Application for granting new Exemption: Lead in solders to PCBs for mounting cadmium telluride and cadmium zinc telluride digital array detectors

1. Name and address of applicant

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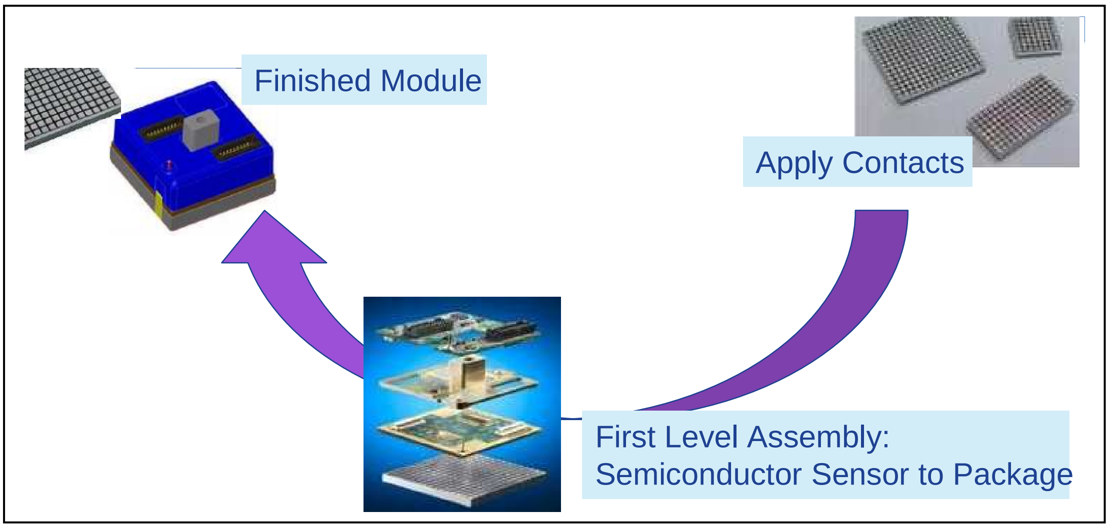
2. Summary of the application

Semiconductor array detectors are increasingly used for X-ray imaging. Cadmium telluride and cadmium zinc telluride (CZT) detectors are relatively new and are significantly more sensitive radiation detectors than silicon detectors and so allow patients to receive lower doses of radiation. This material is however very brittle and fragile and research has shown that poor yields are achieved when these detectors are soldered to substrate circuit boards using lead-free solders whereas high yields are obtained with more ductile lead-based solders. Due to the fragility of CZT, there are concerns that the long term reliability will be compromised if lead-free solders are used and so an exemption for lead in solders is being requested to allow manufacturers more time to develop high yield lead-free bonding processes and to ensure that long term reliability is at least as good as is currently achieved.

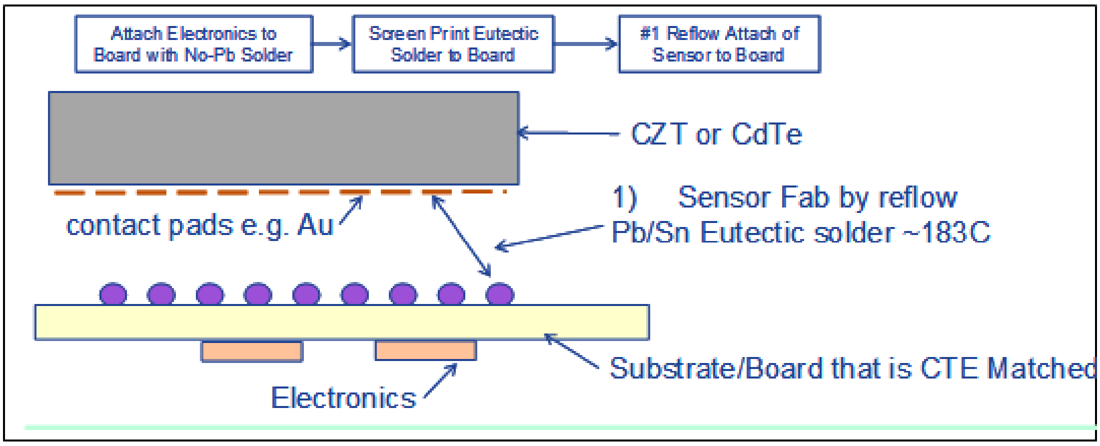
3. Description of materials and equipment for which the exemption is required

