Exemption Renewal Form - Exemption 1 Annex IV

Date of submission: **02 January 2020**

Attached documentation:

- **COCIR - Confidential quantity calculation exemption 1 Annex IV**

1. Name and contact details

1) Name and contact details of applicant

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Function:	EHS Policy Senior Manager	Address:	Blvd A. Reyers 80, 1030 Bruxelles

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: **1 of Annex IV**

Proposed or existing wording: **Cadmium and lead in detectors for ionising radiation**

Duration where applicable: **Maximum validity period**

☐ Other: _____

3. Summary of the exemption request / revocation request

This renewal request includes uses of two of the RoHS substances in two different types of detector. One type contains cadmium and the other contains lead.

Cadmium

Cadmium telluride and cadmium zinc telluride are used in semiconductor flat panel detectors for imaging using ionising radiation. They are used for X-ray imaging as well as γ-radiation imaging with PET and SPECT. They have the advantage of giving superior image quality with lower radiation doses. These materials are superior overall to all other detector materials and so this exemption needs to be renewed to allow their use to continue.

These detectors are also used in category 9 applications because of their superior image quality and so this exemption also needs to be renewed for non-industrial monitoring and control instruments. The health advantage to patients from the use of CT and CZT in reducing the radiation dose to the patients is likely to be much more important than the very small potential of cadmium contamination at end of life.

Lead

Lead is used in ionisation chambers that are used to regulate the quantity of X-radiation that patients are exposed in EU hospitals and clinics. These chambers have been specifically designed to be used in most types of X-ray system sold in the EU and research has shown that all alternative materials and designs are either inferior or unsuitable. Alternative materials can only be used if the entire X-ray system is completely redesigned and this will take many decades before all existing systems can be replaced.

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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: Category 8 applications include: medical imaging including X-ray systems, Computed Tomography (CT), Photon counting CT, Bone densitometry (DEXA method), X-ray radiography, Mammography, Angiography, Gamma camera, Gamma probe, Colorectal cancer screening,

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Capsule X-ray camera, Dental panorama, Dental CT, Cephalometric radiography. Also SPECT and PET.

Category 9 applications would be relevant, although cadmium telluride and cadmium zinc telluride are likely to be used only in industrial monitoring and control instruments (see section 4 (A)1b below).

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: Industrial monitoring and control instruments such as non-destructive testing devices, non-destructive testing via CT, weld inspection, food inspection, level checker (drink bottles), Flat Panel Detector for X-ray Diffraction Analysis, X-ray Fluorescent Analysis, X-ray Fluorescent (lead paint analysers), Gamma camera (radioactivity detector), Gamma-ray spectrometer, Baggage Scanner, Explosive Detection System using X-ray diffraction and veterinary imaging (not in scope of the Medical devices Regulation) such as small animal CT.

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/products?

(Indicate more than one where applicable)

☒ Pb ☒ Cd ☐ Hg ☐ Cr-VI ☐ PBB ☐ PBDE

3. Function of the substances:

a) Cadmium is used in types of semiconductor materials such as cadmium telluride and cadmium zinc telluride that are used to detect X-rays in digital imaging detectors.

b) Lead is used in ionisation chambers.

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

46.7% cadmium in CdTe semiconductor

43% cadmium in nominally $Cd_{0.9}Zn_{0.1}Te$ semiconductor.

Lead metal (99.9%) in ionisation chamber coatings.

5. Amount of substance entering the EU market annually through application for which the exemption is requested:
   - 600kg Cadmium per year
   - 1.6kg Lead per year

   Please supply information and calculations to support stated figure.

Quantity of **cadmium** is from study carried out for the European Commission on the possible inclusion of categories 8 and 9 in scope of RoHS in 2006[1] and assumes that the amount of 300kg has doubled since 2006.

Quantity calculation of **lead** estimated by a manufacturer of ionisation chambers is confidential and so is provided separately:

6. Name of material/component:
   - Cadmium telluride (CdTe) and cadmium zinc telluride ($Cd_{0.9}Zn_{0.1}Te$) semiconducting detectors for ionising radiation.
   - Lead metal coatings in ionisation chambers

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?

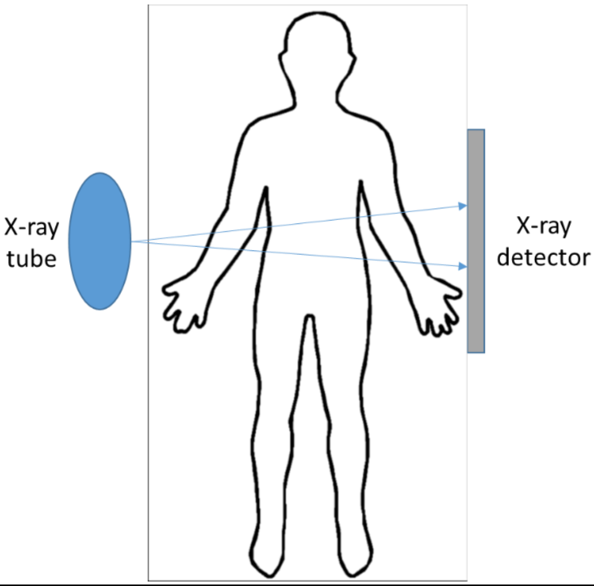
CdTe and CdZnTe detectors.

