Test & Measurement Coalition

Japan Business Council in Europe

CATEGORY 9 INDUSTRIAL EQUIPMENT

ADDITIONAL INFORMATION

Date of submission; 6. July 2020

4.A).1 Description of the concerned application: Category 9 applications including non-destructive (for various such as material identification for recycle, food, pharmaceutical, baggage and many others), quality inspection in manufacturing, X-ray fluorescence analysis and electron microscopes. Please note that the EEEs used for the above applications may also be used by students at universities for study.

4.A).3 Function of the substance: Lead is used to block and absorb ionising radiation to prevent operations personnel, maintenance personnel and the electrical equipment from exposure to radiation.

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

- Commercial purity lead metal of 99.9% and harder alloys such as 95%Pb5%Sb are used
- Transparent glass is also used for some type of category 9 equipment. The glass contains ca. 60 - 70% of lead. The lead-based glass is also important to protect workers when specimen must be visually confirmed. In case risk of mechanical impact to the window is expected, lead-based acrylic is used to avoid breaking and dropping.
- Shielding plastic is used to conveyor type of inspection such as airport baggage etc. Particularly flexible plastic reduces the resistance of the inspected product to the inspection room and enables smooth transport.
  The plastic contains ca. 50 - 60% of lead

4.A).5 Amount of substance entering the EU market annually through application for which the exemption is requested: The quantity of lead shielding used in category 9 devices varies considerably, depending on the design and application as with medical devices. The total amount of lead contained in category 9 devices sold in 2016 in the EU28 is typically estimated to be less than 20 tonnes.

4.A)6. Name of material/component: Lead metal and alloys or lead-based glass or lead-based acrylic or lead-based plastic

4.B) In which material and/or component is the RoHS-regulated substance used, for which you request the exemption or its revocation? What is the function of this material or component?

Lead is used in various forms and shapes as follows:

- Sheet, thicker sections and complex shapes are used as a barrier to X-rays;
- Machined and moulded parts of intricate shapes;
- Lead-bearing transparent glass and acrylic
- Lead-bearing plastic

Lead as ionising radiation shielding has the following uses:

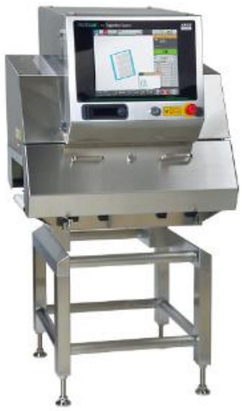
- **Shielding** - this is constructed from sheets of various thickness as well as complex shapes.
- **Collimators** – various types are used to either focus X-rays or to remove radiation that is not travelling in the correct direction to achieve a clear image. Fixed collimator are used at the windows of X-ray tubes for beam trimming and blade-types (made with stacks of thin sheets) are used as movable collimators are also used for beam trimming. Radiation can be scattered (e.g. by the patient and parts of the equipment) and this causes radiation to travel on many unintended directions which can lower quality images if not removed by a collimator (or an anti-scatter grid). The preferred design of lead collimators that are used with flat panel detectors have a hexagonal cell structure that resembles a bee's honeycomb. These are also known as anti-scatter grids.
- **X-ray tubes** – X-ray tubes are either made of high lead content glass or metals. Metal inserts are lined internally with lead sheet. All X-ray tubes contain a high vacuum and so must be perfectly sealed and this is fairly straightforward with glass. Glass is however relatively fragile and so larger heavier inserts are usually metal to prevent damage.

The content of shielding by lead is the same as for medical devices.

The main types of category 9 equipment that utilise lead in radiation shielding are described below.

X-ray imaging equipment.

The content of shielding by lead is the same as for medical devices. Figure 1 shows an example of category 9 X-ray imaging equipment.



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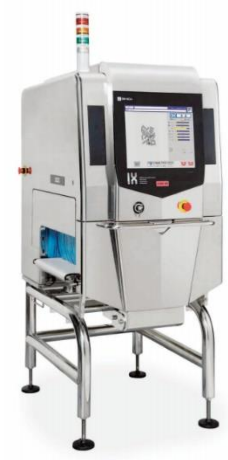

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Figure 1. Inspection for foods, luggage, and others

X-ray analytical instruments.