Cadmium zinc telluride (CZT) is a relatively new semiconductor used to produce high resolution digital images. Cadmium telluride (CdTe) is also a semiconductor candidate for the same applications and has similar mechanical and electrical properties as CZT. Hereafter, CZT is used to indicate Cadmium Zinc Telluride with different zinc concentrations including no-zinc commonly known as cadmium telluride. The CZT detectors are more compact that traditional detectors and provide higher spatial and energy resolution. The semiconductor detectors have fast speed and can provide photon counting capability to high flux rates.
These materials are used in nuclear medicine as the detector in positron emission tomography (PET) and also as the X-ray detector in Computed Tomography (CT). Dental and Bone-mineral densitometry medical exams are also carried out using a CZT detector. Single crystal wafers of CZT are fabricated into detectors by mounting onto printed circuit boards (PCBs) to make the many hundreds of electrical connections using eutectic tin/lead solder. One electrical connection is needed for each pixel of the image. CZT is a very fragile and brittle material which is easily damaged, particularly by stresses imposed by the assembly process. CZT detectors are relatively new and each manufacturer uses their own unique design. As these designs and the capabilities vary the method used to

assemble detectors also varies. The typical assembly process to apply metal contacts to the wafer and assemble the detector module is shown below:



Solder is used either as small solder balls or as reflowed solder paste to form the electrical connections between the CZT and the PCB substrate as below:



To avoid imposing stresses onto the CZT which could cause bond failure or damage to the detector, the PCB must be perfectly flat throughout the manufacturing process. Unfortunately the PCBs used for CZT assembly are complex multilayer boards with a high density of internal vias. Polymer PCB laminates tends to distort and warp when they are fabricated, especially complex boards of this type. Distortion occurs during reflow soldering when electrical components and the CZT detector wafer are bonded with solder to the PCB. It is a general rule for any type of laminate that the amount of distortion increases with temperature. Distortion of laminates will be greater on average during and sometimes also after lead-free reflow than during and after tin/lead reflow due to the 20 – 40°C temperature difference.

CZT detectors are used because of their very high sensitivity to X-ray and other ionising radiation (e.g. gamma ray) compared to other types of detectors such as image intensifiers with optical detectors and also silicon array X-ray detectors. CZT also has an advantage that it operates at room temperature whereas some types of silicon detectors must be cooled to low temperature and so consume far more energy to operate. The higher sensitivity of CZT allows patients to receive lower X-ray doses which results in a lower risk of harmful side-effects such as cancer. The semiconductor wafer must be mounted onto a PCB-type substrate in order to make the detector device in an imaging system; there is no other way of making the many hundreds of electrical connections.

4. Justification for exemption – Article 5 criteria

Criteria permitted to justify RoHS exemptions:

- "No technical substitutes" – Alternative solders give poor yields and long term reliability is uncertain which is unacceptable for obtaining approval for the Medical Devices Directive. Conducting adhesives will be unsuitable as they will degrade on exposure to ionising radiation. The PCB laminate must be TCE matched to CZT to avoid imposing stresses onto the fragile CZT wafer. This limits the choice of laminate materials significantly so that rigid ceramic PCBs (which will not distort during reflow) cannot be used as they cannot be TCE matched, nor can they be made with a sufficiently high interconnect density.
- "Substitutes have greater negative impact on health or the environment" – Alternative digital detectors are not equivalent and the best performing semiconductor X-ray detectors contain Cd or Hg. Silicon digital detectors require higher radiation doses to obtain an equivalent image quality and higher radiation doses increase the risk of cancer.
- "Reliability of substitutes" – This is uncertain with lead-free solders and is likely to be poor with conducting adhesives

The ERA report for the European Commission on whether inclusion of categories 8 and 9 in the scope of RoHS concluded that temporary exemptions for lead in solders may be required[1]. This report was published in 2006 and since then research into substitutes for this application has been carried out but results show that lead-free substitutes are not technically viable (poor yields) and may be less reliable.