Digital flat panel X-ray detectors are used for X-ray imaging as well as for some types of monitoring and control instruments. COCIR believes that most category 9 applications are within the scope of "industrial monitoring and control instruments" and so have been excluded from this exemption renewal request. COCIR believes however that there may be some types of equipment that may be regarded as monitoring and control instruments, but which are not industrial monitoring and control instruments, however this is unclear and there is no official guidance available to clarify scope. This exemption renewal request is intended to include

[1] http://ec.europa.eu/environment/waste/weee/pdf/era_study_final_report.pdf

any types of monitoring and control instruments that used these detectors which are in category 9 and this exemption expires 21 July 2021 (unless renewed). Some example category 9 uses are in Flat Panel Detector for X-ray Diffraction Analysis, X-ray Fluorescence Analysis and X-ray Fluorescence analysers used for lead paint detection. These types of equipment are sold to businesses or Universities, but they may be used by students at Universities and the paint analyser is used in domestic dwellings, but by professionals. If these types of uses are regarded by the European Commission as industrial monitoring and control instruments, then this exemption need only be renewed at this time for category 8. However, if any of these types of equipment may be monitoring and control instruments that are not industrial, then it needs to also be renewed for category 9. The technical reasons for this exemption are explained below and are the same for both categories 8 and 9, which is that image quality is superior and can be obtained with less ionising radiation exposure.

Diagnosis of conditions of patients is carried out using several medical imaging techniques that rely on ionising radiation. The simplest is X-ray imaging where an X-ray tube is located on one side of the patient and which passes X-radiation through the parts of the patient to be imaged and the radiation that emerges from the patient is detected using a digital X-ray detector to create the image.



Other medical imaging techniques are Positron Emission Tomography (PET) and Single-photon emission computed tomography (SPECT) which are used to image internal organs in the body using radioisotopes. The radioisotopes are injected or ingested then are concentrated within the target organs to allow them to be imaged. The radioisotopes emit γ-radiation which is imaged using a digital detector[2]. PET is used to generate three dimensional (3D) images, similarly to Computed

[2] α-emitters are not suitable as they are absorbed within the patient and can be very harmful. β-emitters may be used but are detected with types of scintillators that are specifically suitable to β-radiation.

Tomography (CT) scanners and is used to diagnose cancer, for imaging brain activity, cardiology etc. SPECT is similar to PET using similar γ-radiation detectors but gives better 3D images.

Medical digital detectors, such as cadmium telluride, consist of arrays of discrete semiconductor elements much like the detector of a digital camera where the surface layer consists of an array of these elements. Each element is equivalent to one pixel of the final image and when an X-ray or γ-ray strikes the semiconductor element, several things can happen, but the desired outcome is that an electrical signal is generated that is used to construct the digital image. When an X-ray or γ-ray photon strikes a detector element, the following could happen:

1. It is absorbed and generates a signal. This is the desired outcome
2. It is not absorbed and passes through the detector unaffected
3. It is scattered so that its direction of travel is changed. This is undesirable as it may then be detected by a different element resulting in distortion of the image

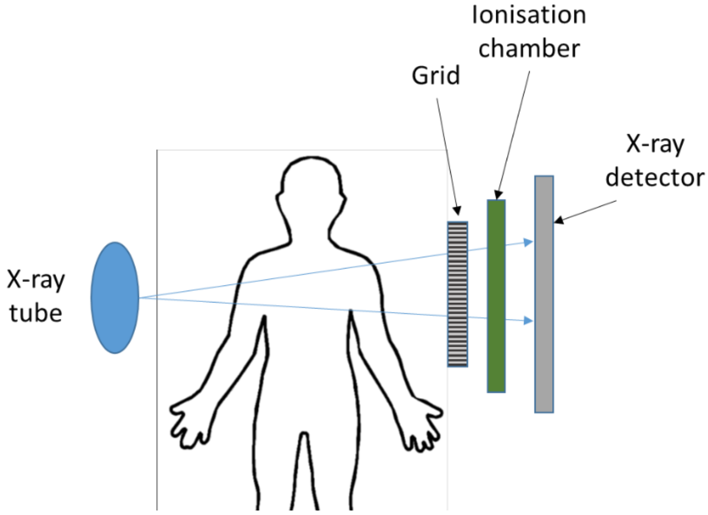
The proportion of incident radiation that is absorbed and generates a signal and not scattered or passing through affects the sensitivity of the detector and the quality of the image. However other variables also affects image quality. Semiconductor detectors are prone to generation of noise which is random signals from detector elements unrelated to the incident X-ray or γ-ray photons. The intensity of this noise depends on the type of detector material and its temperature. Noise intensity can be reduced by decreasing the temperature of the semiconductor. Some types of semiconductor detector must be cooled to reduce the noise to a level such that image quality is acceptable, however cadmium zinc telluride and cadmium telluride can be used at room temperature with an acceptable signal to noise ratio. This avoids the need for additional, energy consuming cooling equipment.

