Exemption Request Form

Date of submission: 19th January 2022

1. Name and contact details

1) Name and contact details of applicant:

Company:	COCIR	Tel.:	00327068966
Name:	Riccardo Corridori	E-Mail:	corridori@cocir.org
Function:	EHA Policy Senior Manager	Address:	Blvd A. Reyers 80, 1030

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

Company:	N/A	Tel.:	_____
Name:	_____	E-Mail:	_____
Function:	_____	Address:	_____

---

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: 1a

Existing wording:

Lead & cadmium in ion selective electrodes, including glass of pH electrodes.

Proposed Wording:

Lead & cadmium in thick film pastes, in ion selective electrodes used for blood gas systems.

Duration where applicable: Until August 2026

☐ Other: _____

3. Summary of the exemption request / revocation request

Blood gas analysis systems use ion selective electrodes in their sensors, to detect blood gases such as pO2 and pCO2 and biomarkers in patients blood. Blood gas systems are used to accurately diagnose various conditions such as asthma, chronic obstructive pulmonary disease (COPD), kidney failure, uncontrolled diabetes and severe infections, as well as treat patients in respiratory and/or metabolic distress.

Lead and cadmium are constituents of thick film screen printable paste used in the sensors. These constituents are used to promote reaction bonding and for ensuring strong adhesion of the paste base metal (typically gold or palladium) to the ceramic substrate material on firing. A planar sensor array can contain up to 10 sensors, with performance integral to the reliability, sensitivity and quick response time of the system. With the sensors themselves reliant on the integrity of the connections formed by the thick film paste. For good connections to be made the paste is required to have a precise viscosity to allow for the printing of fine features and low resistivity (≤ 4.5mΩ @ 10µm) which is determined by the percent solids, the ability to form a dense film with minimal defects and good adhesion to the substrate.

Testing is still ongoing for alternative RoHS compliant thick film pastes, with a focus on alternatives developed by the same manufacturer to minimise the changes to the technical characteristics of the paste, and thus reduce the timeframes for qualification. Alternative technologies which avoid the use of thick film pastes are possible but would require additional time to qualify alternatives due to more major product design and production process changes. In addition to these changes, the many decades of experience and reliability data gathered while using thick film pastes would also have to be overcome, resulting in considerably longer timeframes for qualification.

---

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 blood analysis systems, using ion selective electrodes for the detection of blood gases such as pO_2 and pCO_2 and biomarkers.

   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: N/A

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:

Lead and cadmium are constituents of thick film screen printable paste (also referred to as 'ink'), used in the fabrication of planar sensors, which are used in point of care blood gas systems. The lead and cadmium within the paste is cited[1] as promoting reaction bonding and ensuring strong adhesion of the paste base metal (typically gold or palladium) to the ceramic sensor substrate material on firing.

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

   i. Cadmium up to a maximum of 1.5%.

   ii. Lead compounds (frits) up to a maximum of 3.5%.

5. Amount of substance entering the EU market annually through application for which the exemption is requested:

82g of cadmium and 191g of lead annually.

Please supply information and calculations to support stated figure.

[1] "The Bonding of Gold and Gold Alloys to Non-Metallic Materials" – William S. Rapson

This is provided separately as the calculation includes confidential market information.

6. Name of material/component:
   Thick film screen printable paste (also referred to as 'ink')

7. Environmental Assessment:
   Not applicable as there are no suitable substitutes that have been verified to meet the technical performance required.

   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 and cadmium are used as constituents of thick film screen printable pastes, also known as inks. 'Thick film' technology, uses conductive, resistive and insulating pastes containing glass frit, deposited in patterns defined by screen printing and fused at high temperature onto a ceramic substrate. Compared with solder pastes, the particle sizes are much smaller, and the suspensions therefore more stable. The printable paste is designed to give an appropriate viscosity for the screen-printing process.

The paste is applied (screen printed) onto a substrate in the fabrication of potentiometric and amperometric planar ion selective sensors.

Potentiometric sensors measure the potential difference between two electrodes under the conditions of no current flow. The measured potential is then used to determine the analytical quantity of interest based on the Nernst equation. Amperometric sensors measure the current response to detect the concentration of an analyte at a fixed potential. The applied potential drives the electron transfer reaction of the analytes, and the measured current indicates the analyte concentration.