Lead is needed in solder alloys to attach the CZT detector to the PCB because this solder has a relatively low melting point to minimise laminate distortion, it is more ductile than most types of lead-free solder and its long term field behaviour is fully understood so reliability is good and predictable. The long term field behaviour of these types of detector mounted with lead-field solder is not known as these are very new devices. Early unexpected failure would have serious health implications if the equipment were needed in an emergency because an alternative machine is very unlikely to be available due to their high cost. This would also be a serious problem as the medical equipment could not be used until repaired and patients would suffer as a result of delays in their treatment. Failure of a solder bond is likely to result in the only available CT or PET machine at a hospital being out of action for several weeks. This situation clearly would impose

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

an increased risk to patients' health and so further research by manufacturers is required into possible substitutes for SnPb soldering to minimise this risk.

4.1. Substitute materials

Three substitute materials have been considered but all are unsuitable for technical reasons as described here.

- **Substitute solders**: Development work by one manufacturer found that after fabrication with a SnPb soldering process, the yield of good detectors was better than 98%. However on PCBs produced with lead-free processes, there were 5 – 10% defective assemblies. This level of failure is high and creates unnecessary waste, but of greater concern is that the internal stresses induced by the greater laminate distortion results in more uneven pad dimensions that could also cause more failures to occur after several years in service which would prevent the medical device from being available.
- **Conducting adhesives**: These are not widely used as an alternative to solders because their long term reliability can be inferior and there is also a tendency for the contact resistance to increase over time mainly due to surface oxidation of PCB pads as the copper of the circuit diffuses to the surface where it rapidly forms electrically insulating copper oxide. The conductor particles in some types of adhesive can also oxidise or corrode. If precious metal particles are used, these can form a galvanic cell with the substrate copper accelerating its oxidation. A further reason for not using conducting adhesives is that the detectors will be exposed to ionising radiation. All types of adhesive degrade when exposed to ionising radiation and so bond failure in this application seems highly likely.
- **Alternative laminates**: The laminate must have the same thermal expansion coefficient as CZT and have a sufficiently high interconnect density. This eliminates most options so that very few choices of laminate are suitable and all of these are susceptible to warping at high temperature.

4.2. Alternative designs

CZT replaces silicon digital detectors because of its superior sensitivity to radiation. Silicon is a light element so most radiation passes through undetected and so silicon detectors usually have a surface layer of thallium doped caesium iodide which as these are heavy elements, efficiently adsorb radiation and then convert this to light which is detected by the silicon photodetector array. Cadmium and tellurium are moderately heavy elements which adsorb most of the radiation and so directly convert this into a digital image. If silicon were to be used, patients would need to be exposed to higher radiation doses to achieve the same image quality.

- CT – patients are exposed to relatively high doses of x-ray during a CT scan and so the detector should be as sensitive as possible to minimise the risk of harm from radiation. It is understood that there is a linear relationship between radiation dose and risk of cancer. Huda[2] has established that typical CT doses cause about 1 person in 1,000 (0.12%) to have cancer. In this case, a 10% increase in radiation dose will cause statistically one additional person in 10,000 to have cancer. Clearly, it is

[2] W. Huda, W. T. Rowlett and U. J. Schoef "Radiation dose at cardiac computed tomography: facts and fiction" J. Thorac. Imaging, 2010 Aug; 25(3) p 2014

important to minimise radiation doses and the "Directive 97/43/Euratom – Medical Exposures Directive" requires that all patient exposures are optimised and so if implementation of RoHS were to result in higher doses, this would conflict with existing EU legislation.

- PET – in this technique, patients ingest or are injected with radioisotopes which migrate to specific parts of the body which allows these to be viewed by the radiation detector. As CZT is more sensitive than silicon, lower radioisotope doses can be given which is safer for patients.