High detection rates for X-ray or γ-ray photons and conversion efficiency to an electrical signal are very significant advantages for diagnosis of illness as it allows a reduction in X-ray dose or the amount of radio-isotope given to the patient so reducing the risk to the health of patients and workers from the ionising radiation. Also, a high detection efficiency results in the ability to use thinner detectors which exhibit much less scattering and so give much clearer images which can aid early diagnosis.

Reducing X-ray doses as much as possible decreases the risk posed by ionising radiation which is known to damage cells and this can cause cancer. Image quality is very important as it is essential to detect very small features to be able to diagnose some types of illness, such as small tumours, as early as possible for an improved health outcome.

Lead coatings in ionisation chambers

Ionisation chambers measure the quantity of X-radiation for automatic exposure control to ensure that the correct radiation dose is used to obtain a clear image. These are used in most X-ray imaging systems to compensate for the thickness and density of the parts of the patient being examined. Less X-rays are needed to image a hand than a head and also, obese patients may need a higher dose than thin patients. The ionisation chambers are located between the grid (these help to collimate the X-rays) and the front of the detector, see diagram below. The ionisation chamber is transparent to the X-rays and so gives no image on the detector.



Ionisation chambers contain an anode and cathode and X-rays cause secondary electrons to be emitted from the negative (lead coated) electrode into the chamber and these form electrically charged ions that cause a current to pass between anode and cathode and the measurement electronics. The chamber's monitoring circuit include a capacitor that is charged at a rate which is determined by the quantity of ionisation in the chamber from the X-radiation. When it is charged to a certain voltage, it initiates current flow that actuates a contactor which shuts down the X-ray tube and stops X-ray exposure. Using the correct amount of X-radiation is important to obtain a clear image and minimise exposure of patients to potentially harmful ionising radiation. The quantity of radiation not only depends on the part of the patient and the size of the patient being imaged, but also the X-ray tube voltage and current and also the age of the X-ray tube as this can effect output intensity. It is therefore very difficult for a radiologist to estimate the X-ray exposure time and so automatic control is usually used. Automatic exposure control can reduce the radiation dose by 20%.

X-ray ionisation chambers are made of plastics which are transparent to X-rays and have printed graphite patterns as the positive and negative electrodes (graphite is also transparent to X-rays). The negative electrode is then coated using physical vapour deposition (PVD) with a 3µm thick coating of lead (effectively transparent to X-rays at this thickness). The voltage between the electrodes is several hundred volts. Manufacturers find that alternatives to lead give very different output signals and also the thickness of the metal coating must be carefully controlled as this also affects the output signal.

The ionisation chambers are used with all types of X-ray image detector including digital flat panel detectors as well as photographic film. The ionisation chamber was originally developed for photographic film which is a very variable medium and so required a complex calibration process which uses “look-up tables” with 13 calibration curves. The original design can be used for all types of detector due to their accuracy and flexibility. The ionisation chamber controls X-ray dose over a wide range of x-ray dose. For example, one manufacturer’s design uses 31 exposure points and a change of ±3 points in this range either halves or doubles the quantity of X-rays.

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

Digital detectors

All of the following are required for a digital detector

- High absorption efficiency for ionising radiation
- High conversion efficiency from radiation to electrical signals
- Ability to generate very clear images with very fine detail from safe low levels of radiation
- High signal to noise ratio at ambient temperature
- Must be usable at room temperature and so not require cooling.

Some example requirements for detectors depend on the medical application as follows[3]:

Size of detector panel:

Radiology	minimum 43 x 43 cm
Angiography	minimum 30 x 40 cm
Computed Tomography (CT)	Minimum 4 x 70 cm and these are curved

Frame rate (images per second):

Computed Tomography (CT)	2000 to 6000 s^{-1}
Fluoroscopy and cardiology	15 – 60 s^{-1}
Radiology	0.05 to 2 s^{-1}

Spatial Resolution (pixel size):

Computed Tomography (CT)	1mm^{-1} (1mm)
Soft tissue	1 – 2 mm^{-1} (400 - 150µm)
Bones	3 – 4 mm^{-1} (165 - 125µm)
Mammography	5 – 20 mm^{-1} (100 - 25µm)

The detector's sensitivity also has to be compatible with the radiation energy. For example, mammography utilises lower energy X-radiation energy (17 to 25 keV) than angiography (33keV to match the k-edge energy of iodine that is used as a contrast agent) and CT (60- 140 keV), PET or SPECT may use a variety of energies depending on the isotope that is used. The isotope is chosen that is optimal for imaging the specific organ of interest.

