# Exemption Request Form

Date of submission: 20.01.2023

## 1. Name and contact details

### 1) Name and contact details of applicant:


Company: Dräger Safety AG&CoKGaA

Tel.: +49 451 882 6527

Name: Rolf Eckhardt

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Function: Engineering electrochemical sensors

Address: Revalstr. 1
23560 Lübeck
Germany


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

Company: _____ Tel.: _____

Name: _____ E-Mail: _____

Function: _____ Address: _____

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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 IV where applicable: 1b

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

Duration where applicable: Until the end of 2025 for new instruments that use electrochemical oxygen sensors that contain lead.

Maximum validity period for replacement oxygen sensors.

☐ Other: _____

## 3. Summary of the exemption request / revocation request

This exemption is necessary to allow the use of electrochemical oxygen sensors to measure oxygen concentration in industrial applications. This primarily includes applications in inerting processes, i.e., when organic vapors or gases occur simultaneously with the oxygen in atmospheres for monitoring the lower explosion limit of industrial processes. Lead-containing organic capsules are intrinsically safe here, as they cannot act as a source of ignition, like potential lead-free sensors with electrodes made of platinum black. The latter generate their working potential via a potentiostat circuit and not via a natural potential gradient between the lead and the gold of the working electrode, as is the case with galvanic oxygen sensors. A shift of the reference potential due to penetrating gases from the sensor environment leads here to a failure of the sensor.

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## 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: Sensors for measuring oxygen in industrial processes, such as inerting or in helium atmospheres.

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

| | |
|---|---|
| ☐ 1 | ☐ 7 |
| ☐ 2 | ☐ 8 |
| ☐ 3 | ☒ 9 |
| ☐ 4 | ☐ 10 |
| ☐ 5 | ☐ 11 |
| ☐ 6 | |

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

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:
   Electrochemical oxygen concentration measurement

4. Content of substance in homogeneous material (%weight): >99% lead

5. Amount of substance entering the EU market annually through application for which the exemption is requested: ca 8 to 13.5 kg per year
   Please supply information and calculations to support stated figure.
   Each cell typically contains 8 to 9 grams of lead
   Estimated sales in the EU for industrial applications is expected to be about 1000 to 1500 sensors per year

6. Name of material/component: Lead metal

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?**

Oxygen is measured by small electrochemical sensors that contain lead anodes. These are connected electrically to much larger analyser instruments that calculate and display the oxygen concentration. The sensors are connected to the instrument using electrical cables.

The concentration of oxygen in air needs to be monitored to ensure that they are no highly flammable or even spontaneously combustible atmosphere conditions. Oxygen concentrations need to be accurately monitored if an atmosphere highly flammable gases or vapors, such as hydrocarbons, alcohols or hydrogen.

contains Lead (Pb) is used as the anode in the oxygen ($O_2$) sensor. During the operation of the sensor, oxygen from the gas being analysed permeates through the membrane of the sensor and is electrochemically reduced at the cathode of the sensor. The Pb anode of the sensor is oxidised to PbO / $PbO_2$.

Electrochemical oxygen sensors consist of two electrodes; a high surface area lead anode and an inert cathode which are immersed in an alkali electrolyte. The anode and cathode reactions are:

Cathode:

$O_2 + 2H_2O + 4e- \rightarrow OH^-$

Anode:

$2Pb + 4OH \rightarrow 2PbO + 2H_2O + 4e-$

The electrochemical reaction generates an electrical current which flows through the cell (with an additional load resistor) which is proportional to the partial pressure of $O_2$ in the analysed gas. The voltage across the load resistor is proportional to the current and is measured to calculate the concentration of $O_2$.

The output current of the electrochemical sensor is therefore dependent on the oxygen concentration in the air that enters the sensor. The rate of access of air-oxygen into the sensor is controlled by the design of the sensor, in particular by using diffusion barriers which can be narrow capillaries or a porous layer. The sensor is designed so that the current output is proportional to the oxygen concentration. The diffusion barrier is used to limit the amount of air that passes through the sensor so that only a small amount of oxygen reaches the lead anode so that a proportionally small amount of lead is consumed, ensuring the maximum lifetime of the product .