5. Analysis of possible alternatives

Several substitutes have been considered:

5.1. Substitute solders

The more commonly used lead-free solders that are widely used for many types of electrical equipment all have melting temperatures higher than eutectic tin lead. The most commonly used alloys are compared with eutectic tin/lead below:

Solder alloy	Melting temperature
SnPb	183 °C
SnCu	227°C
SnAg	221°C (3.5%Ag)
Sn3.5Ag0.5Cu	217 °C
Sn-3.5Ag-3Bi	206 – 213°C

Lead-free soldering temperatures tend to be ~30 – 40°C hotter than those used with tin lead solder. This higher temperature has a variety of effects on electrical assemblies but it is known that laminates warp during reflow and the extent is proportional to temperature. Polymer laminates soften as their temperature increases. The conductors and components attached to each side of the laminate will be different and so as the thermal expansion of metals on each side will be different to the laminate material (usually smaller); this difference in expansion will tend to distort the laminate. The extent of distortion is proportional to the laminate's rigidity, which decreases with temperature as well as the differential thermal expansion which increases with temperature. Another effect of high temperature is that heavy components can distort the laminate when it softens and this effect also increases with reflow temperature[3]. Trials by at least one manufacturer have shown that the proportion of defective detector modules made with lead-free solders is higher than those made with tin lead solder. Due to this significant difference, lead-free soldered modules cannot be used in new medical devices until these have been approved under the medical devices directive and this will not be granted until long term reliability has been demonstrated. This will require lengthy testing to simulate a lifetime in use of well over 20 years.

A great deal of reliability testing of lead-free soldered consumer and IT products has been carried out and published but this application has many significant differences. The main difference is that it uses an unusually brittle and fragile CZT semiconductor with an uncommon TCE matched laminate and the main risk is fracture of the CZT. The risk of damage to the CZT is likely to be greater when standard lead-free solders are used as these are harder and less ductile than

[3] NPL report, see page 8 http://publications.npl.co.uk/npl_web/pdf/matc91.pdf

tin/lead and so where stresses are imposed, these are less likely to be relieved by deformation of the solder. Solder hardness depends on its thermal history so it is not always straightforward to compare published values. Values for a selection of solders include[4]:

Solder alloy	Vickers hardness
SnPb	12.9 (not annealed)
Sn3.5Ag	17.9 (or 13.9 for annealed)
Sn3.8Ag0.7Cu	21.9
Sn4.7Ag1.7Cu	(12.45 for annealed)
Sn3Ag3Zn	21.9
Sn3Ag3In	21.3

Hardness depends on thermal history and annealing reduces hardness however it is clear that most lead-free solders are harder and so less ductile than SnPb. SnAgZn and SnAgIn are included (although neither is a standard alloy) in the above table because these are lower melting point alloys but they are equally hard as SnAgCu and SnAg.
Reliability test data with CZT and lead-free solders is very limited as these devices are relatively new so there is data insufficient reliability data with lead-free alloys for obtaining approval for the Medical Devices Directive (MDD).

Lower melting point solders are available but these are not suitable for a variety of reasons. Some are susceptible to corrosion and some are too hard and brittle and so will cause increased stresses to the CZT. The melting points of some alloys are too low and so could melt in service. Low melting point solders include (with SnPb for comparison):

Table of alloys with low melting point compared with SnPb.

Alloy	Melting point °C
63Sn37Pb	183
52In48Sn	118
58Bi42Sn	138
Sn9Zn, Sn8Zn3Bi	189 - 199
Sn20In2.8Ag	175 - 187

The reasons why these are not suitable are as follows:
Tin/zinc alloys: Tin/zinc is very susceptible to corrosion and is suitable only for consumer products that have short lives and where high reliability is not required. Corrosive fluxes must be used that are difficult to remove and so pose a risk of corrosion to other parts of the equipment as well as the solder.
Tin/bismuth; The melting point of tin/bismuth is too low for some types of PCB so that bonds could melt if the equipment or individual components on the PCB (such as power semiconductors) were to operate at elevated temperature. Bismuth alloys are also not good choices as wire is difficult to make so that repairs and rework are difficult and sometimes impossible. SnBi alloys are very hard and brittle and so any stresses will be transferred to the fragile CZT semiconductor. Bismuth also increases the complexity of waste electrical

[4] From http://www.boulder.nist.gov/div853/lead_free/props01.html except Sn3.9Ag0.7Cu which is from Elfnet

equipment recycling processes as it combines with gold and other elements. Comparative tests of SnBi with SnPb showed that SnBi is more susceptible to thermal fatigue failure (i.e. fails after fewer stress cycles) [5]. Stresses will be imposed on solder bonds of electrical components attached to the circuit board because they will have different thermal expansion coefficients (TCE) to the PCB. The PCB's TCE is matched to the CZT's TCE but will not match the TCE of most other components.