[3] http://www.esrf.eu/files/live/sites/www/files/events/conferences/2005/IWORID7/FinalProgramme/hoheisel_1.pdf

Ionisation chambers

Ionisation chambers are designed to be compatible with current designs of X-ray imaging equipment and so any substitutes must also be compatible and respond in an identical manner to achieve optimal image quality and minimise radiation doses for patients.

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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.)

Yes. Medical equipment manufacturers make great effort to collect used equipment that they can refurbish, especially high value equipment such as CT, PET and SPECT. Parts such as radiation detectors remain within a "closed-loop" and can be refurbished for reuse. In addition the materials of old detectors that cannot be reused are intended to be recycled in order to produce new detectors.

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 480kg cadmium and 1.3kg lead (assumes 80% of detectors can be reused)

☐ In articles which are recycled 120 kg cadmium and 0.3kg lead

☐ 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

Radiation detectors

The first X-ray imaging detectors where scintillator screens for real-time imaging and photographic film for recording images. Sensitivity of the detection systems was greatly improved to allow much lower and safer radiation doses to be used by the use of image intensifiers which magnified the weak radiation energy that pass through patients. Modern hospitals increasingly rely on digital records of images and so different techniques are used although the optimum detector depends on several variables. However, most new detectors are various types of very sensitive flat panel detectors that provide a digital image. These detectors are described here and some of the types that have been used with medical devices include:

- Amorphous silicon (a-Si) plat panel detectors – with scintillator material coatings
- Amorphous selenium flat panel detectors – used for mammography
- Evaporated layer of caesium iodide scintillator deposited on an amorphous silicon photodiode detector array
- Deposited layer of Gd_2O_2S (GSO) scintillator deposited onto a crystalline silicon photodiode – has been used for CT
- Scintillators with photomultiplier tubes – used for PET and SPECT
- Cadmium telluride and cadmium zinc telluride (CZT) flat panel semiconductor digital detector

Research into the use of GaAs, HgI_2, InSb, TlBr, PbI and other semiconductors has been carried out and may give superior performance under some circumstances, but are not currently used commercially in medical imaging equipment.

All of the detectors used have advantages and disadvantages and so the type of detector that is most suitable depends on the type of imaging technique that is used and the type of diagnosis required. However cadmium telluride and CZT semiconductor detectors are relatively new and because of their advantages of lower radiation doses and superior image quality, research is being carried out to use these in more types of medical imaging equipment.

The above list of detector types can be divided into two types:

- Scintillator materials, usually deposited onto silicon arrays
- Semiconductor detectors

Scintillators

Large-size silicon semiconductor arrays are easy to make but silicon has a relatively low atomic number and so is a very poor X-ray detector as most X-rays pass through with no interaction (unless the silicon is very thick which causes unacceptable levels of scattering). This is especially a problem at higher energies, for example, with 60keV photon energy, a 5mm thickness of silicon adorbs only 10% of the energy whereas the same thickness of CZT absorbs 100%[4]. This limitation of silicon can be resolved by using scintillator materials as ionising radiation detectors which convert the radiation into visible light for which silicon is a high efficiency detector (silicon detectors are used in modern digital photography cameras). The scintillator materials that are used have relatively high atomic number and density and so are efficient absorbers of ionising radiation. Once a high energy X-ray or γ-ray photon is absorbed, the scintillator then generates a photoelectron which can then be converted into optical light. This light however can be emitted in any direction, not only in the direction of travel of the original photon. This has several negative effects:

- Loss of efficiency as the X-ray or γ-ray photon is converted into light that is not detected by the silicon array
- The emitted light can travel to neighbouring pixels where it is detected giving a blurred image.

The scintillator thickness must be sufficient to interact with a significant proportion of the ionising radiation that is to be detected. However, increasing the detection efficiency using thicker layers of scintillator also increases the amount of light scattering to neighbouring pixels, which gives inferior image resolution. Therefore, a compromise is usually needed which limits both sensitivity and resolution.

