Exemption Request Form

Date of submission: **04 December 2019**

Document submitted with this dossier: "CONFIDENTIAL - Quantity calculation COCIR Ex 1c"

1. Name and contact details

1) Name and contact details of applicant:

Company: **COCIR**
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Function: **Senior Manager Environmental, Health and Safety Affairs**
Address: **Diamant Building - 80 Bd A. Reyers - 1030 BRUSSELS**

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 III or IV where applicable: 1c

Proposed or existing wording: **Lead in infra-red light detectors**

Duration where applicable: **Maximum validity period**

☐ Other: _____

3. Summary of the exemption request / revocation request

Lead selenide infrared detectors are used in medical devices called capnometers, which are used to monitor the breathing of patients in EU hospitals and clinics. Lead selenide is the only detector material that meets all of the essential criteria listed in section 4 (C) and is able to detect small changes in breathing using a capnometer that can be indicative of health conditions as well as difficulties with breathing. All potential substitutes either do not adequately respond to changes in CO_2 concentrations in patients' exhaled breath, they respond too slowly, or the detectors require cooling. Cooling requires extra bulky equipment and would cause condensation of water from exhaled air onto the detector's surface. This will freeze and the ice crystals will block infrared light and so make the PbSe detector insensitive.

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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: Capnometers that measure carbon dioxide in patient's breath

   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: Category 9 applications

   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: Detection and measurement of infrared light

4. Content of substance in homogeneous material (%weight): PbSe = 72.4%

5. Amount of substance entering the EU market annually through application for which the exemption is requested: See separate confidential Annex.
   Please supply information and calculations to support stated figure.

   This information is confidential and so is submitted separately, see separate confidential Annex.

6. Name of material/component: lead selenide is the infrared light sensitive material used to measure carbon dioxide concentration in air.

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 selenide (PbSe) is used as a detector for infrared light. When exposed to infrared light of suitable wavelength its electrical resistance changes and this change is proportional to the intensity of the light. PbSe is sensitive to the wavelength range from 1 to 5.2 µm with a maximum responsivity at 4.0 µm.

Carbon dioxide (CO_2) gas in air and in patient's exhaled breath has a strong infrared absorption peak at about 4.2 µm and so the PbSe detector is ideally suited to measurement of CO_2 concentration.

Infrared detection and measurement is used for many medical procedures as well as in patient monitors to detect and measure breathing (CO_2 analysis). This includes monitoring the breathing of babies. Other medical uses of infrared sensors include:

- Remote body temperature measurement
- Thermal imaging which can be used to detect illness such as tumours
- Medical anaesthesia gas analysis

This exemption renewal request is however limited to the use of PbSe sensors in capnometers used to measure CO_2 in inhaled air and exhaled breath. Lead selenide detectors are used in small electronic components which are inserted into small-size electrical circuits, usually by mounting onto printed circuit boards. The two terminals of the PbSe light detector are connected to an AC power supply via a load resistor and the voltage across the resistor is measured to determine the intensity of infrared light. As these components are small and the measurement circuit is very simple needing few components, these types of infrared detector are ideally suited for small size analysis cells which are the medical devices that monitor CO_2 in inhaled air and exhaled patient's breathe.

The small CO_2 monitors are used to monitor patients with breathing difficulties, during operations and intubated patients to ensure that they are breathing correctly. Any sudden changes, such as if the CO_2 concentration in exhaled air is at a reduced level or it decreases suddenly, can rapidly raise an alarm. It is important therefore that the PbSe sensor responds very rapidly to changes in CO_2 partial pressure.

Two types of capnometer are used; mainstream in which inhaled air and exhaled breath pass directly through the measurement cell and sidestream where samples of air are taken to a separate analysis cell. Mainstream and sidestream versions have different advantages and disadvantages, but both use PbSe detectors[1]. An image of the mainstream analysis cell is shown below.