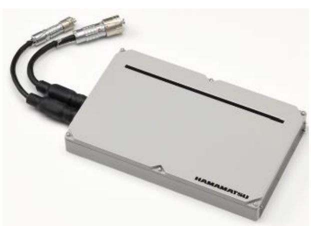
Lead is used in various devices to improve analytical performance where lead is used for its radiation shielding properties, including:

- Collimator for limiting X-ray irradiating area to improve spatial resolution of analysis;
- Collimator for shielding X-ray detector from stray X-ray incidence;
- In glass of capillary plates used for X-ray collimation;
- Viewing windows, to confirm object being analyzed or to confirm analyzed position on the specimen;
- X-ray tube shielding to achieve space effective and radiation safe housing

Examples of X-ray analytical instruments that uses of radiation shielding include:

- X-ray Photo-electron Spectrometers (XPS);
- X-ray Diffraction (XRD) Spectrometers;
- X-ray fluorescence (XRF) coating thickness gauge;
- X-ray fluorescence (XRF) analyzer
  - The kind of important applications of X-ray analysis is screening of RoHS restricted material as defined in IEC 62321-3-1.

Figure 2 shows an example of category 9 X-ray analytical Instruments.



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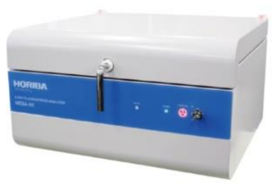

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Figure 2. Radiation line sensor for pipe corrosion inspection, X-ray Fluorescence analyzer, and others

Electron microscopes

Electron microscopes are typically using the accelerated particles (e.g. electrons) with energy of several 100 eV to several MeV, so also require shielding against caused stray ionising radiation.

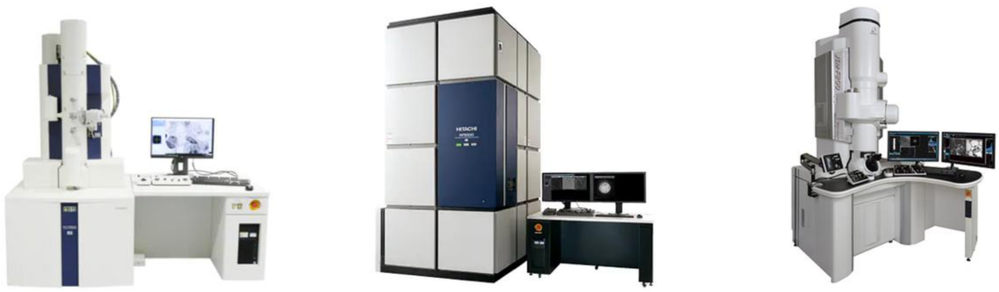

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Figure 3. Electron microscope

Microwave tubes

Microwave tubes are typically using the accelerated electrons with energy of several 100 eV to several MeV, so also require shielding against caused stray ionising radiation.

The content of shielding by lead is the same as for medical devices.

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Figure 4. Microwave tube

Viewing windows

Category 9 applications, the lead-based glass is also important to protect workers when specimen must be visually confirmed. In case risk of mechanical impact to the window is expected, lead-based acrylic is used to avoid breaking and dropping.

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

In the industrial setting, workers need to work close to the equipment, and as in medical settings, effective shielding is needed to protect workers from radiation exposure.

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

Possible alternative substances

The capability of radiation shielding depends on a substance's atomic number and its density. This means that all substances possess this ability to some extent. However, the most appropriate substance for radiation shielding of medical devices or test & measurement equipment is Lead. This is because any potential alternative substance with a lower atomic number and a lesser density invariably require more volume and space to control the same level of radiation as Lead can. This would make it impossible to secure the required performance including the safety for patients as well as workers and could possibly have negative effects on human health and the environment.

In this chapter, potential alternative substances for Lead that are selected based on atomic number and density will be studied below.