The pastes are used for providing the electrical contact within the sensors, and between the sensors and the blood gas system. They are critical for the reliable transduction of the measured sensor response into an electrical signal that is

further converted by the blood gas system and associated algorithms into analysis results.

The sensors are assembled into linear arrays which are incorporated into replaceable measurement cartridges used in point of care blood gas systems.

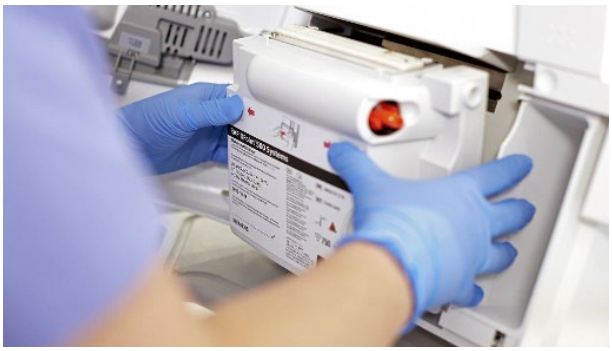

Figure 1 Exemplary image of replaceable blood gas system cartridge

The method for measuring a sample involves flow of the aqueous fluid or patient blood sample (analyte) over the planar sensor and a standard reference electrode, the sensor and reference form an electrochemical cell. The resulting electrical signal from the electrochemical cell is converted by the -system into a meaningful reading of the analyte. An example of the usage of the paste is shown in Figure 2. The pastes are used on the contact pads as well as the 'Via Fills' that connect the planar sensors to make electrical contact with the blood gas system.

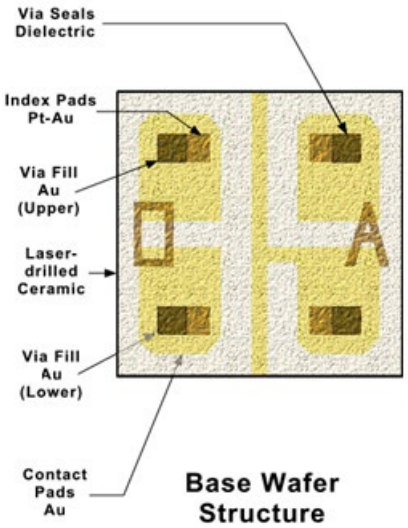

Figure 2 Exemplary schematic showing the printing layers wherein the paste is used on the substrate layer

The sensors are arranged in a linear array of up to 10 different sensors in some blood gas systems, with each sensor designed to detect different analytes. These sensors form a critical part of blood gas systems. The blood gas system measures pH, pCO2, pO2, sodium, potassium, chloride, ionized calcium, glucose, lactate,

total haemoglobin, haemoglobin fractions, neonatal bilirubin, and several calculated parameters. A typical example of such a product is shown in Figure 3.

Figure 3 Exemplary image showing a blood gas system

Blood gas systems are known to help in accurate diagnosis of various conditions such as asthma, chronic obstructive pulmonary disease (COPD), kidney failure, , uncontrolled diabetes and severe infections, as well as treat patients in respiratory and/or metabolic distress. Further details of their application can be found in this referenced document Clinical Utility of Blood Gas[2]. The use of such devices has increased considerably in the recent past and they have become an integral part of intensive care units (ICUs) and emergency medical services.

Blood gas systems have been essential in supporting COVID-19 response efforts, where blood gas systems play a critical role in managing infected patients and monitoring their respiratory distress. Arterial blood gas testing is also performed when patients require critical pulmonary assessment, managing sepsis and kidney function evaluation. These tests provide the clinician with a health assessment of the patient and help direct treatment options.

Arterial blood gas testing is not a routine blood test. The tests are performed on patients who are critically ill in the intensive care units, operating rooms and emergency rooms. In these locations, time is critical for the clinician to provide the best treatment based upon these tests. Analysis results are available in

[2] bg_clinical_utility_poster_fnl4-00278011_1800000000278011.pdf (scrvt.com)

approximately 60 seconds. Faster diagnosis helps prescribe accurate therapy at an early stage of disorder, which helps avoid complications.

The performance of the sensors is integral to the reliability, sensitivity and response time of the system, the sensors themselves are reliant on the integrity of the connections formed by the thick film paste.

A significant advantage of this type of sensing technology is that only a small sample of blood is required (typically 100µL), this is advantageous especially when assessing infants or patients from whom obtaining a larger sample due to their condition would be difficult.