With the increasing conversion of lead to lead oxide, the voltage over the measurement resistor slowly decreases during use. To ensure the correct calculation of the $O_2$ concentration, the instrument and sensor is calibrated with air every 24 hours.

When the voltage with air drops below 8.9 mV (under normal conditions) the medical device detects that the sensor is consumed and informs the user to replace the sensor with a new one. Under normal conditions the sensor can be used for 1 to 2 years.

Ambient temperature also affects the current output of the sensor and so compensation circuits need to be included either within the sensor or in the current measurement instrument. This is straightforward with lead-based sensors, but is also a critical variable with other types of sensor.

Accurate $O_2$-measurement in industrial processes provide explosions by enabeling the user to lower the O2 content of the atmosphere.

One of the main advantages of lead in electrochemical oxygen sensors is that it is not affected by the majority of other gases used in industrial applications, such as inertisiring. The few exceptions to this are acid gases and $CO_2$ will react with the electrolyte (potassium hydroxide or potassium acetate are usually used) and users are warned that this should be minimised, but combustable gases have only a minimal effect on this type of sensor.

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

For monitoring patients, the following characteristics are essential:

- Fast response. For example, <15 seconds to respond to a change from air to 100% oxygen
- High sensitivity to small oxygen concentration changes
- High accuracy
- Long lifetime (at least 1 year, ideally 2 years)
- Measure oxygen in the concentration range of 0% to 100%
- Must be usable and accurate in the presence of commonly used combustable gases (such as hydrogen or organic vapors)
- Usable at 0% – 99% non-condensing humidity
- Accuracy should not be affected by typical $CO_2$ concentrations in inertising atmospheres

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## 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.)**

Dräger has established a take-back system for used sensors and aims to receive up to 100% back from the market. The sensors are recycled for materials recovery.

**2) Please indicate where relevant:**

☐ Article is collected and sent without dismantling for recycling

☐ 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: all parts of the sensors

☐ 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

☒ In articles which are recycled — 8 to 13.5 kg per year

☐ In articles which are sent for energy return

☐ In articles which are landfilled

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## 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**

Since category 9 were included in scope of RoHS, research into substitutes for lead in electrochemical sensors has been carried out. There are also different types of oxygen sensor on the market but these operate in completely different ways to electrochemical sensors and so have very different characteristics. Both alternative metals to lead and alternative types of sensor are described here.

**Lead substitutes in electrochemical sensors**

Research has been carried out and published with alternative anode metals and with various acid and alkali electrolytes. Metals that have been investigated include: antimony, bismuth, copper, tin and its alloys, zinc and aluminium.

Research has shown[1] that the more reactive metals such as tin, zinc and aluminium are unsuitable as they are thermodynamically unstable in suitable electrolytes. Electrolytes such as potassium hydroxide (used with lead) and other alkali solutions, acidic solutions such as phosphoric acid and caesium carbonate solution (mildly alkali) have been investigated.

When a reactive metal anode is combined with an inert cathode, the two different materials generate a galvanic couple which creates a small voltage with the electrode potential of the anode such that they self-corrode, generating a current and generate hydrogen. This generated current between anode and cathode gives a false and incorrect oxygen concentration. Despite this, commercially available oxygen sensors that use tin anodes in a caesium carbonate electrolyte[2]

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[1] Lead-Free Galvanic Oxygen Sensors. A Conceptual Approach, Cornel Cobianu, et. al (Honeywell). CAS (International Semiconductor Conference) 2012, Abstract from https://www.semanticscholar.org/paper/Lead-free-galvanic-oxygen-sensors-%E2%80%94-A-conceptual-Cobianu-Serban/e4cfb461b42eba465ee2410d5637bf7453079bf6

[2] http://www.it-wismar.de/download.php?id=22

are being sold in the EU[3]. The applicants of this renewal request have however evaluated these sensors for their specific applications and found that they do not meet their specifications when used with existing designs of analysing instruments.

Research with less reactive metals such as copper, bismuth and antimony has also been reported, but no commercial products have been developed. The reason why these metals are not used in commercial sensors could be that they can form thin oxide coatings (e.g. during storage before use) which may act as a barrier to further oxidation and so hinder or prevent further electrochemical reaction.