One publication has measured the detection efficiency of 140keV γ-rays comparing CZT with various scintillator materials and at a range of thickness. 2mm thickness material absorbs the γ-radiation with the following efficiency values[5]:

[4] Development of High-Z Semiconductor Detectors and Their Applications to X-ray/gamma-ray Astronomy, T. Tanaka, SLAC Advanced Instrumentation Seminar, 2007

[5] Cadmium Telluride Semiconductor Detector for Improved Spatial and Energy Resolution Radioisotopic Imaging, S. Abbaspour, et al. Word J Nuclear Medicine 15(2) 2017, 101 – 107. Downloaded from https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5436314/

Table 1. Detection efficiency of commonly used types of detectors

Material	Detection Efficiency %
Silicon	~5%
Sodium iodide scintillator	~40%
Cadmium telluride and cadmium zinc telluride	~60%

Scintillators can have other disadvantages over cadmium telluride and cadmium zinc telluride. Many are water soluble salts, such as sodium iodide and caesium iodide and these can be hygroscopic. This cause distortion and disintegration if any moisture reaches the scintillator material. Temperature changes can result is stresses (due to the thermal expansion mismatch between silicon and the scintillator material) that cause cracks in scintillator crystals and the cracks disrupt the emitted light-path.

Visible light is generated by the scintillator material very rapidly by fluorescence ($<10^{-8}$ seconds) which is useful for fast scanning (important for CT, angiography, etc.), but phosphorescence can also occur which gives an “afterglow” or delayed light emission, which blurs images if patients are not perfectly motionless. Inorganic scintillator materials performance is also temperature dependent, which can affect image quality. Light output decay times vary between types of scintillator as well as light output intensity. Decay times should be as short as possible whereas light intensity needs to be as large as possible.

The intensity of light emitted is dependent on the choice of scintillator material. If sodium iodide is 100 units, then Gadolinium orthosilicate (GSO) is only 16 units, although GSO has a faster light decay time at ~60 ns compared to 230 ns for sodium iodide.

Pure sodium iodide is unsuitable and has to be doped with small amounts of thallium to be an effective scintillator material for X-rays and γ-rays, however thallium is very toxic so could pose a health risk to recyclers if not treated correctly.

Another scintillator material that is used is bismuth germanate (BGO) which has a slightly longer scintillation decay time (300 ns) compared to NaI(Tl) (230 ns) and its light output is relatively small causing poor energy resolution. It has however been used in PET applications.

Another limitation of scintillators is that their detection threshold is higher than semiconductor detectors that use CMOS circuitry. Published comparative data[6] including that for photographic film which has largely been phased out are given in the table below.

[6] Energy-resolved X-ray detectors: the future of diagnostic imaging, Danilo Pacella, Reports in Medical Imaging, Dove Press 2015

Table 2. Detection limits of common types of X-ray detection media

Detector	Detection limit, photons / mm^2.
Photographic film	10^6
Flat panel detector with scintillator	10^4
CMOS CdTe semiconductor detector	1

As CdTe (and CZT) semiconductor detectors can detect single photons, they can be used as counting detectors which are far more sensitive (as they can detect one photon) and give superior image quality (because they count numbers of photons to each pixel) than scintillators.

Despite their limitations, flat panel silicon detectors with scintillator coatings are widely used as they are suitable for many medical applications and are easier (and so cheaper) to manufacture than CdTe and CZT detectors of similar size. They are however gradually being replaced by superior performance CdTe and CZT detectors. An exemption to allow the use of cadmium in radiation detectors is required to allow the use of CdTe and CZT detectors in suitable medical equipment to improve image quality and reduce radiation exposure by patients.

Semiconductor detectors

Many types of semiconductor material have been evaluated as radiation detectors. These include silicon, selenium, germanium, mercury iodide, lead iodide, Gallium arsenide, CdTe and CZT.

The optimal sensitivity to ionising radiation depends on several variables including the energy of the radiation. This is because elements have greatly increased sensitivity at energy levels that are higher than the energy of their k-electrons, referred to as the k-edge which is the binding energy of the K shell electrons of an atom. This appears in plots of sensitivity versus radiation energy as a sharp increase in sensitivity at energy levels that coincide with k-edge energies and so selenium has one increase in sensitivity at just above 12.7keV whereas cadmium telluride has two increases corresponding to the k-edge vales of the two elements and these occur at 26.7keV (Cd) and 31.8keV (Te)[5]. Both selenium and cadmium telluride have far superior sensitivity than silicon (of equal thickness), but the sensitivity of selenium is superior to cadmium telluride between 12.7 (the Se k-edge energy) and 26.7 keV (the Cd k-edge energy) and so selenium is slightly more sensitive to x-radiation in this energy range than CdTe, although its other properties may be inferior. As mammography uses energies of 17 to 25 keV, based on sensitivity alone, selenium or even GaAs would be the preferred choice. However all other X-ray imaging, CT, PET and SPECT imaging utilise radiation of higher energies and so cadmium telluride is the most sensitive detector.