Tin/indium: This alloy is relatively soft and ductile and has a low melting point so is susceptible to bond failure if the equipment were to become hot (see SnBi above). As this is a very unusual solder, there is almost no reliability data available and so approval under the Medical Device Directive may not be possible. Solder pastes are unstable (due to particles corroding or cold welding) and solder balls can be made but readily cold weld to each other and so are difficult to use. Indium is a scarce metal with limited availability.

Tin/indium/silver (Sn20In2.8Ag): Patented by Indium Corporation. Availability of indium is an issue. This alloy is expensive due to the high indium content and so is rarely used and very little reliability data published. It is also susceptible to corrosion under high humidity conditions.

5.2. Conducting adhesives

CZT detectors can be bonded to PCBs using a special electrically conducting adhesive. However, in many applications, the interconnection resistance must be lower than is achievable using these materials or there are performance issues making the use of conducting adhesives problematic. The implementation of an under-bump metallization (UBM) is used to allow solder attach of CZT to an interposer or PCB substrate[6].

Figure 1 shows two PCB pads bonded with conducting adhesive to the CZT detector showing the large difference in thickness of adhesive that is caused by PCB distortion (distortion caused by soldering other components). This large difference in bond thickness has been found to increase the risk of either bond failure or cracks in the CZT semiconductor.

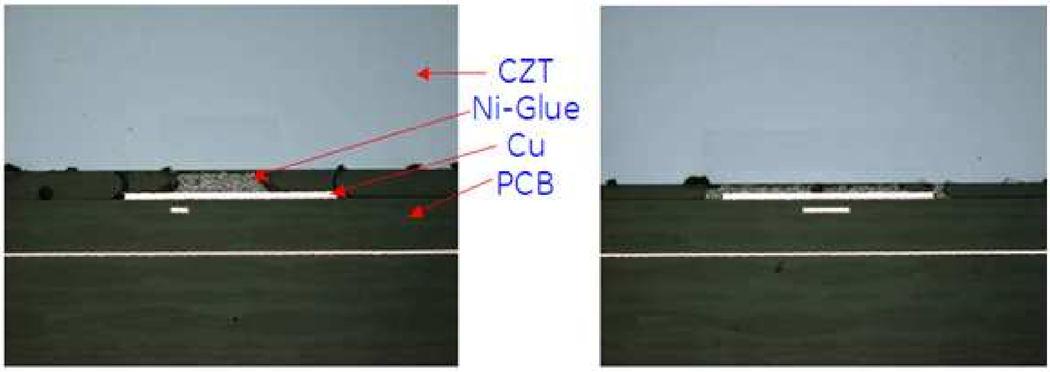


Figure 1: Cross-section through bonds to CZT detector. Left image thick layer of adhesive, right image thin layer

[5] HP tested 58%BiSn with 63%SnPb for cyclic thermal fatigue resistance and found that SnBi bonds failed much sooner than SnPb with all of the package types tested. "Low-Temperature Solders", Z. Mei, H. Holder and H A. Vander Plas. H. P Journal, August 1996.

[6] "Development of Flip-Chip Bonding Technology for (Cd,Zn)Te" Michael Fiederle, Heiko Braml, Alex Fauler, Jürgen Giersch, Jens Ludwig, Gisela Anton, Karl Jakobs, IEEE Transactions on Nuclear Science, Vol. 51 , p232, 2004

Using conducting adhesives to populate the PCB instead of soldering may be suitable for a few applications but this creates bonds with electrical resistance that are higher than with solder and research has shown that the resistivity tends to increase with time as explained above. Any added resistance in the pathway from the CZT sensor to the readout electronics adds error and affects the clarity of the image. In most applications where CZT detectors are used, only a low resistance interconnect path will enable proper detector performance.
Additional reasons why conducting adhesives are not suitable as substitutes are:

- Dynamic, high frequency resistive/dielectric properties of conductive epoxy not best long term solution for high bandwidth signals of photon counting
- Non-planar board substrate & warping of substrate causes gaps that not easily filled with epoxy. There is a difficult balance with expoxy resins as these require good flow rheology and wetting of contact surfaces during part placement but preventing slumping during the slow curing cycle. Precise solder paste printing is straightforward, even with extremely fine pitch and solders have a wetting force on contact surfaces followed by rapid solidification to give very low electrical resistance.
- Solder is more ductile than epoxy and can withstand substrate warpage that may occur during further thermal processes (e.g. to attach other components).