Lead may be the optimal anode choice in electrochemical sensors because it does not self-corrode in the absence of oxygen (such as aluminium and zinc) but it responds rapidly when in contact with oxygen, unlike copper, which reacts and then rapidly passivates so stops working. Nobel metals such as gold and silver do not respond at all as they do not react with oxygen from air.

Combustable gases and vapors are often water soluble to a small extent, so small amounts will dissolve in the sensor's electrolyte and could affect its function. Therefore it cannot be assumed that alternative metals to lead will respond in a similar way when used in oxygen sensors for industrial applications and so extensive testing is essential.

Tests with a type of commercial lead-free electrochemical sensor have been carried out by one manufacturer. Concerning the output signal itself, results indicate that sensors with alternative anode materials should eventually be suitable as a replacement for the lead anode sensors in redesigned instruments. However, test results showed that these sensors have a completely different behaviour in the way that they decrease voltage during operation. The voltage decreases very slowly and does not drop below 8.9 mV even if the anode is complete consumed.

In existing designs of oxygen analyser, a consumed sensor with this behaviour would lead to wrong $O_2$-values with no possibility of detection by the device or the user that the output data was not correct.

Due to the internal design of the cell (which is required by the anode material) it is not possible to adjust the way that the output voltage changes as the anode is consumed by electrical means to reproduce the behaviour of a cell with a lead anode. Therefore lead-free sensors cannot be used as drop-in replacements for the lead anode sensors used in currently available commercial oxygen analysers. The timescale required for instrument redesign is explained in section 7.

[3] Marketed by ITG.

### Other types of oxygen sensor

Many methods of measuring oxygen concentration have been developed but each has different characteristics. These methods are described here:

**3-electrode electrochemical sensors**. One design that has been developed is three electrode cells containing inert lead-free anodes and cathodes with a reference electrode. These have the advantage that the anode is not consumed as the anode reaction is:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

These however have the disadvantage that oxygen is generated at the anode and must not reach the cathode as this would give a false high reading. The accuracy of these sensors is also affected by ambient temperature, humidity, pressure and the presence of other gases.

One advantage of the lead anode sensors is that they carry their "own" voltage power supply in the anode material (which is the reason for the sensors not working when the anode material is consumed). Electrochemical 3-electrode $O_2$ - sensors require a bipotentiostat which needs an additional power supply. Also, the capacity of a small enough battery that would fit into the available space would not allow the operation over 1-2 years.

Experiments with this sensor also showed that electromagnetic requirements cannot be fulfilled without additional means, which are problematic at the installation place of the sensor (e.g. metal housing and control electronics).

**Solid metal oxide semiconductor sensors**

These are known as lambda probes and are often used in vehicles to measure the differences in oxygen concentrations in supplied air and in exhaust gases by measurement of the current between electrodes. They do not measure the actual oxygen concentration (only a difference) and these usually need to be heated to 300°C and so are unsuitable in medical applications as they pose a safety risk due to the high temperature.

### Mass spectroscopy

Mass spectrometers can analyse all substances in patients' breath but the response time is too long taking many minutes to obtain a single concentration[4].

### Paramagnetic oxygen gas analysers

These rely on oxygen gas being strongly paramagnetic and this method can give very fast response times. However, they have several disadvantages. The response is affected by the concentrations of other paramagnetic gases which includes $CO_2$ (in exhaled breath), $N_2O$ (used for anaesthesia) and most other

[4] https://academic.oup.com/bjaed/article/9/1/19/465989

anaesthesia gases. It is also affected by water vapour concentrations (water is diamagnetic so opposes the paramagnetic effect[5]). Because of these limitations, paramagnetic oxygen sensors are unsuitable in anaesthesia applications and can be difficult to use with ventilators.

Paramagnetic sensors have already replaced lead anode based $O_2$ measurement in diverting (side-stream) respiratory gas monitors. However, due to requirements for the flow of the measurement gas to be very continuous, without pressure and flow peaks, it is not possible to use this type of sensor for the inspiratory $O_2$ measurement for industrial applications.
Another disadvantage of this type of sensor is that they need an additional power supply, which cannot be made available near the sensor due to a lack of space. The current peaks and power needed by this principle would require quite a large battery, which is mechanically and dimensionally not possible at the installation location of the sensor.