Sensitivity is only one criteria that is important when selecting the optimum type of detector and the following variables are also important:

- Band gap (eV) – Dark currents (current generated with no incident radiation) is lower with materials having larger band-gap values

- Effective Charge Pair Formation Energy (eV) – Lower values increase gain of the detector
- Mobility Life-time Product (cm^2/V) – higher values increase charge collection which improves sensitivity
- Atomic number – materials with high atomic number are superior at interaction with ionising radiation

These criteria are compared below for some of the more widely studied X-ray and γ-ray detector semiconductor materials.

Table 3. Comparison of properties of semiconductor materials

Semiconductor	Band gap	Effective Charge Pair Formation Energy (eV	Mobility Life-time Product (cm^2/V)	Atomic number
Cadmium telluride (CT) and cadmium zinc telluride (CZT)	1.5 to 2.2	4.5	>10^{-3} to 10^{-5}	48, 30, 52
Mercury iodide (HgI_2)	2.1	~4.2	1.5 x 10^{-5}	80, 53
Lead iodide (PbI_2)	2.3	5 – 5.5	(h) 7 x 10^{-8} [(7)]	82, 53
Selenium (Se)	2.2	5,4	(h) 0,02	34
Germanium (Ge)	0.67	3.0	(e-) 3.9	32
Gallium arsenide (GaAs)	1.43	4.2	(h) 8 x 10^{-5}	31, 33
Silicon (Si)	1.1	3.6	(e-) 1.4	14

Silicon, selenium and germanium are inferior materials mainly because of their lower atomic number and so low absorption. Cadmium telluride and cadmium zinc telluride (CZT) have higher atomic numbers than gallium arsenide and so gives superior absorption performance. Some materials can only be used when cooled, e.g. germanium which must be cooled with liquid nitrogen, which is impractical in hospitals but cadmium telluride and cadmium zinc telluride are used without cooling.

Research has been published on detectors using cadmium telluride and cadmium zinc telluride (CZT), mercury iodide and lead iodide, but only CdTe and CZT have been used in commercial

[7] This value varies, depending on the literature source, but is roughly $1x10^{-8}$

medical devices, although imaging with mercury iodide and lead iodide detectors has been demonstrated[8]. A list of peer reviewed publications that explain why CdTe and CdZnTe are superior are given in the Annex at the end of this exemption renewal request.

Comprehensive research by a medical equipment manufacturer has evaluated alternative semiconductors for CT detectors. This work assessed 23 materials by assessing variables such as their absorption performance, count rate, diffusion radius (affects spatial resolution) and charge carrier loss (likelihood that an X-ray results in a charge reaching the pixelated electrode). Elements with k-edge of 80 – 90keV were reported to be less suitable for CT as this is close to the X-ray energy used for CT, which makes mercury compounds (83.1 keV) and lead compounds (88.0 keV) less suitable.

This assessment resulted in three materials that are potentially suitable; CdTe, Lead sulphide and germanium, however of these, lead sulphide and germanium must be cooled to low temperature which requires additional, quite bulky, cryocooling equipment or the use of liquid nitrogen. Liquid nitrogen cooling is not technically practical for a CT detector as the detector rotates around the patient. Also, of the 23 semiconductors assessed, only a few material, including CdTe are commercially available of suitable thickness and size.

Lead in ionisation chambers

As explained in section 4B, the response of ionisation chambers to X-radiation depends on the metal coating thickness and the type of metal. This is because the ionisation chamber functions by emitting secondary electrons from the metal coating and the energy and number of these electrons depend on both variables. Light elements (such as graphite) generate very weak signals (graphite emits only 2% of the emission from lead of similar thickness) and the signal is too small to give accurate control.

As each element emits secondary electrons with different energies, there is no possible drop-in replacement for lead as every alternative element will generate a different signal. As the ionisation chamber design, control circuits and especially the calibration curves were developed with lead, it is not possible to use a different metal coating and achieve the same automatic exposure control; patients' images will be over or under-exposed if a different metal were used.

One manufacturer has designed an ionisation chamber using tin to replace lead, but the behaviour of this chamber is very different to those with lead and so cannot be used with types of X-ray imaging equipment that was designed to work with lead-based ionisation chambers. The manufacturer has also found that the output of the tin-based chamber can drift outside of the calibration range of the calibration curves developed for lead based ionisation chambers and so is not able to control exposure. The tin coated ionisation chamber can however be used with a very few newly designed X-ray imaging products which were designed to be compatible with the tin coated ionisation chamber.