Table 1. Atomic number, density, limitations, melting, price, and CRM

Element	Atomic number	Density	Limitations	Melting Point	Price[1]	CRM[2]
Uranium	92	19.05	Radioactive	1135 ℃	—	—
Bismuth	83	9.8	Less dense so thicker material needed	271.406 ℃	8.76 USD / lb	✔
Lead	82	11.3	Currently used	327.46 ℃	1.090 USD / lb	—
Thallium	81	11.8	Very toxic (as also is mercury atomic number	304 ℃	2,689.8 USD / lb	—

[1] Price information is based on the average price per a pond in 2010.
USGS, *Metal Prices in the United States Through 2010*, 2012. https://pubs.usgs.gov/sir/2012/5188/sir2012-5188.pdf

[2] Critical Raw Material （https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en）

			80)			
Gold	79	19.3	Very expensive, likely to be stolen if used, making medical device un-usable and so harming patients	1064.18 ℃	19,640 USD / lb	—
Platinum	78	21.1	Very expensive, likely to be stolen if used, making medical device un-usable and so harming patients, same with other platinum group metals.	1768.2 ℃	25,856 USD / lb	✔
Tungsten	74	19.3	Limited suitability as shielding but see discussion below.	3414 ℃	9.7 USD / lb	✔
Tantalum	73	16.7	Has been evaluated but is difficult to fabricate and brittle so thin sheets are easily broken.	3017 ℃	54 USD / lb	✔
Hafnium	72	13.3	May be suitable, but less so than tungsten, difficult to fabricate and difficult to extract from minerals	2233 ℃	255.37 USD / lb	✔
Barium	56	3.51	Too reactive as a metal and gives inferior shielding glass due to lower atomic number and density	727 ℃	—	—
Molybdenum	42	10.3	Similar density as lead but much lower atomic number so needs to be much thicker	2622 ℃	15.80 USD / lb	—

Any elements having an atomic number greater than 84: Polonium are classified into radioactive element with no stable isotopes. So, we should find potential alternative substances in the list of elements having an atomic number lower than 83: Bismuth[3]. And, since atomic number 81: Thallium is well known for its toxic property, we should exclude it from the potential alternative list.

Furthermore, aside from safety concerns, we should also take market availability into consideration because EU citizens would lose access to state of the art medical and scientific

[3] Bismuth was long considered as a stable isotope. But in 2003 it was demonstrated to be a radioactive isotope (Belle Dumé, "Bismuth breaks half-life record for alpha decay," in Physicsworld, 23 Apr. 2003.). However, this paper lists Bismuth as a potential alternative substance because it has a tremendous long half-life.

technology if the manufactures would not be able to use alternative substances due to high costs. According to the report of the United States Geological Survey (USGS), the metal price of atomic number 79: Gold is ＄19,640/lb and that of atomic number 78: Platinum is ＄25,856/lb, meaning they are 18,018 and 23,721 times respectively more expensive than Lead. In addition, European Commission has announced the Critical Raw Materials(CRM) for European economy. According to this, atomic number 74: Tungsten, 73: Tantalum, and 72: Hafnium are designated as CRM. As for Hafnium, it can be found in zirconium minerals and produced as a by-product of zirconium extraction. According to the report of the Japan Oil, Gas and Metals National Corporation (JOGMEC), the world production of Hafnium in 2011 was around 120 tonnes[4], which is not enough to meet the high demand for radiation shielding. Now, we can exclude atomic number 79: Gold, 78: Platinum, and 72: Hafnium from the potential alternative list.

Considering atomic number 82: Lead from a technological aspect, its physical properties are as follows: high density, low melting point (327.46 ℃), soft, and malleable. For atomic number 84: Tungsten, its physical properties are as follows: very high melting point (3414 ℃) and extreme hardness, although it has a higher density than Lead. For atomic number 73: Tantalum, its physical properties are as follows: very high melting point (3017 ℃) and brittleness[5], althogh it has a higher density than Lead. For atomic number 56: Barium, although its meltingpoit is enough low (727 ℃), its density (3.51 g/cm^3) is very lesser than Lead, so it does not meet the required performance for radiation shielding. And for atomic number 42: Molybdenum, it has high melting poit (2622 ℃) and its atomic number is lower than Lead, so it does not meet the required performance for radiation shielding as well.

In addition to the above physical properties, the environmental impact has to be added into it. Table 2 shows each metal's Global Warming Potential considering its three main stages: (1) mining, (2) purification, and (3) refining.[6]

[4] Japan Oil, Gas and Metals National Corporation (JOGMEC), “39. Hafnium (Hf),“ in Mineral Sources Material Flow, 1 May 2012. http://mric.jogmec.go.jp/wp-content/old_uploads/reports/report/2012-05/39.Hf_20120619.pdf

[5] Tantalum finds use in areas: high-temperature applications, such as aircraft engines; electrical devices, such as capacitors. It is rarely used as an alloying agent because it tends to make metals brittle (https://www.lenntech.com/periodic/elements/ta.htm).

