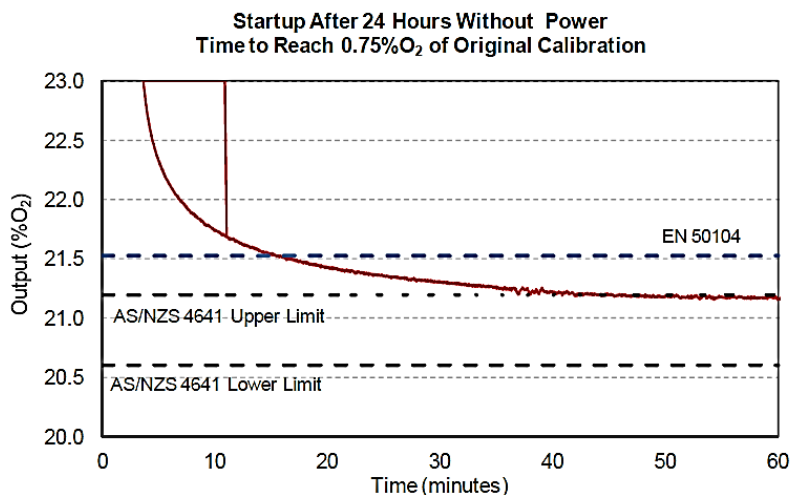


Figure 7. Response of three electrode electrochemical sensor after being powered after 24 hours without power

- It can be difficult or impossible to tailor the activity of the sensing electrode to avoid cross sensitivity to contaminant gases that might also be present. This can be achieved with lead anode sensors but with three electrode oxygen pump sensors it is difficult to find an anode material and bias voltage combination that gives sufficient activity for rapid oxygen reduction that does not give unacceptable cross sensitivity.

Solid metal oxide semiconductor sensors (e.g. zirconia)

These sensors are also known as lambda probes and use a zirconium oxide solid state semiconductor. They are used, for example, in vehicles to measure the oxygen concentrations in hot exhaust gases (to control air/fuel ratios) and also in industrial applications such in flue gas emissions from furnaces. They do not measure the actual oxygen concentration, only a difference between the analysed gas and fresh air so a source of fresh air is also needed, which will be impractical with many applications. The sensors usually need to be heated to at least 300°C and so are ideal for analysis of hot gases. However, they are not suitable for use in portable personal oxygen analysers as they pose a safety risk due to the high temperature and also, the energy required to heat the sensor would be large (hundreds of milliwatts to watts) and require too large and heavy batteries. The high temperature of operation would also prevent them from being used in ATEX applications.

Mass spectroscopy

Mass spectrometers are useful laboratory instruments that can be used to analyse gases. However, these take several minutes at least to obtain a single concentration value. It is not possible to use these for continuous monitoring.

Paramagnetic oxygen gas analysers

This technique utilises the paramagnetic properties of oxygen gas molecules. Oxygen molecules are attracted by strong magnetic fields and so the oxygen concentration can be determined by the attraction force. Unfortunately, many other gases are also paramagnetic (e.g. nitrogen oxides and CO₂) so this analysis method is unsuitable in many industrial environments where other magnetic gases may occur. Other disadvantages are that it is not accurate at low oxygen concentrations (<1%) and cannot be used where there is vibration or movement of position.¹⁴

Optical sensors (e.g. fluorescence/luminescence)

Many types of optical sensors have been developed, but many are suitable only for measurement of oxygen dissolved in liquids. One type that is used for gases is luminescence sensors. These function by using luminescent dyes that fluoresce when exposed to ultraviolet light. This light is quenched when the dye is exposed to oxygen and the reduction in fluorescent light emission can be used to measure the oxygen concentration. This type of sensor has a main limitation that many other substances also cause quenching, such as water vapour and nitrogen oxides and so these are often unsuitable in industrial installations.

Ultrasonic sensors

Ultrasonic oxygen sensors measure the concentration of oxygen in a gas or liquid by measurement of the speed the ultrasonic sound waves through the gas or liquid. These are suitable when the composition of the gas is known as every substance in the gas will affect the speed of sound differently. They are therefore usually unsuitable in industrial environments where the air composition is unpredictable.