5.3. Alternative laminates

As CZT is a very fragile material, it is necessary to use a laminate with a very similar coefficient of thermal expansion (TCE). This severely limits the choice of materials that can be used with heavily loaded polymer laminates being the only suitable choices. The evaluation of some types of laminates using lead-free solders to attach the detector has been evaluated but this was found to cause delamination or cracking in the CZT especially where there is a mismatch in coefficient of thermal expansion. The higher temperature associated with lead-free solders results in larger differential expansion and therefore more stress in the CZT than with SnPb whatever the laminate material is used. Rigid cCeramic thick-film circuits will not warp and have a relatively low TCE close to that of the CZT detector but it is not possible to construct these with a sufficiently high interconnect density. As a result detectors with ceramic substrates would not provide sufficient spatial resolution for many medical imaging applications. Standard PCB laminates are unsuitable as their TCE is too large and so do not match that of the CZT detectors.

5.4. Alternative detectors

Alternative detectors are available as two types. The traditional radiation detector is based on scintillator materials coupled with large form factor photomultiplier tubes or silicon photodiodes. The most commonly used alternative digital detectors are silicon detectors with thallium-doped caesium iodide scintillators (thallium is very toxic). These all require larger doses of radiation to achieve the same sensitivity as CZT and this increases the risk to patients (as explained above).
Of the modern high performance detectors that have been developed which give equal or better sensitivity to radiation and gives images with equal or better details, all are made of brittle and fragile semiconductors based on lead, cadmium and mercury. Theses will all be equally susceptible to damage by soldering with lead-free solders because of the high temperature processing, as explained above and lead, cadmium and mercury are all RoHS-restricted substances.

Semiconductor detectors made from lead or mercury of similar size to CZT will be equally fragile and so suffer from the same limitations as CZT.

6. Life cycle assessment

6.1. Alternative solders

Alternative lead-free solder alloys are of two types, those with higher melting temperature than SnPb and those with melting temperature that are similar or lower than tin lead.
Although no suitable alternative alloy has been found as described above, the main constituents of the apparent alternative alloys are considered here. Each alloy has different environmental impacts at different phases of the equipment life cycle as follows:

Mining and refining of metals used to make solders
Tin is used in all options so can be ignored for this assessment.
Lead is mined in large quantities as a primary metal with about 8 million tonnes per year being produced. Consumption world-wide is increasing despite the RoHS restrictions due to its main uses for batteries and buildings. Extraction and refining of lead from its ores is well controlled in developed countries and many developing countries so that lead pollution does not occur. Sulphur dioxide is produced as a by-product which is used to make sulphuric acid.
Silver mining **c**reates large amounts of waste and the quantities of emissions of hazardous substances can be greater than from lead refining[7]. Cyanide is used for refining (and sometimes also for extraction from rock).
Zinc is also mined in very large quantities as a sulphide ore but much less is recovered by recycling as this is less straightforward than for lead. As with lead, smelting zinc ores releases sulphur dioxide which is recovered as sulphuric acid. Although zinc itself has a relatively low toxicity, its ores often contain cadmium which can be separated but is often left with the zinc if it is at concentrations below 100 ppm (the RoHS limit for cadmium in homogeneous materials). During all high temperature processes including smelting, some of this cadmium may volatilise to generate toxic emissions. At end of life, zinc is not usually recovered from printed circuit board scrap due to its reactivity and so forms a waste by-product.
Bismuth arises as a by-product from mining other metals including lead. It is a relatively rare metal occurring at low concentrations so that significant quantities of energy are required to extract and refine this metal. Availability is not an issue.
Indium arises as a by-product from extraction of other metals and occurs at very low concentrations and so significant quantities of energy are required to extract and refine this metal. Availability is very limited with demand equal to or exceeding supply with most being used to manufacture displays.