Ionisation chambers have mostly replaced the previously used method of automatic exposure

[8] Cannot be regarded as substitutes as these also contain RoHS substances

control using phototimers. Phototimers use scintillator panels that convert X-rays into light and then the light output is measured with photomultipliers or photodiodes. As most X-rays should be absorbed to be measured, these are positioned after the X-radiation has passed through the patient. This has disadvantages that have resulted in the change to ionisation chambers, as summarised below:

Table 4. Comparison of ionisation chambers with phototimers

Characteristic	Ionisation chamber	Phototimer
Position	Between X-ray source and patient,	After X-rays emerge from patient.
Effect on X-ray beam	Does not block X-rays so no scattering or image generated	Must absorb radiation to measure dose. Scattering does occur which requires lead shielding and can affect image quality
Behaviour with implants	No effect as energy from X-ray tube is measured before reaching patient	Can block X-radiation so that patient receives a dangerously high dose and image is over-exposed
Shielding	Not needed	Lead shielding required

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

Flat panel detectors

The possible substitutes described above in section 6A are not unreliable, but require higher radiation doses, which can be harmful to patients, and inferior image quality which may prevent early or accurate diagnosis.

Ionisation chambers

Alternatives to lead give different signals which prevent accurate automatic exposure control. This is not a reliability issue, but poor control can cause repeat X-ray imaging if the first image is over or under exposed and this exposes patients unnecessarily to extra harmful X-radiation.

Phototimers were used before being replaced by ionisation chambers. One reported reason was that they have inferior reliability due to their greater complexity[9].

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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.

Flat panel detectors

Significant research has been carried out to investigate alternative semiconductor materials as X-ray detectors as described above in section 6A with the aim increasing performances. All substitute semiconductors give inferior performance to cadmium-based detectors.

Ionisation chambers

Alternative metals to lead have been considered, but all give different output signals so that the ionisation chamber is incompatible with the X-ray imaging system. Chambers have been made with tin instead of lead as described above in section 6A, but these tin coated chambers can be used only with a very few new systems that have been designed to be compatible with tin-coated ionisation chambers.

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

Flat panel detectors

Manufacturers are searching for even better detector technologies than cadmium zinc telluride that give superior image quality and lower radiation doses. At present there are no known

[9] https://radiologykey.com/automatic-exposure-control

materials that are equal to or superior to CdTe or CdZnTe and COCIR cannot exclude that cadmium could be a key substance for future technologies bringing even more benefits to patients in the future. Recently, research into thallium bromide flat X-ray panel detectors was published, but these are not available commercially and so cannot be evaluated in medical devices. Moreover, thallium bromide is much more toxic than cadmium telluride[10].**Ionisation chambers**

It is impractical to use alternatives to lead in ionisation chambers that are used with most X-ray systems currently available on the EU market. Replacement of lead by tin may eventually be possible when new X-ray systems are designed and replace the current range. Designing a new X-ray system is extremely complex and typically takes over 10 years from design to construction of prototypes, testing, clinical trials and gaining Medical Device Regulation approval by a Notified body. Each manufacturer is able to develop one new system at a time (due to limitations on the availability of trained engineers) and each manufacturer will have many systems designed for different purposes as briefly summarised in section 4.

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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 – lead added June 2018

   ☒ Candidate list – lead added June 2018

   ☐ Proposal inclusion Annex XIV

   ☐ Annex XIV

   ☐ Restriction

   ☐ Annex XVII – although cadmium is listed, restrictions do not include semiconductor radiation detectors

   ☐ Registry of intentions

   ☒ Registration

   Cadmium telluride is registered (as it is used in photovoltaic panels) - https://echa.europa.eu/registration-dossier/-/registered-dossier/12227/3/1/6

   Lead is registered - see https://ila-reach.org/our-substances/lead-metal/

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

[10] LD50 (oral, rat) of thallium compounds are about 23mg/kg, whereas LD50 (oral mouse) of cadmium telluride is 2100/kg so the thallium compound is about 100 times more toxic.

(B) Elimination/substitution:

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

☐ Yes. Consequences? _____

☒ No. Justification: Substitutes give inferior or less accurate performance

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

☐ Yes.

☐ Design changes:

☐ Other materials:

☐ Other substance:

☒ No.

Justification: Substitutes give inferior or less accurate performance

3. Give details on the reliability of substitutes (technical data + information): Not applicable to this exemption
4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
    1) Environmental impacts: Not applicable to this exemption renewal request
    2) Health impacts: Substitutes could have negative health impacts as explained above in section 6A
    3) Consumer safety impacts: Not applicable to this exemption renewal request (apart from negative health 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: No

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? Not applicable

(D) Socio-economic impact of substitution:

⇨ What kind of economic effects do you consider related to substitution?

☐ Increase in direct production costs - Not applicable although cadmium zinc telluride is more expensive than substitute detectors

☐ Increase in fixed costs - Not applicable

☐ Increase in overhead - None

☒ Possible social impacts within the EU – There would be negative health impacts to EU citizens (as explained in section 6) if this exemption were not renewed. This is especially applicable for ionisation chambers as most X-ray imaging systems rely on these, but only a very few types can use tin-based chambers. All currently available types of system need to be available to provide the full range of healthcare currently available to EU citizens. EU citizens are typically X-rayed more than once per year on average and there is a concern that repeated high X-ray doses can increase the risk of cancer. The risk is highest with imaging techniques that require larger doses such as fluoroscopy and CT, which are used with about 50 – 100 people per 1000 inhabitants or about 25 million people per year[11]. The likelihood of these 25 million contracting cancer from X-ray exposure would be reduced if CZT detectors were used, although it is not possible to quantify the numbers of fewer cancers that would result.