Tunable diode laser absorption spectroscopy sensors

These are a type of infrared sensor in which the diode laser produces an infrared light beam that passes through the analysis gas to a photodiode that measures the infrared light received. By tuning the laser to specific wavelengths, they can analyse a variety of gases including oxygen. However, other gases also absorb infrared light at the absorption wavelengths of oxygen gas and so these sensors cannot be used where these gases might occur.

(B) Please provide information and data to establish reliability of possible substitutes of application and of RoHS materials in application

Not applicable. There are no lead-free drop-in replacements that can be used.

7. Proposed actions to develop possible substitutes

¹⁴ <https://alphaomegainstruments.com/products/oxygen-sensors/>

(A) Please provide information if actions have been taken to develop further possible alternatives for the application or alternatives for RoHS substances in the application.

As described in section 6, many alternative types of oxygen gas concentration analyser have been developed and each type has specific uses. The three-electrode electrochemical pump-cell sensor has been developed and can be used for some applications. Honeywell and others have also carried out research into substitute metals in the two-electrode galvanic cells and a few types of these are sold in the EU, although all have limitations and none are drop-in replacements, as described in section 6. For most industrial applications, lead anode cells still need to be used as there are no alternatives. For example, of Honeywell's competitors that sell lead-free galvanic sensors, there are none suitable for ATEX, diving gas or vehicle exhaust gas emission applications and most types that are available are lead anode sensors. The current status of substitution is shown in Table 3.

Table 3 Status of substitutions.

Type of sensor	Advantages / Disadvantages
Lead anode galvanic	Fast response, accurate and no power consumption
Tin anode galvanic	Larger sensor size needed, passivation risk and different characteristics to lead-anode sensors
Antimony, bismuth and copper anode galvanic	Anodes passivate and self-corrosion under some conditions
Zinc anode galvanic	Self-corrosion occurs
3-electrode pump-cells	Longer cell lifetime but different control circuit so not a drop-in replacement. Consumes at least 0.5W so not suitable for lightweight small-size personal oxygen monitors. Technical issues prevent use in ATEX applications
Zirconia sensors	Operates only at high temperature
Fluorescent analysers	Interference from many gases that also quench dyes. Suitable only in clean environments. Different characteristics and circuit design to lead anode sensors so not a drop-in replacement
Others	Several other types are used commercially and are suitable for certain specific uses, but not as replacements for lead-anode sensors

(B) Please elaborate what stages are necessary for establishment of possible substitute and respective timeframe needed for completion of such stages.

For most end-uses, more research is needed to develop alternative sensors that are suitable. It will also be necessary to design suitable analyser instruments for the alternative sensors as these are unlikely to be drop-in replacements as described above in section 6. Honeywell is developing alternative sensors and also replacement analyser instruments. For most end-uses, validation testing and approvals are also required before the new instruments can be sold in the EU or globally.

However, depending on the end use application in question it is expected that different levels of redesign work will be required and hence different timeframes will be needed. The following timescales refer to instruments that currently use membrane cell sensors. In all cases below, the sensor development phase is uncertain. This would be up to 4 or 5 years if a totally new sensor design is needed, but perhaps only about six months if an existing Honeywell sensor such as a pump cell could be used. The actual timescale will not be known until further development work and testing has been carried out although it is likely that new sensors will be needed for at least some applications.

- Oxygen gas concentration monitor for safety applications including portable analysers. For portable applications, these must be small and lightweight and need to be accurate and reliable with new batteries or after recharging during at least a working shift. This is an issue with 3-electrode sensors as these have higher power consumption than the lead anode sensors. Likely steps and timescales are outlined in Table 4.

Table 4 Lead-free oxygen gas concentration monitor development for safety applications

Development stage	Time required
Sensor development	Ca. 6 months
Analyser instrument development	3-4 years
Approvals	1 year
Total	4 to 5 years

- ATEX approved analysers. The generation of oxygen inside the housing, which must be vented is a serious limitation and currently, this is not technically possible. If a suitable sensor is available, then the following would be required. Likely steps and timescales are outlined in Table 5.