[6] Philip Nuss, Matthew J. Eckelman, Life Cycle Assessment of Metals: A Scientific Synthesis, July 7, 2014. [abbr. : Philip]

https://journals.plos.org/plosone/article?id=10.1371/journal.pone.0101298

Table 2. Global warming potential from mining, refining and production of heavier metals

Metal	Global warming potential from production (kg CO_2-eq/kg)
Lead	1.3
Bismuth	58.9
Thallium	376
Mercury	12.1
Gold	12,500
Platinum	12,500
Iridium	8,860
Osmium	4,560
Rhenium	450
Tungsten	12.6
Tantalum	260
Hafnium	131
Molybdenum	5.7

Metal refining to sufficient purities frequently requires energy-intensive and precisely-controlled melting stages.[7] So, the purer the ore and the lower its melting point is, the lower Global Warming Potential is also. The substance with the lowest Global Warming Potential is Lead. Atomic number 73: Tantalum has 200 times more Global Warming Potential than Lead.
Therefore, based on substance physical properties and the environmental impact, we can exclude atomic number 73: Tantalum, 56: Barium, and 42: Molybdenum from the potential alternative list.

Bismuth and Tungsten

Some studies show that atomic number 83: Bismuth and 74: Tungsten could be very good alternative substances.[8] Although these contexts are connected to lead aprons used in

[7] Philip p.1.

[8] Mehdi Zehtabian, Zahra Molaiemanesh, Elham Pirouzan, Sedigheh Sina, "Design of Light Multi-layered Shields for Use in Diagnostic Radiology and Nuclear Medicine via MCNP5 Monte Carlo Code," in Iranian Journal of Medical Physics Vol. 12, No. 3, Summer 2015.

medical sites, it is necessary for us to discuss Bismuth and Tungsten as alternative substances for lead shielding in medical or test & measurement applications.

Assessment of Tungsten

Althogh Tungsten's atomic number (74) is smaller than that of Lead (82), it could be considered as a very good alternative substance because its density(19.3 g/cm3) is higher than Lead (11.3 g/cm3) and it is not classified into toxicity categories.
But our renewal application demonstrates that Tungsten has a bigger negative impact than Lead. We refer to the following points as this reason[9]:

- Tungsten composite shielding material needs to be more thicker than Lead shielding material to achieve the same level of radiation schielding performance as Lead can. The space available for radiation schielding is so limitted that it is difficult for some applications to adopt Tungsten composites in exchange of Lead metal.
- Tungsten is too hard and inflexible to form into compex shapes such as anti-scatter grid.
- Thin sheet of Tngsten metal is too brittle and fragile.
- Composite shielding materials including Tungsten composites are non-recyclable materials.
- LCA of Tungsten shows a wider and bigger negative environmental impact than that of Lead.

Besides, in the stages of Use-phase and End-of-life, a radioactivation issue should be considered. Radioactivation means that a stable isotope changes to a radioactive isotope through the influence of strong ionizing radiation. For example, Cobalt-60, which is used as a γ-ray source for medical/industrial appications, is artificially produced in nuclear reactors where Cobalt-59 is irradiated with neutrons. Radioactivation could occure if the element in the shielding material is affected by strong irradiation.[10] In fact, there was a case where Tungstesn was radioactivated and had a cooling time of three years.[11] Lead, however, cannot be radioactivated.[12]

Assessment of Bismuth

Nadin Jamal AbuAlRoosa, Noorfatin Aida Baharul Amina, Rafidah Zainona "Conventional and new lead-free radiation shielding materials for radiation protection in nuclear medicine: A review," in Radiation Physics and Chemistry 165, December 2019. [abbr. : Nadin]

[9] COCIR, JBCE, TMC, 'Exemption Reniewal Form – Exemption 5, Annex Ⅳ', 2020, pp.20-26.

[10] Typical shielding materials and product radioactive nuclides with very long half-life are shown in the following table.