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

In order to be able to manufacture the sensors the paste has to be suitable for application by screen printing. Screen printing is attributed to be a reproducible and efficient method for large scale production of planar sensors.[3]

The key attribute of the paste to ensure printability is the viscosity, this is required to be in the range 190 - 350 Kcps. This not only determines the flow of the paste but also the ability to print features to the required resolution (typically >75µm lines and spaces), which is critical to minimising the size of the sensors.

The paste must also provide consistent physical and chemical properties after firing (the process of heating the paste to temperatures of >800°C, often multiple times to facilitate bonding to the substrate).The key attribute required from the paste after firing is resistivity, this is required to be ≤ 4.5mΩ @ 10µm fired film thickness, which is determined by the percent solids, the ability to form a dense film with minimal defects (pin holes) and good adhesion to the substrate. Defects or pin holes in the fired paste act as air gaps increasing the overall resistivity. These attributes also ensure the integrity and reliability of the connections made by the paste.

The lead and cadmium within the paste is cited[4] as promoting reaction bonding and ensuring strong adhesion of the paste base metal (typically gold or palladium) to the ceramic sensor substrate material on firing.

Manufacturers have built up many decades of experience, with some utilising the principles of this technology for over 45 years and as such have refined both the hardware and software of the system to maximise the analytical capability.

---

[3] https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3872359/

[4] "The Bonding of Gold and Gold Alloys to Non-Metallic Materials" – William S. Rapson

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.)

A closed loop system does not exist as the sensors are disposed of as infected medical waste.

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: _____
☐ 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 _____
☒ In articles which are sent for energy return 82g of cadmium and 191g of lead annually (as used blood gas systems are contaminated medical waste, they must be incinerated)
☐ 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

Replacement Thick Film Pastes:

Lead and cadmium have been used in thick film pastes for many decades[5] and have known to have been used successfully for the manufacturing of sensors for blood gas systems for the past 20+ years.

A number of manufacturers of thick film paste exist, for example; Du Pont[6], Koartan[7], Ferro[8] and Heraeus[9]. All of which have been developing lead and cadmium free alternatives, the exact formulation of each paste however is proprietary to the paste manufacturer.

There are a number of variables inherent to each of the thick film pastes based on the following, which influence the technical characteristics;

- The constituents themselves, including rheology modifiers,
- The ratios of constituents,
- The constituent particle size and shape etc.

These variables in turn impact the firing temperature, viscosity, shear rate and printability of the paste including the ability to print and resolve sufficiently fine features. They also impact the performance of the paste after it has been fired to form a conductor, in terms of resistivity, bond strength and reliability. Consequently to optimise the chances of success in transitioning to a new paste for a particular application it is prudent for manufacturers to minimise the number of variables by first testing alternatives with the same paste manufacturer. This helps to minimise these differences, but also utilises the close technical relationship which usually is already in place to minimise the qualification timeframes.

One thick film paste manufacturer launched a lead and cadmium free paste in late 2018[10] which was intended to be the replacement for pastes containing lead and cadmium. As well as changing the constituent formulation, changes have also

---

[5] "The Bonding of Gold and Gold Alloys to Non-Metallic Materials" – William S. Rapson

[6] https://www.dupont.com/mobility-materials/thick-film-materials.html

[7] https://koartan.com/thick-film-pastes/conductor-pastes/gold-pastes

[8] https://www.ferro.com/

[9] https://www.heraeus.com/en/group/home/home.html

[10] https://www.heraeus.com/en/het/company_het/press_and_news_het/2018_het/09_imaps.html

been made to the particle size and shape of the constituents, with the intent of improving performance.

Initial trials of this particular paste, by a manufacturer of blood gas systems and the sensors therein, were started in early 2019, with a batch of 6 wafers manufactured. Of this batch, 2 wafers failed due to print voids and the production associate which produced the samples noted it was difficult to work with. The sensors are required to pass a 100% conductivity test, which only 66% of the samples passed, compared to the typical passing rate of the current paste >95%. As such, the investigations into this potential alternative were halted to try to investigate a more promising alternative.

A second alternative paste was investigated which printed well and showed no continuity issues. However, the sample was only able to achieve an average use life of 21 days, with some samples failing at as early as 12 days, rather than the warranty use life of 30 days which is currently offered for one system. For the full testing details please refer to the histogram of use life (Figure 1) in the confidential submission.