[1] The advantages and disadvantages of each type are explained at http://www.oem.respironics.com/Downloads/Main%20vs%20Side.pdf

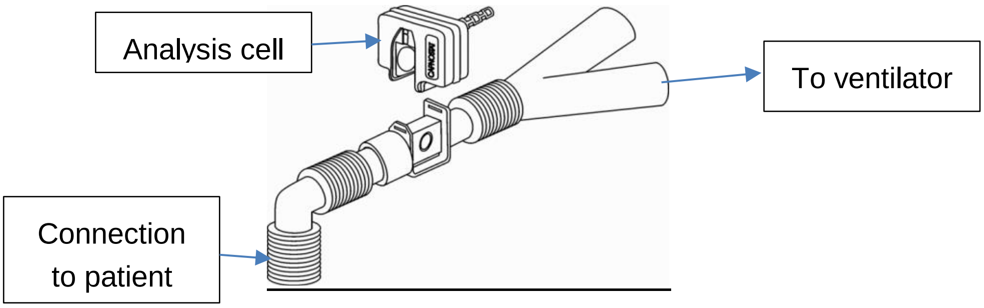

Figure 1. Design of mainstream capnometer that analysis for CO2 in inhaled and exhaled air[2]

Infrared analysis of inhaled air and exhaled breath provides a graphical and numerical display of the partial pressure (related to concentration as wt%) of carbon dioxide within the patients' airway. A detailed analysis of the waveform (capnogram), can reveal to the clinician both complex and subtle changes of the patient's ventilation status and is used for diagnosis of conditions (such as asthma) as well as to identify breathing difficulties.

[2] https://philipsproductcontent.blob.core.windows.net/assets/20170523/47502cc99e2941faaf55a77c01453ed7.pdf

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

The infrared detector must have the following properties:

- Photoconductor with an electrical resistance that decreases as the level of incident infrared light increases.
- Must be able to operate at room temperature and up to above human body temperature without cooling (sometimes heating is needed to prevent condensation).
- High sensitivity to small infrared light level changes so as to detect small changes in CO_2 concentration that are needed for diagnosis of medical conditions (such as asthma).
- Relatively low electrical resistance when not exposed to infrared light (measured as MΩ/square).
- Low noise (measured as $\mu V/Hz^{1/2}$). One publication reports a signal to noise ratio of 1000 to one[3].
- Very fast response to changes in CO_2 concentration. Typical "time constants" (the time taken for the sensor to fully respond to a change of CO_2 concentration) of PbSe are 4µS[4].
- No interference from other infrared adsorbing molecules that may be present in exhaled air, such as anaesthetic gases, nitrous oxide and water vapour. Heat detectors (such as pyroelectric types) will be sensitive to all infrared absorbing gases so will be inaccurate.
- Small size and light-weight of detector module so that it does not cause the breathing tube or mask to be pulled away from the patient.

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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.)**

Not for these sensors or for capnometers

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3 A value is published for the similar lead sulphide detector at https://www.spiedigitallibrary.org/conference-proceedings-of-spie/2021/1/Lead-sulfide-infrared-detectors/10.1117/12.164933.short

4 https://www.lasercomponents.com/fileadmin/user_upload/home/Datasheets/lcdgp/pbse-pb45-series.pdf

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 See separate confidential Annex.
☐ 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

Lead sulphide and lead selenide function as photoconductors which change their electrical resistance with the level of incident infrared light. Alternative infrared light detectors are available but are a) not sensitive in the same wavelength range as PbSe, b) they operate in different ways, c) are too insensitive or slow to respond or d) require cooling. Most alternative types of semiconductor detector, when exposed to light, generate either a voltage or a current that is proportional to intensity of the incident infrared light. These types cannot be used as drop-in replacements for PbSe which functions by a change in electrical resistance.

Design change using different circuits with alternative types of infrared detector are also not possible, as explained here. Many types of detector are sensitive to heat (infrared wavelengths are 0.7 to 1000µm) so that they respond by changing temperature. The resultant change in output signal is relatively slow because the materials take time to increase or decrease in temperature compared with the changes in resistance caused by the excitation of PbSe molecules when exposed to 4.2µm radiation photons. As a result, pyroelectric, thermopile and bolometer detectors take much longer to respond than PbSe and this timescale is too slow for capnometers where changes that occur in less than 1 millisecond need to be easily and instantly detectable for diagnostic purposes as the shape of the CO_2 concentration curve with time is used to identify medical conditions. Another limitation of pyroelectric, thermopile and bolometer with heat sensors is that they will respond to heat from all infrared absorbing gases including moisture, although bandpass and cut-off filters may be used to limit the range of wavelengths that these detectors respond. Heat detectors however have inferior sensitivity and responsivity.

Some types of infrared semiconductor detectors are not sensitive at 4.2µm (such as InGaAs). Many types require cooling to eliminate "noise" that would make them too insensitive at room temperature. Noise is random changes in voltage or current, which, if too large, hides genuine changes caused by incident infrared radiation. Electrical noise can be reduced by cooling the semiconductor material. Some can be cooled with thermoelectric coolers, but some need liquid nitrogen temperatures to function, but cooling is impractical with capnometers for two reasons:

- Exhaled breath contains moisture. This would condense and freeze at low temperature onto the detector surface acting as a physical barrier blocking the infrared radiation. Some types of capnometers need to be heated to prevent condensation.
- The capnometer must be close to the patient, be small and light-weight. Adding a refrigeration system or a liquid nitrogen dewer would make it too bulky and heavy (it could pull a mask off the patient's face) as well as posing a safety risk to patients from the very cold surfaces. Some types of detector are available as small thermoelectrically cooled detectors but will suffer from the condensation issue described above as well as using more power (a limitation with battery powered devices).

The table below summarises the parameters of a range of the more commonly used types of infrared detector that are used commercially.

Table 1. Comparison of parameters of a range of the more commonly used types of infrared detector compared with PbSe

Detector type	Wavelength range	Responsivity*	Response time	Operation temperature of detector
PbSe	Optimal for 4.2µm	High responsivity. Ca. 1,000V/W for 2mm x 2mm at 25°C Detectivity = 10^9 cm $Hz^{0.5}$/W at 25°C	Very fast, time constant typically 4µS	Ambient

InGaAs	Not in optimal CO_2 absorption range Detects in range 0.5 to 2.55µm	No response at 4.2µm	OK	Can be used at ambient
InSbAs	Detects in a much wider range than PbSe, from 1 to 11µm	Inferior responsivity at ambient. Has about 10 times smaller detectivity than PbSe: Ca. 50V/W for 2mm x 2mm at -10°C Also has inferior detectivity, can achieve 10^9 cm $Hz^{0.5}$/W only at -10°C or below	OK	Requires cooling
InSb (photoconductive and photovoltaic types are made)	Can detect from 1 to 5.5µm.	OK only when cryogenically cooled	OK	Cryogenic cooling needed (liquid nitrogen)
PtSi	Detects in a much wider range than PbSe	Inadequate responsivity	OK	Needs cooling (to ≤0°C, usually cooled cryogenically) and has low quantum efficiency
Pyroelectric	Responds to heat in all of heat spectrum	Inadequate responsivity as much less sensitive than PbSe	Slow response[5]	Ambient
Deuterated L-alanine doped triglycene sulphate (DLATGS)	Responds to heat in all of heat spectrum (these are a type of pyroelectric detector)	Inadequate responsivity	Slow response	Ambient
Thermopile	Responds to heat in all of heat spectrum	Inadequate responsivity and much less sensitive than PbSe	Slow response	Ambient
Bolometer	Not in optimal CO_2 absorption range, detects in all of heat spectrum.	Much less sensitive than PbSe	Fairly slow (typically 50mS[6])	Ambient

* Note that "responsivity" is a measure of the detectors' signal size per watt of incident infrared energy. A larger size of the response gives superior sensitivity to small changes in CO_2 concentration and superior accuracy of concentration measurement.

Detectivity is the inverse of the "Noise Equivalent Power" and is a measure of

5 For example, a thermal time constant of 150mS and an electrical time constant of 2 seconds, https://www.infratec.co.uk/downloads/en/sensor-division/detector_data_sheet/infratec-datasheet-lie-202-_.pdf

6 http://www.xenics.com/en/faq/what-thermal-time-constant

sensitivity, but also takes into account signal noise generated by the detector. Detectors with high signal to noise ratios tend to have higher (superior) detectivity values.

All types of pyroelectric detector including DLATGS, have lower responsivity and much slower response times compared with PbSe. Commercial thermopiles and bolometers[7] also have relatively low responsivity and slower response times compared with PbSe.

Only PbSe is sensitive to 4.2µm radiation, has sufficient sensitivity, a very fast response to changes in CO_2 partial pressure and does not require cooling. Capnometer sensors are required to have a responsivity with a sufficiently large change in measurement parameter, such as electrical resistance or voltage measured across a load resistor, to enable accurate measurements of small changes in CO_2 concentration.

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

Reliability is not an issue because there are no alternative types of detector that meet all of the essential criteria listed in section 4 (C).

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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.

Many different types of sensor have been evaluated for the of measurement of CO_2 in patient's breath, but only one has been found that meets all of the essential requirements listed in section 4 (C) above. PbSe is very sensitive to small changes in CO_2 concentration and its peak sensitivity coincides with the optimal absorption wavelength of CO_2. It responds to changes in CO_2 concentration almost instantly and the change in electrical resistivity that occurs when small CO_2 concentrations changes occur to give accurate analytical results. The sensor which is attached to patients breathing tubes must be small and lightweight and so this prevents the use of the types of sensor that need cooling. Also cold sensors pose a safety risk to patients as well as

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7 Commercial bolometers are very small silicon based devices and have much lower sensitivity and detectivity than PbSe. Large-size bolometers are more sensitive but are impractical in the small space available inside capnometers. Also, large-size bolometers are not produced commercially as fabrication is very complex.

condensation from patient's breath freezing on cold surfaces which would block infrared radiation making the sensors insensitive and unresponsive.

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

A new type of sensor is needed that meets all of the essential criteria listed in section 4(C). It is not possible to predict when one might be discovered as all known semiconductors and other types of detector have been evaluated and none of these meets all of the essential criteria listed in section 4(C). Semiconductor development is now relatively mature so that it seems unlikely that a new one will be discovered that could replace PbSe. If a detector were to be discovered, although this seems unlikely based on current knowledge, then this would need to be thoroughly tested for performance under all conditions of use, tested for reliability, clinical trials carried out to monitor and assess its effect on a cross-section of patients' medical conditions before gaining approvals world-wide. This is likely to take 8 to 10 years.

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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 selenide has a registration dossier on the ECHA database

2) Provide REACH-relevant information received through the supply chain. Name of document:

PbSe registration dossier https://echa.europa.eu/registration-dossier/-/registered-dossier/11183

(B) Elimination/substitution:

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

   ☐ Yes. Consequences? _____

   ☒ No. Justification: No substitutes exist that meet all essential criteria

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

   ☐ Yes.

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

   ☒ No.

   Justification: No substitutes exist that meet all essential criteria

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: Not applicable as no alternatives exist
   2) Health impacts: Not applicable as no alternatives exist
   3) Consumer safety impacts: Not applicable as no alternatives exist

⇨ Do impacts of substitution outweigh benefits thereof? Not applicable as no alternatives exist

Please provide third-party verified assessment on this: _____

(C) Availability of substitutes:

a) Describe supply sources for substitutes: None exist

b) Have you encountered problems with the availability? Describe: Not applicable, as none exist

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? A substitutes that meets all criteria listed in section 4 (c) first needs to be developed. It then needs to be tested, etc., as described in section 7 (B).

(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 Patients in EU hospitals and clinics would be seriously harmed if these sensors could not be obtained in the EU because this exemption were not renewed. If their breathing cannot be accurately monitored using capnometers, deaths and serious harm could occur. It is not known how many patients in the EU would be affected annually, but the number is likely to be of the order of thousands of people. One study reports that 64,000 patients per year are ventilated in critical care units in the UK alone[8]. Capnography is also used in operating theatres and when transferring critical patients between hospital wards.

☐ 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:

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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:

The calculation of the quantity of lead 4(A).5 and in answer to 5.3 includes confidential market information (on sales and sensor design) and so is provided as a separate confidential submission.

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[8] https://onlinelibrary.wiley.com/doi/pdf/10.1111/j.1365-2044.2011.06793.x