Target material	Product nuclides
Alminium	^{22}Na, ^{7}Be, ^{3}H, ^{54}Mn
Iron	^{54}Mn, ^{56,60}Co, ^{55}Fe, ^{3}H, ^{44}Ti
Concrete	^{22}Na, ^{7}Be, ^{3}H, ^{60}Co, ^{152}Eu

Shuichi Ban, Hajime Nakamura, Hideo Hirayama, "Estimation of Amount of Residual Radioactivity in High-energy Electron Accelerator Component by Measuring the Gamma-ray Dose Rate," in Journal of Nuclear Science and Technology, 27 Aug 2014, p.169.

[11] In the case where the smmothed filter (Copper-tungsten alloy) of the particle accelerator for therapy was radioactivated, the radioactive isotope : Tungsten-181 was produced (https://ndrecovery.niph.go.jp/trustrad/activated_target.html).

[12] http://www.mesco.co.jp/materials/mat_section/mat_onshut/mat_onshut_tokusei/

Bismuth is a convenient substitute substance for Lead as it shares many of the similar properties of Lead. Lead-replacement is expected to take place in applications including solders. Although some Bismuth is produced by refining its ore, its production mainly stems from a by-product of lead extraction. According to the USGS report, the world refinery production of Bismuth in 2016 was 17,100 tonnes, of which China produced 14,000 tonnes.[13] Considering Lead's negative iampact on human health and the environment, the world demand for Lead will go down from now on and the source of lead metal will be changed form lead ore to lead-acid battery waste thanks to lead's highly effective recycling scheme. On the other hand, although the collection of Bismuth from lead-free solders was expected , the recycling scheme of it has not been well developed yet because the collection of Silver from lead-free solders was more economical.[14] Therefore, we cannot hope so much that the supply of Bismuth will grow, and also we fear its unstable supply because of geopolitical reasons.
The following are the technical reasons why Bismuth could not be an alternative substance for lead shielding. To apply a shilding material to medical devices or test & measurement equipment, a pure metal with a large atomic number and its easy processing are desireable. For a bismuth shielding, it shall be made of not pure Bismuth but a bismuth alloy because Bismuth is so brittle in its pure form. [15] And, as for a bismuth alloy containing 43 of Bismuth (atomic number 83) and 57 of Tin (atomic number 50), its density is 8.2 g/cm3, which is inferior to a lead shilding performance because its density is 11.3 g/cm3 and its atomic number is 82.

About Composite Shielding Materials

New shielding materials, Tungsten or Bismuth sheet with a polymer coating have been available in the market. Since a polymer coating would make their densities lesser, their capability of radiation shielding cannot compete with lead. And, since ionizing radiation damages a polymer and makes it hard, it is difficult to find a polymer that can bear against the abrasion and radiation conditions for many years.[16] Normally, shielding materials are stored inside equipment and their replacement is never considered. Therefore, polymer-based shielding materials are not suitable for medical devices or test & measurement equipment because thier life time is very long.

Conclusion

Although some studies argue that Bismuth and Tungsten could be good alternative for lead shielding, we have to consider that this context is connected to lead aprons used in medical sites. As for lead shieldings stored inside medical devices or test & measurement equipment, there is no possibility of human or the environmental exposure to lead during their Use-phase, meaning that it is highly unlikely for lead dust to be inhaled or ingested by a person.[17]

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[13] USGS, Mineral Commodity Summaries 2018
https://www.usgs.gov/centers/nmic/bismuth-statistics-and-information
The production of Bismuth in China mainly stems from a by-product of Tungsten refineing process.

[14] Japan Oil, Gas and Metals National Corporation (JOGMEC), "34. Bismuth (Bi)," in Mineral Sources Material Flow, 1 May 2012.
http://mric.jogmec.go.jp/wp-content/old_uploads/reports/report/2012-05/34.Bi_20120619.pdf
ISHIHARA Shunso, " On bismuth resources of Japan and world," in journal of the Society of Resource Geology No. 58(2), 2008.

[15] Nadin p.3.

[16] Nadin p.3.

[17] Lead dust is a major source of lead exposure in children (Nadin p.2.).

Although we cannot exclude the possibility of lead exposure in a person at the Production phase and End-of-life phase, this exposure can only occur when specially trained workers handle lead shildings under well controlled conditions. In addition, a lead shielding is almost pure lead[18] which is collected at the disposal phase and can be recycled very easily. Therefore, we can coclude that Tungsten and Bismuth are not appropriate alternative substances for lead shielding in medical devices or test & measurement equipment.

[18] The hard lead contains approx. 96.2 of Lead and 3.71 of Antimony.