Also during this time, the signal produced by the sensor (recovery) was also identified as being different to that of the current paste. Testing showed that the potential alternative had a mean recovery less than that of the current paste of 37 mg/dL, which was confirmed when a second lot was tested. Full testing details are shown in the confidential submission (Figure 2 and 3) which would require further changes to the sensor design to resolve.

This difference in sensor signal was investigated by repeating the fabrication and creating a second batch (lot 2) of the sensors, and installing the sensors in other cartridges but keeping the same reagents as the first test; all of which showed the same difference in sensor results. Full testing details are shown in the confidential submission (Figure 4).

Given all of these issues and with the advent of the COVID pandemic, which impacted resource availability (due to a combination of a 31%[11] rise in product demand and lockdown restrictions), trials at this stage were halted until late 2021.

Trials are still on-going for the currently selected alternative with feasibility, conductivity testing completed and use life testing for 5 out of 13 of the analyte

[11] 2019 to 2021

sensors, across multiple models of blood gas systems. However, additional time is still required to undertake all of the required testing, as outlined in Section 7B.

Potential Alternative Technologies:

It has been established[12] that thick films based on nano-scaled powders offer better sensing properties than thin films deposited through methods such as sputtering, chemical vapor deposition, or laser ablating. As detecting analyte to very small quantities is one of the defining technical characteristics of blood gas systems these technologies are unsuitable for this application.

Photolithography is used on silicone wafers in the integrated circuits industry. However, such technology requires extremely clean operating conditions which are not currently in place. Although there have been some academic papers exploring photolithography and its use on ceramics, the work has been limited thus far and has not demonstrated this technology is suitable for the ceramic wafers used in blood gas systems.

Microprinting and inkjet printing was deemed as an unsuitable alternative methodology as the resulting process was thought to be too inconsistent. The inconsistency arises from the head space within the print heads, which would cause different pressures to be applied to the print as the volumes of ink in the print head changes. It is conceivable that the optimisation of such parameters to overcome this, and other design characteristics such as the redesign of the printer head, may be possible given sufficient time. However, more crucially the areas of the printed ink are quite large, with the smallest droplets deposited by this method being about 100µm across[12] which is not suitable for sensors in blood gas systems.

There are six main manufacturers[13] of blood gas systems, of these it is known that some manufacturers do not use planar sensors, instead they are likely to use macro sensors. However, even if manufacturers relying upon planar sensors were

[12] Tomchenko, Alexey. (2006). Printed Chemical Sensors: from Screen-Printing to Microprinting.

[13] Blood Gas Systems Manufacturers:

Radiometer: https://www.radiometer.co.uk/

Siemens: https://www.siemens-healthineers.com/blood-gas/blood-gas-systems

Nova: https://www.novabiomedical.com/

Medica: https://www.medicacorp.com/products/blood-gas-analyzers/

Synergy Medical Systems:http://www.synergymedsys.com/Blood-Gas-Analyser.html

Eshweiler: https://www.eschweiler-kiel.de/en/eschweiler-automatic-analysing-systems/

Sensa Core: https://www.sensacore.com/product/blood-gas-analyzer-abgem

Roche: https://diagnostics.roche.com/global/en/products/product-category/blood-gas.html

to switch technology to macro sensors, the development cycle of a new gas system is typically ten years so a suitable time period to allow for this development to occur would need to be permitted.

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

Both manufacturability and finished product performance need to be established in assessing the suitability of alternatives.

In the first instance the following properties determine the manufacturability or suitability for screen printing and achieving the desired pattern resolution.

Viscosity: 190 - 350 Kcps

% Solids: 84.5 – 88 ±2%

The precise values can impact the printing mesh required, the print speed and achievable thickness and resolution.

The following are sought after the firing step(s) has been completed, firing is typically at a peak of between 850 and 950°C, the precise firing cycle, overall duration and dwell time at peak temperature will need to be assessed for alternative pastes under consideration.

Resistivity: ≤ 4.5 mΩ @ 10 µm fired film thickness

These features impact the performance and reliability of the sensors themselves which in turn impacts the performance and reliability of the blood gas system.

In some blood gas systems the sensors are arranged in a linear array of up to 10 different sensors each for detecting different analytes, it has been shown that changes made to one sensor in these arrays can impact the performance of other sensors, so changes to the paste used in the construction of each sensor need to be assessed sequentially rather than making changes to all of the sensors.