Assembly of equipment
Where higher melting point solders such as SAC (SnAgCu) are used, the energy consumption of the soldering process is increased. Various values for the percentage increase have been estimated with ~ 10 – 20% more energy consumed being typical.

[7] See full life cycle analysis of lead-free and lead-based solders http://www.epa.gov/dfe/pubs/solder/lca/index.htm

Use of medical equipment
The choice of solder affects the use phase only if it affects equipment reliability. The reliability with lead-free solders is uncertain for this application and there is a risk that it may be inferior causing unexpected failures that have a negative impact on healthcare.

6.2. Alternative laminates

Although ceramic substrates are unsuitable as explained above, these are manufactured from metal conductors bound with low melting point glasses which are often lead – based. Theses circuits are heated to high temperatures to melt the glass binder and so much more energy is consumed than with traditional polymer PCB laminates.

6.3. Alternative detectors

All of the alternative types of detectors with the required performance are equally or more fragile than CZT and so would also require tin/lead solders to avoid a high proportion of waste during production and to produce products with known high reliability. Therefore this option cannot be considered. Silicon digital detectors require the use of higher radiation doses which increases the risk to patients from the larger radiation dose.

7. Re-use and recycling of materials from waste EEE

At end of life, imaging equipment will be recycled due to its high metals content which has a high value. Printed circuit boards are separated for separate recycling as required by Annex II of Directive 2002/96/EC before being recycled. In the EU and in many facilities elsewhere, PCB scrap is recycled using smelters which are large furnaces that melt some metals such as copper and convert others including lead into oxides which are collected then converted into metals for re-use. Lead is recovered with a very high efficiency and emissions are extremely low and meet EU environmental limits. Unsafe recycling of WEEE is carried out in some developing countries but this is mostly with IT, telecom and consumer equipment. Waste medical equipment is very unlikely to be recycled except by professional recyclers using well controlled safe processes.

Lead: Large quantities of recycled lead are produced from lead scrap including printed circuit boards. No lead is released in the circuit board fabrication phase or the use phase of the life cycle. At end of life, CT, PET and other machines that contain these circuit boards contain large amounts of valuable metals and so are always recycled.
Silver: It is likely that recyclers will want to recover silver from equipment at end of life. There are safe and efficient processes used by professional recyclers in the EU but there is a risk that unsafe methods using very hazardous chemicals such as nitric acid and cyanide might be used in developing countries where unsafe recycling occurs.
Other solder constituents including tin (Bi, In and Zn) may also be recovered by modern efficient recycling processes but are very difficult to recycle without suitable processes.
Thallium doped caesium iodide and silicon: Silicon and these uncommon elements are not recovered by recycling processes. Thallium is also not normally

recovered and would pose a risk if uncontrolled and unsafe recycling processes were used.

8. Other information

The quantity of lead in the solder required for each CZT detector circuit is 1 g.
~ 1 - 2 kg of lead is expected to be used in the EU annually for this application.

9. Proposed plan to develop substitutes and timetable

The only potential alternative to lead in solders is lead-free solders. Manufacturers are carrying out research to find alloys and processes that give high yields. This work is likely to need to evaluate less commonly used alloys which are more ductile than the lead-free alloys most often used in consumer and IT electronics such as tin/silver/copper. If high yield processes can be identified, then the assembled detectors will need to be tested using realistic conditions to determine whether these alloys will be reliable long-term in use. Reliability testing of new alloys must be thorough for medical devices as this data is needed before applying for approval under the Medical Devices Directive. To gain approval, it will be necessary to show that the alternative alloy is no less reliable than lead-based solders and so do not pose a risk to patients. The likely time-scales are:

Evaluation of alternative alloys and processes	2 – 3 years
Reliability testing of assemblies made with high yields	at least 2 years
Submission for MDD approval	1 year
Total timescale	minimum 5 years

This exemption is therefore likely to be needed until 2018 at least.

10. Proposed wording for exemption

Lead in solders used on PCBs for mounting cadmium telluride and cadmium zinc telluride digital array detectors