☐ Possible social impacts external to the EU – None as cadmium and lead can continue to be used in equipment sold outside of 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:

Calculation method for the amount of lead in ionisation chamber placed on the EU market annually

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[11] https://ec.europa.eu/energy/sites/ener/files/documents/RP180web.pdf see figure 5.2.

Annex.

Peer reviewed publications are as follows;

- Most relevant papers are 1, 2, 5, 16, 17, 18
- Papers on high resolution: 2, 6, 7, 18
- Spectral information with more than two energies: 1,2,14, 15
- Better quantitative information: 3, 4, 5, 13, 16, 17
- Better Dose-Efficiency: 3, 5, 7, 8, 18

1 Pourmorteza A et al. Abdominal Imaging with Contrast-enhanced Photon-counting CT: First Human Experience. Radiology. 2016 Apr; 279(1):239-45.

2 Yu Z et al. Evaluation of conventional imaging performance in a research whole-body CT system with a photon-counting detector array. Phys Med Biol. 2016 Feb 21; 61(4):1572-95.

3 Gutjahr R et al. Human Imaging With Photon Counting-Based Computed Tomography at Clinical Dose Levels: Contrast-to-Noise Ratio and Cadaver Studies. Invest Radiol. 2016 Jul; 51(7):421-9.

4 Symons R et al. Low-dose lung cancer screening with photon-counting CT: a feasibility study. Phys Med Biol. 2017 Jan 7; 62(1):202-213.

5 Symons R et al. Feasibility of dose-reduced chest CT using photon-counting detectors: initial human results, Radiology

6 Leng S et al. A High-Resolution Imaging Technique using a Whole-body, Research Photon Counting Detector CT System. Proc SPIE Int Soc Opt Eng. 2016 Feb; 9783. pii: 97831I.

7 Leng S et al. Dose-efficient ultrahigh-resolution scan mode using a photon counting detector computed tomography system. J Med Imaging (Bellingham). 2016 Oct; 3(4):043504.

8 Yu Z et al. Noise performance of low-dose CT: comparison between an energy integrating detector and a photon counting detector using a whole-body research photon counting CT scanner. J Med Imaging (Bellingham). 2016 Oct; 3(4):043503.

9 Sandfort V et al. Optimized energy of spectral CT for infarct imaging: Experimental validation with human validation. J Cardiovasc Comput Tomogr. 2017 May - Jun; 11(3):171-178.

10 Harrison AP et al. Multi-Channel Block-Matching Denoising Algorithm for Spectral Photon-Counting CT Images. Med Phys. 2017 Mar 23.

11 Li Z et al. An effective noise reduction method for multi-energy CT images that exploit spatio-spectral features. Med Phys. 2017 May; 44(5):1610-1623. doi: 10.1002/mp.12174. Epub 2017 Apr 12.

12 Yu Z et al. Spectral prior image constrained compressed sensing (spectral PICCS) for photon-counting computed tomography. Phys Med Biol. 2016 Sep 21; 61(18):6707-6732. Epub 2016 Aug 23.

13 Zhou W et al. Lung Nodule Volume Quantification and Shape Differentiation with an Ultra-High Resolution Technique on a Photon Counting Detector CT System. Proc SPIE Int Soc Opt Eng. 2017 Feb 11; 10132.

14 Symons R et al. Dual-contrast agent photon-counting computed tomography of the heart: initial experience. Int J Cardiovasc Imaging. 2017 Mar 13.

15 Symons R et al. Photon-counting CT for simultaneous imaging of multiple contrast agents in the abdomen: an in vivo study. Med Phys. 2017 Apr 26.

16 Pourmorteza A et al. Photon-Counting CT for Vascular Imaging of the Head and Neck: First in Vivo Human Results, Invest Radiol. 2018 Mar; 53(3):135-142. doi: 10.1097/RLI.0000000000000418

17 Symons R et al. Photon-counting CT of the brain: first in-vivo human results, AJNR Am J Neuroradiol. 2017 Dec; 38(12):2257-2263. doi: 10.3174/ajnr.A5402

18 Pourmorteza A, Symons R, Henning A, Ulzheimer S, Bluemke DA.Dose Efficiency of Quarter-Millimeter Photon-Counting Computed Tomography: First-in-Human Results. Invest Radiol. 2018 Jun; 53(6):365-372. doi: 10.1097/RLI.0000000000000463.