It is known that a manufacturer will carry out 100% electrical conductivity testing on sensors, scrapping any non-conforming product. Sample performance testing of sensors (between 0.27 & 1.7 % of sensors), to verify performance in measuring analytes is also carried out, all sample sensors are scrapped after testing. The slope of the signal produced by the sensor over time when exposed to a known analyte and any drift of this signal are the key parameters assessed to ensure suitable performance is achieved from each batch.

---

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.

A newly developed RoHS and REACH compliant paste, from a known paste manufacturer is being evaluated.

Initial trials of a RoHS compliant paste, by a manufacturer of blood gas system and the sensors therein, were started in 2019. However with the advent of the COVID pandemic, which impacted resource availability (due to a combination of a 31%[14] rise in product demand and lockdown restrictions), trials were halted until late 2021.

When undertaking changes to thick film processing a number of different factors can influence the quality of the final product, which include:

- Screen type, mesh size, filament diameter, frame size, wet print thickness.
- Requirement for an emulsion layer to ensure that the stencil can seal onto the substrate whilst holding the mesh filaments clear of the substrate at the edge of the stencil apertures. This ensures that pastes can flow underneath the wires to the edge of the apertures therefore producing clean print edges.
- Tension of screen and squeegee design and pressure, all of which influence the ability to deposit the correct amount of paste on the surface of the substrate.
- Screen-substrate gap needs to be tailored to ensure smudging doesn't occur when it is too small, but also not too large to allow distortion of the print.

After printing the substrates must be fired, according to the thermal profile specified by the paste manufacturer and assembled into its final form. Due to the critical nature of the end product, such factors needed to be considered and trialed during the manufacturing feasibility testing. Currently there are 13 affected sensors, on

[14] 2019 to 2021

multiple model types, which require testing. Testing has been completed for 5 out of 13 of the analyte sensors. The remaining testing is on-going.

Other alternative paste manufacturers are also being considered alongside the primary alternative paste of interest, however for the reasons discussed earlier this is less likely to yield the required results.

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

The steps for a change from an existing paste to a newly developed RoHS compliant paste involves the following steps. In total the whole process requires

an additional 4 $^{1}/_{2}$ years to complete. This timeframe allows for the assessment of up to two potential replacement pastes from two different paste manufacturers.

Each of the steps noted below have to be performed sequentially and following strict internal change control procedures.

Step	Description	Detail	Est. Duration
1	Feasibility (completed for 5 out of 13 sensors)	Determining the equivalency of the paste in terms of manufacturability, to include thick film printing and subsequent process steps, conductivity, and performance testing for up to 13 different sensors.	18 months remaining
2	Use - Life Testing (completed for 5 out of 13 sensors)	Manufacture of lots and testing of sensors against a known control sensor. Measurement of spiked blood samples with different levels of analyte for a period of up to 30 days depending on the system. This test needs to be undertaken on multiple lots of sensors, inks, and systems. Testing timeframes are limited by capacity and test cycles.	14 months remaining
3	Shelf-life testing	Storage of the sensors and then conductivity and performance testing repeated to verify there has been no degradation in function.	8 months
4	Verification	Repeat of conductivity and performance testing for up to 13 different sensors to verify there has been no degradation in function.	8 months
5	Implementation	Transfer of the new paste from R&D into mainstream manufacturing.	6 months

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:

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

(B) Elimination/substitution:

1. Can the substance named under 4.(A)1 be eliminated?
   - ☐ Yes. Consequences? _____
   - ☒ No. Justification: There are no currently qualified alternatives that provide a technical solution.
2. Can the substance named under 4.(A)1 be substituted?
   - ☐ Yes.
     - ☐ Design changes:
     - ☐ Other materials:
     - ☐ Other substance:
   - ☒ No.

     Justification: Refer to Section 6.
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: _____
   3) Consumer safety impacts: _____

⇨ Do impacts of substitution outweigh benefits thereof? Not applicable.
Please provide third-party verified assessment on this: _____

(C) Availability of substitutes:

a) Describe supply sources for substitutes: Not applicable.

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? _____

(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 Without this exemption certain blood gas systems would not be able to be sold in the EU.

☐ 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:

Confidential market data has been used to calculate the quantity of restricted substance entering the EU market annually. This information has been submitted separately.

Details of the testing of alternatives has been summarised in Section 6, with full details provided in the confidential submission.