**Optical sensors**

There are many types of optical oxygen concentration analysis methods, but most are either unsuitable or are designed for analysis of dissolved oxygen only (e.g. in blood)[6]. Infrared absorption spectroscopy analysis can be used to analyse many substances in industrial applications, but this technique does not respond to oxygen gas and so is unsuitable.

One technique uses substances that change colour when exposed to oxygen and the colour is measured electronically. Response times can be slow and colour measurement is not very accurate and so this method cannot be used for industrial oxygen analysers where fast response times and high accuracy are essential.

Another type of optical sensor uses an oxygen permeable polymer containing a luminescent compound. The luminescent compounds emit light when excited by exposure to light of a shorter wavelength (e.g. UV), but this is quenched when exposed to oxygen and the change in luminescence intensity is used as a measure of oxygen concentration.

Many luminescent oxygen sensors have been developed and a few types have been commercialised. A recent review[7] reports that many luminescent dyes can be used in aqueous solutions, but some are effective only within specific pH ranges, so are used only to measure dissolved oxygen (not the gas). Many types of dye are not stable as they photo-bleach and become unresponsive. Response time of some types is a disadvantage; one commercial product is claimed to have

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[5] https://www.sablesys.com/wp-content/uploads/Sable-Systems-International_White_Paper_O2-Analyzer.pdf

[6] https://www.optimedical.com/

[7] Optical methods for sensing and imaging oxygen: materials, spectroscopies and applications, Xu-dong Wang and Otto S. Wolfbeis, Chem. Soc. Rev., 2014, 43, 3666.

a response time of less than 30 seconds[8], however electrochemical sensors respond typically in less than 10 seconds and some are <5 seconds. A fast response time is essential for analysing oxygen in industrial applications. A few types of luminescent oxygen sensors have much faster response times but only function at very low oxygen concentrations that are not applicable to industrial applications.

Luminescent oxygen sensors respond by quenching by oxygen molecules, however many other substances including organic vapors, water vapor, nitrogen oxides and many other contaminants also causes quenching and so these sensors are not sufficiently selective for oxygen to be useful in industrial applications.

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

Reliability is not believed to be an issue and substitutes are technically unsuitable as explained in section 6 (A).

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## 7. Proposed actions to develop possible substitutes

**(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.**

Research has been carried and published on a wide variety of new lead-free oxygen sensors. Industrial device manufacturers evaluate any commercial products that meet their specifications and appear to be suitable. As stated above, paramagnetic sensors are now used in side-stream applications, but cannot be used where rapid and accurate measurements are required such as in industrial applications.

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

New lead-free electrochemical oxygen sensors are being evaluated and tests have shown that these respond very differently and so are not drop-in replacements. As a result, analyser instruments that are used with the sensors will have to be completely redesigned.

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[8] Luminox O2 sensors available from SST (technical datasheet)

## 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 lead has been registered – see https://ila-reach.org/our-substances/lead-metal/ and https://echa.europa.eu/registration-dossier/-/registered-dossier/16063

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: None of the potential substitutes achieve all of the essential performance criteria

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

☐ Yes.

☐ Design changes:
☐ Other materials:
☐ Other substance:

☒ No.

Justification: None of the potential substitutes achieve all of the essential performance criteria

3. Give details on the reliability of substitutes (technical data + information):_The substitutes are technically unsuitable therefore reliability is unable to be investigated.

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to; Not applicable to this exemption renewal request as substitute is technically unsuitable

   1) Environmental impacts:
   2) Health impacts:
   3) Consumer safety impacts:

⇨ Do impacts of substitution outweigh benefits thereof? Not applicable to this exemption renewal request

Please provide third-party verified assessment on this:

**(C) Availability of substitutes:**

a) Describe supply sources for substitutes:
Lead-free oxygen sensors have recently become available **but are not** drop-in replacements, as explained in section 6

b) Have you encountered problems with the availability? Describe:
No as there are no drop-in alternatives available

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 sections 6 and 7

**(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

Insufficient monitoring of oxygen in certain industrial applications may cause harmful condition for workers (e.g. hydrogen production plants, hydrogen storage plants) thus this application has a direct influence on occupational safety issues.

☐ Possible social impacts external to the EU

☐ Other:

⇨ Provide sufficient evidence (third-party verified) to support your statement:

## 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:**