Table 5 Lead-free ATEX approved analyser development timescale

Development stage	Time required
Sensor development	Up to 3-4 years
Analyser instrument development	3-4 years
Testing for compliance with applicable ATEX standards	1 year
Approvals by ATEX Notified Body	1 year
Total	8 – 10 years

- Vehicle exhaust analysis, SCUBA diving gases, Bio-ox and medical applications

Table 6 Lead-free analyser development timescale

Development stage	Time required
Sensor development	Up to 4 - 5 years
Analyser instrument development	4 - 5 years
Instrument validation and approvals	2 years
Total	10- 12 years

Honeywell also produce analysers with capillary sensors. These will also require sufficient time once suitable sensors designs have been identified. Instrument redesign, testing and approvals etc. will be required with alternative sensors. Most time will be needed for more difficult applications such as the following example which uses a capillary sensor.

- More technically difficult applications such as 0 – 2ppm O₂.

Table 7 Lead-free analyser development timescale

Development stage	Time required
Sensor development	Up to 3 – 4 years
Analyser instrument development	5 years

Approvals	1-2 years
Total	Up to 11 years

8. Justification according to Article 5(1)(a):

(A) Links to REACH: (substance + substitute)

1) Do any of the following provisions apply to the application described under (A) and (C)?

- Authorisation
 - SVHC
 - Candidate list
 - Proposal inclusion Annex XIV
 - Annex XIV
- Restriction
 - Annex XVII
 - Registry of intentions
- Registration

2) Provide REACH-relevant information received through the supply chain.

Name of document: _____

(B) Elimination/substitution:

1. Can the substance named under 4.(A)1 be eliminated?

- Yes. Consequences? _____
- No. Justification: **Substitutes have different performance characteristics and so are unsuitable**

2. Can the substance named under 4.(A)1 be substituted?

- Yes.
 - Design changes:
 - Other materials:
 - Other substance:
- No.

Justification: **Substitutes have different performance characteristics and so are unsuitable**

3. Give details on the reliability of substitutes (technical data + information): **Not applicable**

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
- 1) Environmental impacts: _____
 - 2) Health impacts: [There could be serious harm to workers if oxygen analysers were no longer available \(see below\)](#)
 - 3) Consumer safety impacts: _____
- ⇒ Do impacts of substitution outweigh benefits thereof?
Please provide third-party verified assessment on this: [Not applicable](#)

(C) Availability of substitutes:

- a) Describe supply sources for substitutes: [Honeywell and others manufacture a wide range of oxygen analysers](#)
- b) Have you encountered problems with the availability? Describe: [Not applicable](#)
- c) Do you consider the price of the substitute to be a problem for the availability?
 Yes No
- d) What conditions need to be fulfilled to ensure the availability? [See above](#)

(D) Socio-economic impact of substitution:

- ⇒ What kind of economic effects do you consider related to substitution?
- Increase in direct production costs
 - Increase in fixed costs
 - Increase in overhead
 - Possible social impacts within the EU
 - Possible social impacts external to the EU
 - Other: _____
- ⇒ Provide sufficient evidence (third-party verified) to support your statement:

[If this exemption is not renewed, then EU users of lead anode oxygen sensors will not be able to obtain new instruments. This will negatively affect all of the industries and end-users listed in section 4 above. Many would be forced to stop operations because not being able to measure oxygen gas concentrations in their work environments would be too dangerous. Some end-users may decide to risk operating without monitoring oxygen concentrations, and this would pose a very severe risk to workers safety, such as when in confined spaces, tunnels, mines, etc. Deaths from asphyxiation are potential outcomes. Some EU manufacturers who produce analysers as well as end users of these analysers may cease to operate in the EU with loss of employment. Honeywell is not able to provide quantitative estimates of these impacts as they are dependent on many other industries.](#)

9. Other relevant information

Please provide additional relevant information to further establish the necessity of your request:

10. Information that should be regarded as proprietary

Please state clearly whether any of the above information should be regarded to as proprietary information. If so, please provide verifiable justification:
