Exemption Request Form

Date of submission: November 22, 2019

1. Name and contact details

1) Name and contact details of applicant:

Company:
LASER COMPONENTS GmbH

Tel.:
49-8142-2864-27

Name:
Sven Schreiber

E-Mail:
s.schreiber@lasercomponents.com

Function:
Head of Sales

Address:
Werner-von-Siemens-Str. 15,
82140 Olching, 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 IV where applicable: 1c

Proposed or existing wording: The existing wording is **"Lead, cadmium and mercury in infra-red light detectors"**. Laser Components make infrared detectors containing lead but not cadmium or mercury and so we are requesting renewal of 1c which could be "**Lead in infra-red light detectors**", although other manufacturers are likely to require this exemption to include mercury and cadmium.

Duration where applicable:

At least the maximum seven years validity, starting from:

- 21 July 2021 for medical devices and monitoring and control instruments;
- 21 July 2023 for IVD medical devices; and,
- 21 July 2024 for industrial monitoring and control instruments.

☐ Other: _____

3. Summary of the exemption request / revocation request

Lead sulphide and lead selenide infrared detectors have unique characteristics that enable them to be used in a wide variety of applications. They are used in near infrared analysers used by very many diverse industries, medical devices for analysis of carbon dioxide in patients' breath and in spark detection systems. These detectors are used because of their high sensitivity in the near infrared range and can be used without cooling. Another advantage over thermal heat detectors is the very fast response times of the lead based detectors, which is essential in many applications.

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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: Spark detectors, physical property and chemical analysers and spectrometers, rapid remote temperature measurement, carbon dioxide analysers (capnographs), gas analysers, etc.

   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: There are other applications of 1c used in category 9 products that this renewal request does not consider because Laser Components do not make these types of detector. For example,

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mercury cadmium telluride infrared detectors are used in high performance infrared spectrometers.

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 sulphide and lead selenide are photoconductors used to detect and measure infrared radiation

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

86.6% lead in lead sulphide (PbS)

72.4% lead in lead selenide (PbSe)

5. Amount of substance entering the EU market annually through application for which the exemption is requested: Estimated to be about 8 grams per year

Please supply information and calculations to support stated figure.

We estimate that one 2 x 2 mm detector chip will contain 38.4µg of lead assuming these are 100% dense single crystals. However these materials are polycrystalline and so we have estimated that they contain about 60% of this figure, so 23µg lead. Although the total number of detectors produced by all manufacturers annually is unknown, we estimate that this could be about 1 million of 2 x 2 mm equivalent size and one third of these are used in the EU. 1 million x 23 µg = 23 grams lead, so one third is 7.7 grams

6. Name of material/component: lead sulphide and lead selenide in photoconductor detectors

7. Environmental Assessment: _____

LCA: ☐ Yes

☒ No

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(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?

The original exemption 1c of Annex IV is for lead, cadmium and mercury in infrared detectors. Lead is used as two types of semiconductor materials; lead sulphide (PbS) and lead selenide (PbSe), both of which are sensitive to infrared radiation. Cadmium and mercury are used in cadmium mercury telluride detectors, but this material and its uses are not included in this exemption renewal request.

PbS and PbSe are infrared sensitive at different wavelengths as follows:

- PbS: From 1 to 3.0µm with a peak sensitivity at about 2.4 µm
- PbSe: From 1 to 4.7µm with a peak sensitivity at about 4.0 µm

PbS and PbSe are photoconductors that change electrical resistance when exposed to infrared radiation in the wavelength ranges as above. Resistance decreases as the intensity of infrared radiation increases. The PbS and PbSe are used as very thin layers inside small electronic components that are usually mounted onto printed circuit boards so that the entire detector module is very small and can be used at locations where there is very little space available. In some applications, it is used with an infrared source to analyse the composition of gases through which the infrared light passes and in other applications, infrared radiation from hot materials is detected and measured. Examples of uses of PbS and PbSe include:

Spark Extinguishing Systems

PbS and PbSe detectors are used in spark extinguishing systems where the detector is used to detect hot small particles (sparks) (e.g., from cutting metal) that could cause a fire if they reach flammable materials. In some processes that emit sparks, these can, for example, be removed by ventilation in which the hot particles travel rapidly along fume extraction ducting. As soon as a spark is detected, it can be immediately extinguished (e.g. with a water spray) to prevent fires. The sensors must be very sensitive to low intensity infrared radiation as the particles can be very small and they must respond very quickly by actuating the water spray to extinguish the spark before they can set alight flammable materials.

PbS and PbSe are essential for detection of all types of spark and small hot particle In systems that are used in daylight- or artificial light conditions, such as with open conveyors. Optical filters are used to remove visible light to allow the detection of very small hot particles.

Spark detector systems for the detection of hot particles, which can occur, for example, during comminution processes (this can create sparks) use PbSe detectors which are sensitive to longer wavelengths than PbS, although PbS is more sensitive. PbS is sensitive to 1 – 3 µm whereas PbSe can detect infrared radiation of up to 4µm.

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Spark detectors must operate very rapidly as follows:

The edge length of a PbS detector can typically be 6mm. Sparks move typically at 30m/second in air and so will be visible to a 6mm length PbS detector for only 200µSeconds. If there is other material (e.g. dust) in the air flowing past the detector, the detection time can be even shorter. Therefore the detector must detect and respond with an output signal in less than 200µSeconds.

Near infrared chemical analysers

Near infrared chemical analysers are used for a wide variety of materials and in many different industries. A few are described here.

Food analysers: They are used to analyse flour, grains, dairy products, etc. for moisture content and concentrations of protein, fat, gluten, lactose and other substances. These are used in laboratories and in factories to analyse flour, grains, and dairy products before and during processing to ensure that their composition is correct and is as labelled on product containers. They need to be able to rapidly analyse the materials without complex sample preparation (the milk or flour powders are simply inserted into a compartment of the analysers) and analysed within 1 minute to avoid stopping the production process or producing material with an incorrect composition that has to be disposed of as waste. Water, protein, fat, gluten, lactose, etc., all have characteristic infrared spectra in the 400 to 2500nm range. The analysers use a silicon detector for the 400 to 1100nm range and PbS for the 1100 to 2500nm range. The spectra of most of these materials are complex consisting of many absorption peaks, but absorption peaks occur at characteristic wavelengths for each type of molecular group such as carboxyl groups, hydroxyl groups, etc. The spectra of milk, flour and grains will be complex and so special prediction algorithms have been developed that are used to determine the materials constituent concentrations with a high level of accuracy. These prediction models are based on the sensitivity range and the temperature response of the PbS sensor that is used, which, like all semiconductor detectors, is non-linear and is temperature dependent. If a different type of material is analysed, the user can develop their own calibrations to provide accurate analysis.

The response of PbS detectors versus wavelength and temperature is complex as shown in the spectra below for real PbS detectors.

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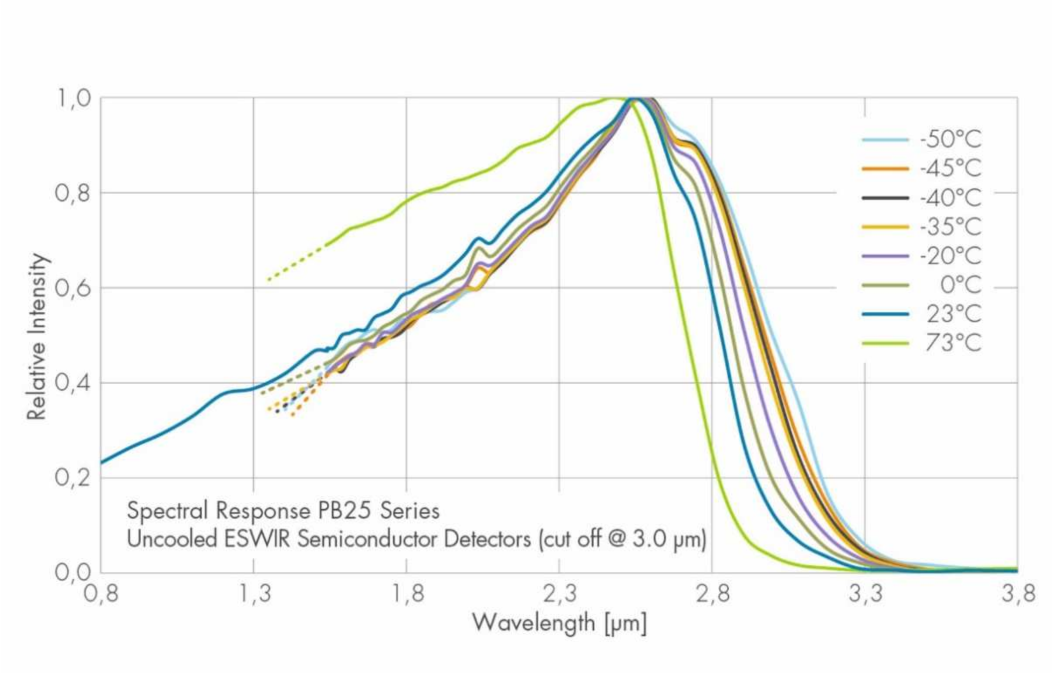

Figure 1. Relative intensity versus wavelength of lead sulphide detectors at temperaturtes between -50° to +73°C

The shape of the curve is complex because the PbS layer is very thin and may not absorb 100% of incident light so that the small amount that is not absorbed, passes through and is then reflected back so is absorbed during the second pass. The prediction models have to use the real response of the detectors that are used and it is very difficult to design a new analyser with a completely different type of detector as this will respond differently.

Laboratory chemical analysers: A commonly used laboratory instrument analyses substances and mixtures of substances by passing light through the material and measuring the proportion of light within the wavelength range that is absorbed. Most substances absorb light at specific wavelengths and so have characteristic spectra that can be used to identify these substances and/or measure their concentrations. Some laboratory analysers use special lamps, optics and detectors that allow analysis in the ultraviolet, visible and near infrared wavelength ranges, typically from 190nm (0.19µm) to 3300nm (3.3µm) where PbS is used for the near infrared range from 860, 1800 or 2300 to 3300nm, depending on which other types of detectors are also used. PbS is always needed however between 2300 to 3300nm as no suitable alternatives exist. To achieve maximum sensitivity over the entire wavelength range, one spectrometer may use three different detectors as follows:

- A photomultiplier tube to detect UV and visible wavelengths 190 to about 900nm;
- InGaAs for part of near infrared range – up to 1800nm with standard types and up to 2300nm if the extended range (wideband) types are use; and

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- PbS for the rest of the near infrared wavelengths up to 3300nm.

Organic and inorganic substances have characteristic spectra in the near infrared range that depend on the characteristics of bonds in the molecules. As a result, analysis in this wavelength range is used in pharmaceutical research, forensic science, failure investigations, chemical process development and in many other industries. These analysers need to be very sensitive to detect substances at fairly low concentrations in mixtures and to analyse small quantities of substances. These laboratory analysers are very widely used because they are straightforward to use, very sensitive, accurate and do not require liquid nitrogen cooling (of detectors). It is also helpful to users that one instrument can analyse one small sample in the UV, visible and near infrared ranges as this allows the analysis of very small quantities that may be available, for example for forensic analysis, but insufficient is available for analysis by UV/visible and separately by infrared analysis..

Optics analysers

Lead sulphide and lead selenide detectors are used in spectrometers used to measure the properties of optical components such as lenses and in particular for the spectroscopic analysis of optical coatings on lenses and lens assemblies during coating and etching processes. These materials need to be analysed in the wavelength ranges up to 3.5 µm (PbS) and 5.0 µm (PbSe) to ensure that they meet the required specification for quality and thickness.

Optical components such as lenses that operate at infrared wavelengths use special coatings that must have the specified thickness and quality and this can only be measured by using PbS and sometimes also lead selenide detectors. Infrared optics are used in a very wide range of industries including automotive (collision avoidance systems etc.), aviation, medical, military, etc. The following is an illustrative list of applications that use infrared sensitive optics:

- Medical instrumentation
- Volcanic ash detection
- Imaging devices
- Mine safety
- Flame detection
- Food analysers
- Environmental monitoring
- Analysis and control of gaseous effluent from power stations
- Detection instruments and safety systems on oil rigs
- Security systems
- Sensing instruments
- Spectroscopy
- Infrared cameras
- Avionics

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- Space applications
- Ozone layer monitoring
- Analysis of vehicle exhaust gases for MOT requirements
- Blood alcohol meters (Breathalysers)
- Imaging devices
- Mine safety
- Flame detection
- Food analysers

PbS detectors are critical in the production of high quality optical coatings. Most optical coatings used for any products in the near to far IR region, for wavelengths from 1.5 to 15 microns, will use PbS and PbSe detectors. The most important wavelength range that the PbS detector technology needs to operate in is the 1000nm to 2400nm region, because many of the materials used in the IR "film stacks" (these are multiple thin layers of coatings on the surface of glass or other materials) will be absorbing below 1500nm.

PbS detectors are not needed for all of the components used in the above applications, but the coating spectrometers must be able to analyse a wide wavelength range including those where PbS and PbSe are especially suitable. Therefore, PbS detectors are needed in the manufacturing processes of all of the above listed applications.

Non-contact temperature measurement

The use of non-contact temperature measurement is used in a variety of applications. Three examples are described below. Infrared detectors can be used to measure temperature of objects without making physical contact by measurement of the intensity of infrared radiation emitted. As an object's temperature increases, the intensity of the emitted radiation in the range of infrared wavelengths increases. Many of the types of infrared detector on the market can be used, unless temperature measurements must be made very quickly.

Railway wheel temperature measurement

Very fast measurements are required, for example, using semiconductor sensors (based on lead sulphide or selenide, depending on variables such as temperature being measured) built into "Hot Box Detectors" and "Hot Wheel Detectors" of trains. The sensors are built into a train's track and used to monitor the temperature of the bearing boxes, wheels and brakes of the passing rolling stock. Trains may pass over the sensors at over 200km/hour and so measurements need to be very fast (only semiconductor types are suitable). When the temperature of bearings, wheels or brakes are measured and it is found that these have overheated, alarms are immediately sent to the train operators and the trains can be stopped before damage to the rolling stock occur, or more critically, to prevent a derailment. In this way Hot Box and Hot Wheels Detectors have drastically decreased the number of derailments occurring since they began to be introduced in the 1960s and as such have greatly increased

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the safety of train travel and transport[1].

Infrared temperature control in microwave digestions

Chemical analysis of inert materials, such as plastics, ceramics and alloys, can be carried out by first dissolving them in hot corrosive chemicals. The problem is preventing these chemicals from also dissolving the containment vessel in which the materials are dissolved. Ceramics, glass and quartz, for example are attacked by strong alkalis and by acidic fluoride solutions. A widely used method is to place the materials and dissolution solution into a sealed fluoropolymer (such as PTFE) vessels which is heated internally using microwave heating. The microwave-heated pressure digestion vessel is sealed to prevent loss of substances as vapours, but it is essential that the temperature is controlled to prevent overheating which would increase the internal pressure to a level where it would burst open the vessel. Microwave heating is very rapid so a fast non-contact temperature measurement method is needed and lead sulphide detectors are ideal. Temperature is determined by measurement of the infrared energy emitted from the inside of the vessel. At 50°C to 300°C, the emitted radiation is at a maximum in near infrared frequencies detectable using lead sulphide detectors of about 3µm. Conveniently, PTFE is transparent to infrared radiation of about 3µm, so that the temperature inside the vessel can be measured externally by measurement of the infrared radiation passing through the vessel wall. Infrared radiation is however also emitted from the cooler external surface of the vessel which would interfere with the internal measurement, but this lower temperature radiation can be removed using a suitable optical filter. The diagram below illustrates the method used.

[1] These are built according to the European Railway Norm EN15437-1 which outlines the following required temperature measurement tolerances for trains travelling up to 250km/h. As part of installed railway infrastructure (large-scale fixed installations) these may be excluded from RoHS, but portable or temporary devices would be in scope.

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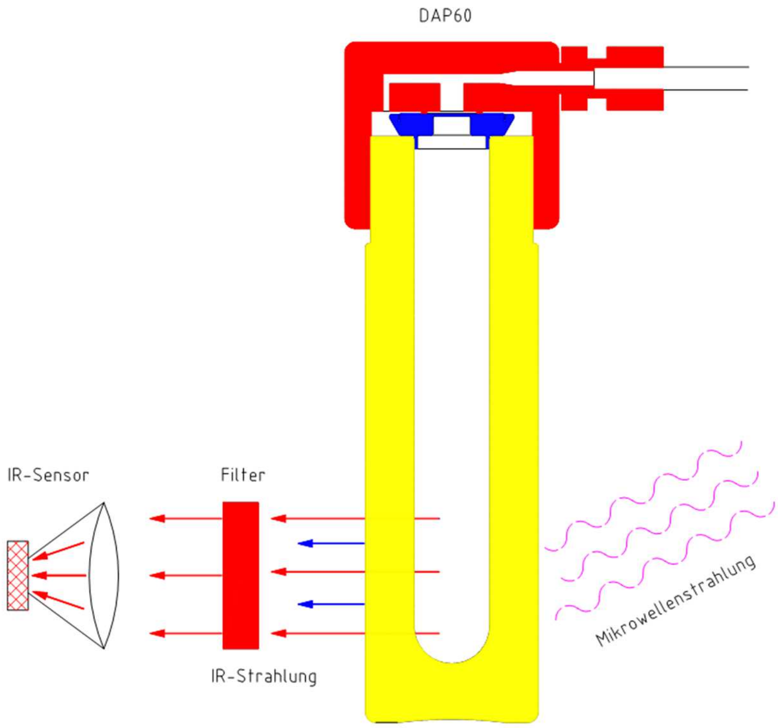

Figure 2. Remote temperature measurement of a microwave heated vessel

Vessels are sealed and fitted with rupture discs that burst when a specified pressure is excceeded. A rapid temperature drop occurs when the disc bursts and when this happens or when a specified temperature is reached, the microwave's magnetron is switched off. Very rapid temperature measurement accuracy of +/- 1 ° C is needed for this equipment.

Remote temperature measurement

PbSe infrared detectors are used to measure surface temperatures remotely during production processes. Temperature control is essential to maintain quality and performance. This is used for production of plastic thin film, metals, glass, food products, paper, textiles, etc., which may be moving so contact temperature measurement is not possible. Typically it is necessary to measure temperatures between 100 and 200°C, but higher temperatures may need to be measured in some applications. The wavelength of emitted infrared radiation from surfaces in this temperature range is about 3 - 5µm which coincides with the sensitive range of PbSe detectors and these instruments have an accuracy of 0.3%. Hotter surfaces such as at 600°C and hotter emit at shorter wavelengths and so different types of detector are used. PbSe has the advantage of other types of detector in this temperature range that it can measure surface temperatures that are behind flames or through infrared absorbing gases. The PbSe detector is located at the outer edge of the process and measures emitted radiation from the surface that has passed through the intervening gases and sometimes through a flame.

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The main difficulty of remote measurement of surfaces is that the emitted radiation varies due to the emissivity of the surface. This variation can however be minimised by using the shortest wavelength detectors possible for the applicable temperature range. For 100°C to ca. 300°C, this is PbSe. Heat detectors such as pyroelectric and bolometer detectors detect all wavelengths (e.g. up to 14 µm) and so are as a result much less accurate.

Medical carbon dioxide analysers

In the medical field, infrared sensors are used for monitoring the carbon dioxide (CO_2) gas concentration of the air inhaled and exhaled by patients in need of ventilation. This application is called capnography, and the sensor is used in intensive care units (in hospitals) and in emergency care (e.g. in ambulance cars or helicopters) paired with ventilators and monitors. The device itself is rather small (6x3x2cm), weighs approximately 40g, features a cable to the host system (ventilator or monitor) and is plugged onto the ventilator tubing near the patient's face.

The application of capnography on ventilated patients from pediatrics to adults is state of the art in medicine. There are two types; sidestream capnographs (using a pump and tubing to extract a gas sample for measurement) and mainstream capnographs (directly applied to the ventilator tubing). Mainstream capnographs offer the advantage of fast rise times and small delays with respect to CO_2 concentration versus time. The operation principle is a non dispersive infrared (NDIR) measurement, where the attenuation of gases (here CO_2) in characteristic wavelength ranges (here around 4.3µm) is used to quantify the gas content of the air. Infrared light is sent from a broadband (e.g. thermal) source through the sample gas to a detector, the spectrum being narrowed down by a bandpass filter. The higher the CO_2 concentration in air that is present, the less infrared light reaches the detector. A second detector and bandpass filter combination is used to correct for changes in the total light intensity present (e.g. depending on dirt in the optical path or intensity fluctuations in the source) by comparing the two signals. The infrared detectors contain a small amount of lead selenide as the infrared sensitive material.

In order to be suitable for clinical use, all medical capnographs have to fulfil tight accuracy specifications in the relevant concentration range from 0 to 10 vol.% CO2. For outdoor use in emergency applications, additional requirements such as suitability within a broad temperature range from -20 to +50 degrees Celsius plus robustness against shock and vibration (use in ambulance cars and helicopters) are essential. This combination of requirements is met by using PbSe detectors, but which cannot be substituted without loss of performance, as explained in more detail below.

The performance of the mainstream capnograph is fine tuned to the host systems with respect to concentration accuracy, signal-to-noise ratio and rise time. For the clinician, it is important to see exactly how much CO_2 is present during inhalation and exhalation and how the shapes

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of the concentration / time curves appear. From this he/she can deduce if the ventilation parameters are set correctly or if there is an issue with the air delivery and removal. A short rise time results in meaningful clinical data even for patients with high breath rates or steep breathing patterns. Longer rise times tend to suppress data that otherwise can be useful to the clinician and so a fast response time is essential.

The use of mainstream capnographs is state of the art and essential for supporting clinicians using ventilators and patient monitors worldwide on patients in intensive care units and in acute care. If these sensors were not to be available, this would seriously deteriorate the quality of ventilation and consequently of the medical care given to patients with breathing impairments.

Other uses of PbS and PbSe infrared detectors include:

- CO_2 detection such as in gas analysers used in factories, mines, etc., to warn workers if levels become dangerously high
- CO_2 sensors for SCUBA diving, analysis of atmosphere in bioreactors, stowaway detectors, etc.
- Flame control and flame detectors
- Moisture monitoring
- Gas analysers (e.g. hydrocarbons, SF6). Many of these are portable battery powered handheld monitors that are used to detect gases (such as hydrocarbons, refrigerants, CO_2 and CO) and are mainly used by workers. Many gases have characteristic infrared absorption in the near infrared and can be monitored using PbSe detectors. These analysers must be small and lightweight to be carried for an 8 – hour shift without being recharged and therefore uncooled detectors need to be used because electrical cooling of detectors shorten battery lifetime to < 8 hours or requires batteries that are too heavy to be carried for 8 hours.

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

PbS and PbSe infrared detectors have the following characteristics that are essential in applications where they are used:

- Sensitive in required wavelengths: PbS: From 1 to 3.0µm with a peak sensitivity at about 2.4 µm, PbSe: From 1 to 4.7µm with a peak sensitivity at about 4.0 µm
- Photoconductor with a significant electrical resistance change when infrared intensity changes
- Functions at room temperature and does not require cooling
- Small size and lightweight detector circuits
- Fast response to changes in infrared radiation intensity
- High "detectivity" (this characterises performance, and is equal to the reciprocal of noise-equivalent power (NEP), normalized per square root of the sensor's area and frequency bandwidth). Higher detectivity values are equivalent to larger signal to noise ratios and superior sensitivity.
- High detectivity is especially important with spectrometers that analyse over a wide range of wavelength so that more than one type of detector is used. Each type of detector needs to have a similar high detectivity so that accuracy in each wavelength range is equivalent.
- Can be made in large size (up to $1cm^2$) required for measurements in inhomogeneous environments. For example for remote temperature measurements and spark detectors
- Low power consumption in monitoring circuits when used in battery powered applications, such as portable hazardous gas monitors
- CO_2 sensor technology features 2 detectors with the following basic requirements: 1) Fast rise time and 2) High signal-to-noise ratio (S/N) and sensitive to around 4.3µm. These requirements are fulfilled by using lead selenide (PbSe) photoresistors of $2x2mm^2$ sensitive area.

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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.)

EEE containing PbS and PbSe detectors are disposed of by a variety of routes, as permitted by the EU WEEE directive, so no closed loop exists for these components.

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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:**

The following is based on published EUROSTAT data for 2016[2], using data for category 9 (the main user of these detectors) and German data (as data for many other countries is not published). It is likely that close to 100% of category 9 equipment is collected for recycling or reuse, but no accurate data is published as most category 9 WEEE is not recorded by official WEEE schemes. The following are based on proportions of 8grams used per year.

☒ In articles which are refurbished	0.22% = 0.0176 grams
☒ In articles which are recycled	86.7% is recycled = 6.94 grams
☒ In articles which are sent for energy return	11.6% = 0.93 grams
☐ In articles which are landfilled	Proportion of end of life WEEE collected is not known so this cannot determine.

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

There are many types of infrared detector and lead sulphide and lead selenide are two of these types of sensors. However, each type of infrared sensor has different characteristics so that each type is used for different applications and uses. Some of

[2] http://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do

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the characteristics of the main commercially available infrared sensors are compared in the table below.

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Table 1. Comparison of PbS and PbSe with other types of infrared sensor.

Detector	Type	Wavelength range (µm)	Peak wavelength (µm)	Typical detectivity (cm Hz½/W)	Response time	Operating temperature
PbS	Photoconductor	1 to 3.3	2.4	3.5×10^{10} (90Hz) 1.1×10^{11} (650 Hz)	Fast, 200µS	Ambient
PbSe	Photoconductor	1 to 4.7	4.0	6.0×10^{9} (90Hz) 1.8×10^{10} (1 kHz)	Very fast, time constant typically 4µS	Ambient
InGaAs	Photodiode (can be used as a photoconductor)	0.5 to ~2.55µm (several types exist with different ranges[3])	Standard range 1.55 Extended range 2.25	From 4.8 x 10^{10} to ~10^{11} (1kHz for extended range type)	Fast	Can be used at ambient
InSbAs	Photodiode	1 to 11µm (but may be supplied with cut-off filters)	Depends on temperature	5.0×10^{9} (1.2 kHz)	Fast	Requires cooling
InSb	Can be used in both photovoltaic and photoconductive modes	Photovoltaic 1 to 5.5µm. Photoconductor 1 to 6.7 µm	5.3 5.5	Photovoltaic = 1×10^{10} Photoconductor at -10°C, 1×10^{9} (1.2kHz)[4]	Fast response	Cryogenic cooling needed
PtSi	Schottky barrier detector	Ultraviolet to far infrared. Detects in a wider range than PbS & PbSe	Not applicable	Ca. 1×10^{9} (at 80K[5])	Fairly fast, used for imaging	Needs cooling (to ≤0°C)
Pyroelectric	Pyroelectric	Responds to heat in all of heat spectrum	No peak	4×10^{8} (10 Hz)[6]	Slow response[7]	Ambient

[3] Standard types have a range of up to 1.7µm, whereas extended range types are sensitive up to 2.55µm. However, the dark current values of extended range types is much larger (typically 20 times larger) so that they have an inferior detectivity.

[4] https://www.hamamatsu.com/resources/pdf/ssd/p6606_series_kird1026e.pdf

[5] http://photonics.intec.ugent.be/education/IVPV/res_handbook/v1ch23.pdf

[6] https://www.infratec.co.uk/downloads/en/sensor-division/detector_data_sheet/infratec-datasheet-lie-202-_.pdf

[7] 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

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DLATGS	Pyroelectric	Responds to heat in all of heat spectrum	No peak	2.7 x 10^8 (1.3mm element size[8])	Slow response	Ambient
Thermopile	Generates a voltage from temperature change	Responds to heat in all of heat spectrum	No peak	10^8 (1Hz), 10^6 (at 1kHz[9])	Slow response	Ambient
Bolometer	Change electrical resistance with temperature	Responds to heat in all of heat spectrum	No peak	1 to 3 x 10^8	Fairly slow (typically 50mS[10])	Ambient

Another type of semiconductor detector that operates in the infrared range is mercury cadmium telluride (MCT). These have to be cooled(usually with liquid nitrogen) to be used and are very sensitive, but cannot be considered as possible substitutes for PbS or PbSe as they contain two RoHS substances, although these substances are also in scope of exemption 1c. MCT is used for the mid to far infrared range, but cannot be used uncooled.

[8] https://fscimage.fishersci.com/images/D10942~.pdf

[9] https://www.ama-science.org/proceedings/getFile/ZGL0BN==

[10] http://www.xenics.com/en/faq/what-thermal-time-constant

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Wavelength range and sensitivity

The range of wavelength that the sensor is sensitive is important for applications where only certain wavelengths need to be detected. This is important, for example, in CO_2 monitors, gas analysers and moisture monitoring because these all rely on measurement of infrared intensity at specific characteristic wavelengths. Cut-off and band-pass filters can remove ranges of unwanted wavelengths but they cannot allow discrimination between gases or substances that have characteristic absorption wavelengths that are similar to each other. Also, for analysis of gases such as CO_2, the sensor must be sensitive in the main characteristic absorption range and the main absorption wavelength of CO_2 is 4.2µm and so InGaAs is unsuitable. Each semiconductor type of detector is sensitive within a different range and the spectral response curve also depends on temperature, not only becoming overall more sensitive as temperature decreases, but the shape of the curve also changes with temperature[11]. The spectral responses (sensitivity) of indium gallium arsenide, lead sulphide and lead selenide sensors are shown below.

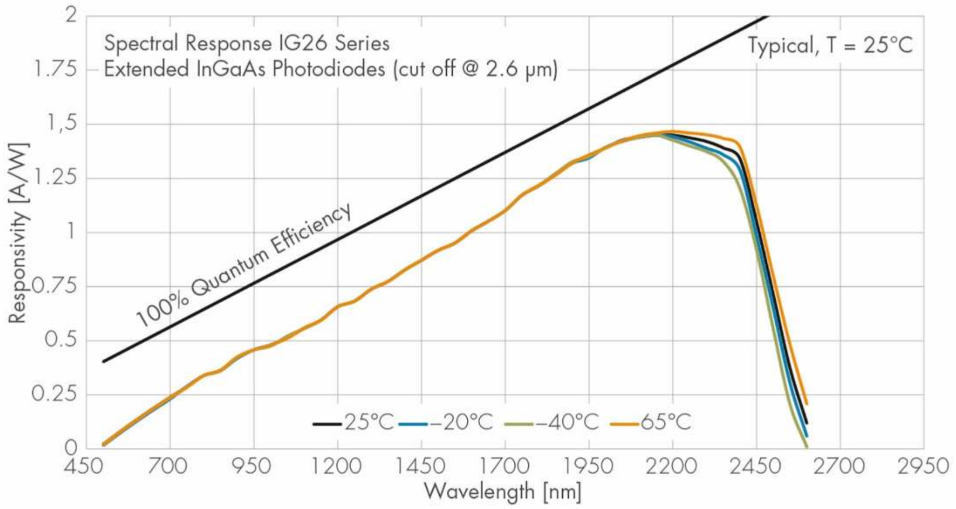

Figure 3. Relative sensitivity versus wavelength of indium gallium arsenide detectors in the temperature range 25° to 65°C

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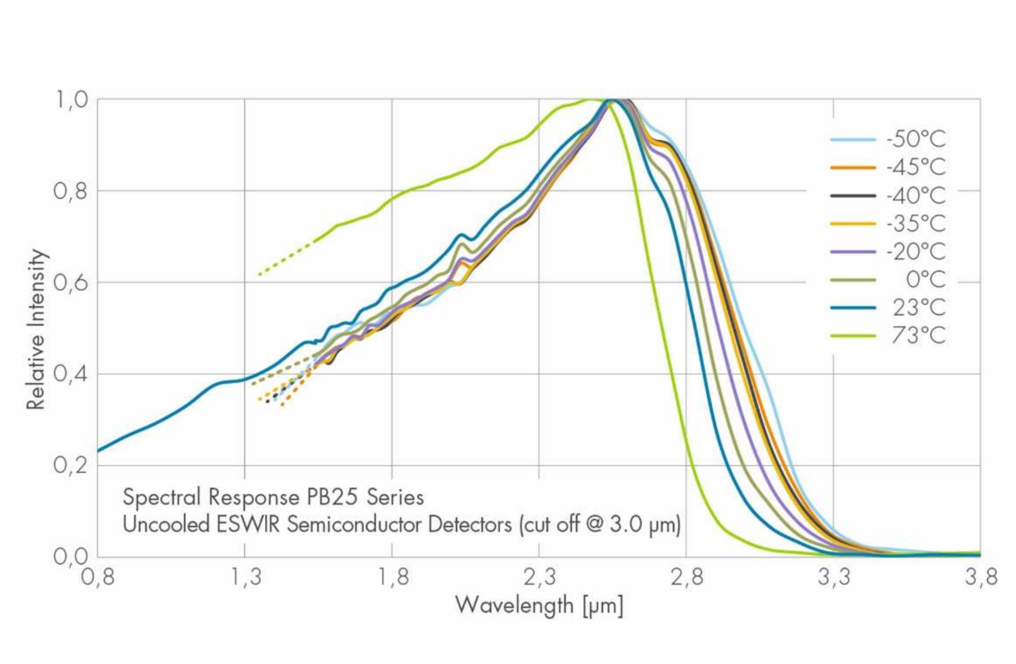
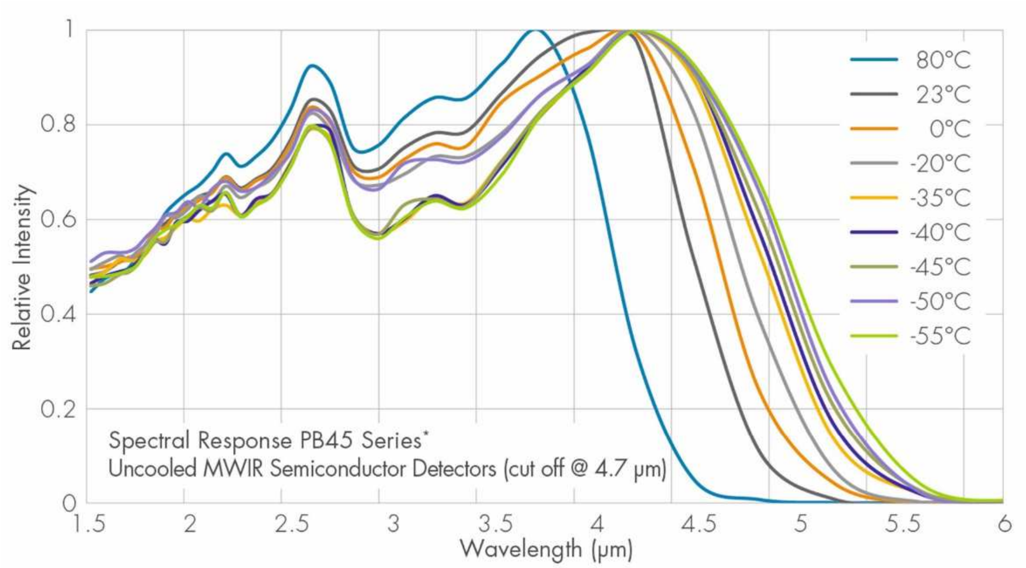


Figure 4. Relative sensitivity versus wavelength of lead sulphide detectors in the temperature range -50° to +73°C



*Spectral Responsivity Modulation is "Substrate Enhanced".
This means that not all photons are initially captured by the absorbing region. A portion of the light passes the absorber, travels through the quartz substrate, is reflected, and passes through the substrate again until it is finally captured by the PbSe material. Therefore, the detailed spectral responsivity curve is a little complex since it is a product of the infrared absorption of the active material itself, the substrate and once again the active material. Older literature curves tend to hide this feature for simplicity reasons. Please note, that a spectrally simple curve can be generated on special request by blackening the backside of the substrate. However, the drawback of blackening is less signal.

Figure 5. Relative sensitivity versus wavelength of lead selenide detectors in the temperature range -50° to +80°C

Near infrared analysers automatically analyse for constituents in milk, flour, grains and many other materials. These instruments do this by the use of special prediction algorithms that take into account the non-linear response of the sensor, as shown above, as well as the complex spectrum of the material being analsed and the temperature which also affects the sensor's spectral response curve shape. Also a different algorithm is needed for each material being analysed and for each combination of substance concentrations being measured. It is therefore not technically practical to replace a lead sulphide sensor with one of a different type as new algorithms will be needed which will take many years work to develop for each analyser, that is, if a suitable alternative detector be developed.

Similarly, spectrometers used to analyse the properties of coatings on lenses need to operate at wavelengths of up to 5µm and so InGaAs is unsuitable (other types either need cooling or are not sufficiently sensitive).

Laboratory spectrometers that anayse in the ultraviolet, visible and near infrared ranges use lead sulphide to analyse at up to 3.3µm, which is the upper limit for this material. The upper limit of wideband types of InGaAs is 2.6µm and is used in some spectrometers as well as PbS to achieve maximum sensitivity across the near infrared range. Some organic and inorganic substances have characteristic absorption wavelenths in the 2.6 to 3.3µm range and so could not be analysed if PbS could not be used. The 2.6 to 3.3µm wavelength range is especially useful for analysis of molecules with C-H, O-H, alcohol (C-OH), amide ($CONH_2$), amines ($C\text{-}NH_2$) and C≡N nitrile bonds.

Operating temperature

Some semiconductor sensors can be used only when they are cooled. This is because the semiconductors generate random electrical signals called "noise" and at ambient temperature, this noise is sufficiently intense to prevent the detection and measurement of infrared radiation. Cooling has several disadvantages:

- It requires additional electrical equipment and power consumption.
- Condensation will occur on cold surface and ice or water droplets will scatter infrared radiation so that it cannot be measured
- The additional energy consumption will result in shorter time periods that battery powered equipment can be used. This can pose a safety risk to workers who rely on portable hazardous gas monitors and there is a safety risk if the battery cannot provide sufficient power for a full working day. Cryocooling also adds weight so may be impractical with handheld portable devices
- Very cold surfaces pose a safety risk to users
- Some detectors, such as InSb, can be used only by liquid nitrogen cooling. This makes the equipment much more bulky as a dewer and insulation are required. Also the user has to frequently replace the liquid nitrogen which is a hazardous process due to its

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very low temperature which can rapidly freeze human flesh causing severe frostbite that can result in loss of limbs. Use of liquid nitrogen is also impractical with portable equipment and at remote locations.

Cryocooled semiconductor sensors are used where their superior performance (e.g. high sensitivity) at low temperatures is needed for specific applications but are not suited to the applications where PbS or PbSe are used.

Some types of detectors, such as InSbAs, are made into small discrete electronic components that include electrically powered thermoelectric cooling. These small components consume more power than uncooled semiconductors and condensation can occur on the detector windows.

Sensitivity

The sensitivity of infrared detectors is very variable. In general, semiconductors are much more sensitive than heat sensors such as pyroelectric, bolometer and thermopile detectors[11]. This is important when the infrared intensity is low so that it can be detected and measured accurately. Lead sulphide is much more sensitive than lead selenide, but the wavelength range of the sulphide is smaller and different than that of the selenide and so each is used in different applications.

A manufacturer of spectrometers used to measure the properties of coatings on lenses has evaluated DLATGS and other types of pyroelectric detectors and found that these have much lower sensitivity by a factor of 100 or 1000 times, which makes them too insensitive to be used. They also found that the sensitivity of bolometer detectors are also too insensitive.

Detectivity

Detectivity is a measure of the sensitivity of sensors that depends on their power output, noise generation and is usually normalised for surface area. High signal output and low noise give high detectivity values. Detectivity depends on temperature as noise emission of semiconductor sensors decreases as they are cooled. For photodiode sensors, the frequency also affects detectivity.

Manufacturers of near infrared food analysers have evaluated InGaAs as a possible substitute for PbS. However, to obtain the required sensitivity for accurate analysis, the GaInAs needs to be cooled with liquid nitrogen, which is not practical and is also very hazardous in the locations (e.g. food factories) where these instruments are used. The additional hazard of using liquid nitrogen is also undesirable in analysis and test laboratories where spectrometers are used and so is avoided wherever this is technically possible.

Response time

Response times are dependent on the type, size and temperature of the detector.

---

[11] As shown in figure 2-1 on page 8 of https://www.hamamatsu.com/resources/pdf/ssd/infrared_kird9001e.pdf

Semiconductors respond very quickly because when a photon impacts the semiconductor molecule, it excites electrons and this causes the change in electrical resistance, voltage or current. Pyroelectric, thermopile and bolometer sensors respond to heat and so take time for their temperature to increase. This time depends on the thermal mass although modern pyroelectric, thermopile and bolometer sensors use very small thermal mass so that the time to respond is not very long, although it is always much longer than semiconductor detectors, as shown above in Table 1.

The response time of semiconductors also varies, depending on the atomic structure of the material as well as other variables, including their temperature.

Detector size

Some applications require measurements to be made in inhomogeneous environment. For example with spark detectors where a very small hot particle must be detected within a much cooler environment. This can be achieved by using a larger size of detector and PbS can be made at up to 1cm^2 and PbSe at up to 6 x 6 mm. This is because these are homogeneous polycrystalline materials. Other semiconductor detectors such as single crystal InGaAs wafers are more difficult to make with the result that these contain inhomogeneities in the semiconductor and these must be avoided when producing detector chips. As inhomogeneities in InGaAs are quite common, it is not practical to make detector chips of larger than 3 x 3 mm which makes these unsuitable for measurement in environments that are not homogeneous. If larger InGaAs chips were to be to be made, most from each wafer would be unsuitable (due to the presence of defects) and so would become waste.

Operating mechanism

There are several different types of infrared sensor, each of which operates in a different way, gives different outputs, requires different circuitry and has different characteristics (such as those described above).

Lead sulphide and lead selenide sensors are photoconductors which have an electrical resistance that decreases when exposed to infrared radiation in the responsive wavelength range. This makes them easy to use as the resistance can be measured using a bias voltage supply in series with the photoconductor with a load resistor across the voltage supply.

Most other types of semiconductor sensor are photodiodes, as in Table 1, which generate a voltage or current that depends on infrared intensity. These output voltages or current are very small and so pre-amplifiers need to be provided. This complicates the measurement circuit as well as adding another variable that needs to be taken into account when determining infrared intensity.

Pyroelectric, thermopile and bolometer sensors are completely different to semiconductor sensors in that they respond to changes in their temperature induced by the incident radiation. They are less sensitive than most semiconductors and respond much more slowly. Their output is either a voltage or a current and these also need pre-amplifiers to operate.

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

No substitutes exist that have all of the essential properties that are required by the end uses of PbS or PbSe detectors and so poor reliability is not the reason why this exemption is justified.

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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 sensors have been developed that are sensitive in the near infrared range, but as described in section 6, all have different responsivity and other characteristics compared with the lead-based photoconductor sensors and so they cannot be used as drop-in replacements. Manufacturers of electrical equipment that use PbS or PbSe sensors are evaluating whether substitution is possible. For example:

Spark detectors

Alternative types have been considered but all were found to be unsuitable. Cooling of semiconductor spark detectors is impractical as condensation will prevent them working, so most types of semiconductor detectors cannot be used. Also, they must operate very rapidly as explained in section 4, and therefore heat detectors (pyroelectric, bolometer and thermopile) cannot be used as they are too slow. InGaAs can be used without cooling and is a fast detector but has disadvantages compared with PbS and PbSe.

- InGaAs does not operate in the sensitive range of PbSe so it cannot be used when infrared light detection of >2.6µm is needed.
- PbS is about 2.3 times more sensitive to infrared radiation than InGaAs and is sensitive over a wider wavelength range (than the more sensitive standard InGaAs with 1.7 µm cut-off).
- PbS detectors are available with larger surface areas than InGaAs which enables them to detect sparks at a larger range of angles so that sparks

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are detected in a much larger volume of the air that is moving past the detector.

Near infrared chemical analysers

As explained in section 6, manufacturers are carrying out research into alternative detector materials, but as explained, substitution with different semiconductor detectors is at present technically impractical

Mainstream capnography (CO_2 measurement) for medical applications

This CO_2 sensor technology uses a pair (i.e. two) of detectors with the following basic requirements: 1) Fast response time, 2) high signal-to-noise ratio (S/N) and 3) high sensitivity at around 4.3µm. These requirements are fulfilled in the design of the sensor by using lead selenide (PbSe) photoresistors of 2x2mm2 sensitive area. In recent years, manufacturers of capnographs have been searching for alternative detector materials, but without success for the reasons explained in section 6. The graph below shows a comparison of the relevant figure of merit which is the specific detectivity D* of PbSe and other detector types. It can clearly be seen that PbSe is technically superior to all known alternative materials, so substitution of PbSe with another material yielding the same performance has not been possible. The detectivity of PbSe at 4.3µm is about 10 time better than the next best material, InAsSb. The performance of InAsSb can be improved by cooling the detector but this causes condensation to form from patient's breath and which interferes with the transmission of IR light resulting in poor accuracy.

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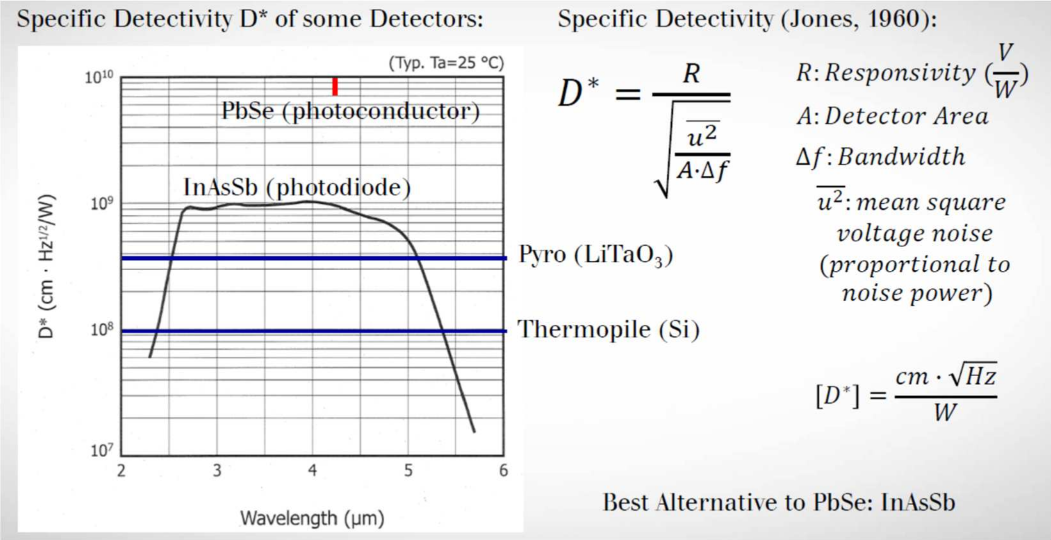

Figure 3: Specific detectivity around 4µm at room temperature for several CO_2 detectors.

Optics analysers

Although there are alternative types of infrared detector that function in the same wavelength range as PbS (see Table 1), research has shown that the performance of potential substitutes (sensitivity, detectivity, etc.) is insufficient for use in optics analysers (pyroelectric types were found to be up to 1000 times less sensitive) and so no suitable alternatives have been identified.

Substitutes for microwave-heated pressure digestion

Manufacturers have considered alternative methods of temperature measurement inside these vessels. Inserting a sensor inside the dissolution solution is impractical as many of the solutions used will chemically dissolve the sensor. Light guides (to conduct infrared radiation to an external sensor) made of glass or polymer will be attacked and so are also unsuitable. Inert metals (such as platinum resistance thermometers) are unsuitable as these are very rapidly heated by microwave radiation and any electrically conductive detector may similarly be heated. The only option is an external infrared detector[12]. Vessels are made of PTFE or quartz, both of which are transparent to infrared radiation of wavelengths that can be used to measure temperatures of 50°C to 300°C. However heat detectors such as pyroelectric, thermopile and bolometer sensors are not wavelength-selective and so cannot be used to measure temperature. These also respond more slowly and are less sensitive than lead sulphide detectors and so would not switch off microwave power when the required temperature is reached or the bursting disc

[12] German patent no. 4412887, "Device for in-situ temperature measurement of a sample in a pressure vessel". Berghof Labor und Automationstechnick GmbH, 29 October 1998

actuates.

Other infrared detectors

Equipment manufacturers are able to use only commercially available infrared detectors. Research has been published on semiconductor detectors other than those discussed in section 6. Although these are not commercially available, they are also not suitable due to their being responsive in different wavelength ranges than PbS and PbSe. Research into the following lead-free infrared detectors is being carried out:

- Tin sulphide: This operates in the near infrared but has a peak sensitivity of 850nm which is much lower than PbS or PbSe, so is not suitable as a replacement.
- Tin telluride: This is sensitive only in the far infrared range (ca. 15µm and higher) so cannot be considered as a substitute.
- Bismuth telluride: This is sensitive in the medium infrared range being responsive mainly at above 6 µm and so also cannot be considered as a substitute.
- Copper antimony sulphide: This is sensitive at up to 800nm only[13].

Research into new infrared detectors is continuing, but only those materials listed in Table 1 are commercially available. New materials other than those in Table 1 that are currently being researched are not suitable as substitutes because they all operate in different wavelength ranges to PbS and PbSe.

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

Research into infrared detectors has been carried out for many decades with many types being developed including those described in section 6. All potentially suitable commercially available semiconductors have been tested, but none meet all of the essential requirements that PbS and PbSe provide, as described in section 6. Also, electrical equipment manufacturers are aware of the temporary nature of exemptions and try to avoid PbS and PbSe in new designs, but where these are still used in the applications described in this renewal request, redesign has not been possible. For all existing uses of PbS and PbSe, no substitutes are foreseeable at present. Therefore the maximum validity of a renewed exemption is requested with start dates as listed in

13 https://pubs.rsc.org/en/content/articlepdf/2018/ra/c8ra05662e

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section 2 and to expire 7 years later. Research will continue by looking for new materials, as discussed above in 7(A) and also into the possibility of alternative designs, but it is not envisaged that substitutes will be developed before the requested expiry dates and most likely this will take considerably longer. As fast response and high detectivity are both essential, only semiconductor detectors are suitable. There are a limited number of elements in the periodic table and only some combinations of these elements are semiconductors that are sensitive in the infrared range. Most, if not all combinations of elements have been considered, but this has shown that none can replace lead in PbS or PbSe where these are currently used and so the timeframe for substitution is likely to be very long and replacement may never be possible.

---

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 sulphide is registered as an intermediate: https://echa.europa.eu/registration-dossier/-/registered-dossier/11485

Lead selenide is registered as an intermediate https://echa.europa.eu/registration-dossier/-/registered-dossier/11183

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: No alternative materials or designs exist that meet all essential performance criteria

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

☐ Yes.

☐ Design changes:

☐ Other materials:

☐ Other substance:

☒ No.

Justification: No alternative materials or designs exist that meet all essential performance criteria

3. Give details on the reliability of substitutes (technical data + information): None exist so not applicable
4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
   1) Environmental impacts: No substitutes exist
   2) Health impacts: No substitutes exist
   3) Consumer safety impacts: No substitutes exist. Consumer safety may be at risk if these types of detector could not be used in the EU, as fires that would have been prevented by spark detectors and rail derailments could increase and consumer safety may be negatively affected by inferior chemical analysis and less accurate medical capnography

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

Please provide third-party verified assessment on this: _____

(C) Availability of substitutes:

a) Describe supply sources for substitutes: Many types of infrared detectors are available, but all have different characteristics

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 Prices of other types of infrared detector are similar to PbS and PbSe.

d) What conditions need to be fulfilled to ensure the availability? New substitute semiconductor detector with suitable properties needs to be discovered.

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(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 There will be a negative socio-economic impact if this exemption is not renewed. Many different industry sectors would be affected and a few examples are described here.

- Spark detectors: Fires in factories can cause damage to the infrastructure, deaths and injuries as well as emitting harmful fumes. Any measures to reduce the risk of fires is therefore beneficial. Some data exists for factory fires in a few EU Member States[14], but the number that are prevented by spark detectors is not known, although this could be a significant number.
- Capnography: Many thousands of hospital patients require their breathing to be carefully and accurately monitored. This is to ensure that they are breathing correctly as well as to diagnose medical conditions. If the capnograph is too slow to respond or insufficiently sensitive, medical conditions may not be diagnosed and patients may deteriorate or even die if changes to their breathing are not detected. Most critically ill patients require that their breathing is monitored by capnography and many of these may not survive without this equipment. One study reports that 64,000 patients per year are ventilated in critical care units in the UK alone[15]. It is also essential for anaesthetised patients (3 million per year in the UK) whose chances of survival would be reduced without capnography. EUROSTAT data is also available for surgical operations in the EU[16], many of these require anaesthesia and capnography is used.
- Near infrared analysis: Factories, research laboratories, universities and colleges use near infrared analysers. If these were no longer available in the EU, the socio-economic impact would be:
    - EU researchers would be at a very significant disadvantage compared to their non-EU counterparts. EU statistics indicate that research and development

[14] Extensive and detailed data exists for the UK. For example, there were 1,842 accidental fires in industrial premises in the UK in the year 2017/2018 with 2 fatalities and 93 non-fatal casualties https://www.gov.uk/government/statistical-data-sets/fire-statistics-data-tables#non-dwelling-fires-attended

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

[16] https://ec.europa.eu/eurostat/statistics-explained/index.php/Surgical_operations_and_procedures_statistics

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accounts for over 2% of gross domestic product in the EU and employs 1.2% of the EU workers in 2016[17], equivalent to 2.7 million jobs[18].

  - Many factories rely on near infrared analysers to maintain quality. Without these, quality would negatively affected. Large quantities of food products may need to be disposed of if they subsequently are discovered to not meet quality standards. This would be unacceptable as the costs would make EU manufacturers uncompetitive compared with non-EU manufacturers and as a result, there could be significant job losses.

- Optical components: There are many optical component manufacturers located in the EU, many of which are SMEs. Those that coat optical components would not be able to operate in the EU if this exemption were not renewed because they could not buy new analysers. About 5,000 companies operate in the photonics sector in the EU employing 300,000 people[19].

☐ 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:

_____

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[17] GDP = Gross Domestic, data from Product from https://ec.europa.eu/eurostat/statistics-explained/index.php/Europe_2020_indicators_-_R%26D_and_innovation

[18] EU employment is estimated to be 228.7 million employees. https://www.statista.com/topics/4095/employment-in-europe/

[19] https://www.photondelta.eu/news/news/promising-european-photonics-results-are-in/

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