Japan Business Council in Europe

Exemption Request Form

Date of submission: 19 January 2023

1. Name and contact details

1) Name and contact details of applicant:

Company:	Japan Business Council in Europe	Tel.:	+32.2.386.5330
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This exemption application is submitted with the endorsement of the business associations listed below:

JAIMA Japan Analytical Instruments Manufacturers' Association

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

☐ 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:	9
Proposed or existing wording:	Helium cadmium laser
Duration where applicable:	7 years.

☐ Other: _____

3. Summary of the exemption request / revocation request

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase and polymorphy, crystallinity and molecular interactions. It is based on the interaction of light with the chemical bonds within a material. Helium cadmium lasers enable wavelengths of 325 nm to be used in Raman spectroscopy measurements. Diode Pump Solid State (DPSS) lasers, as an alternative to helium cadmium lasers, can be used in many applications. However, although DPSS lasers can be used for Raman spectroscopy, at the moment 325 nm DPSS lasers for Raman spectroscopy are not available commercially, due to a lack of stability and precision. Therefore, the extension of the exemption is required for helium cadmium lasers to continue to be used in Raman applications.

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4. Technical description of the exemption request / revocation request

(A) Description of the application concerned:

1. To which EEE is the exemption request/information relevant?

   Name of applications or products: Helium cadmium laser

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: _____

c. Please specify for equipment of category 8 and 9:

   The requested exemption will be applied in

   ☒ monitoring and control instruments in industry

   ☐ in-vitro diagnostics

   ☐ other medical devices or other monitoring and control instruments than those in industry

2. Which of the six substances is in use in the application/product?

   (Indicate more than one where applicable)

   ☐ Pb ☒ Cd ☐ Hg ☐ Cr-VI ☐ PBB ☐ PBDE

3. Function of the substance: Helium cadmium lasers enable wavelengths of 325 nm to be used in Raman spectroscopy measurements. Please see 4(B) for more detail.

4. Content of substance in homogeneous material (%weight): Cadmium 100 %weight.

   Amount of substance entering the EU market annually through application for which the exemption is requested: The amount of Cadmium is approximately 800g in Europe.

5. Name of material/component: Helium cadmium laser

6. 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?

The main components are the mirrors at the front and rear of the laser and the laser tube. Cadmium (Cd) and helium (He) gas are enclosed in the laser tube (Figure 1). The cadmium is heated to convert it to its gas phase. Collisions with He atoms which have been excited by electrical discharge then excite the Cd atoms into the laser-emitting excited state. This generates lights of a specific wavelengths (325 nm and 442 nm) in the laser tube, which is amplified by mirrors at both ends (Figure 2).

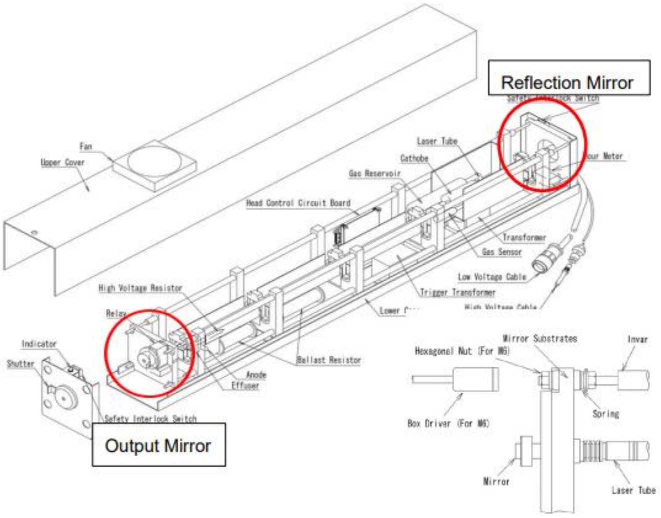

Figure 1: Detailed structure of the He-Cd laser

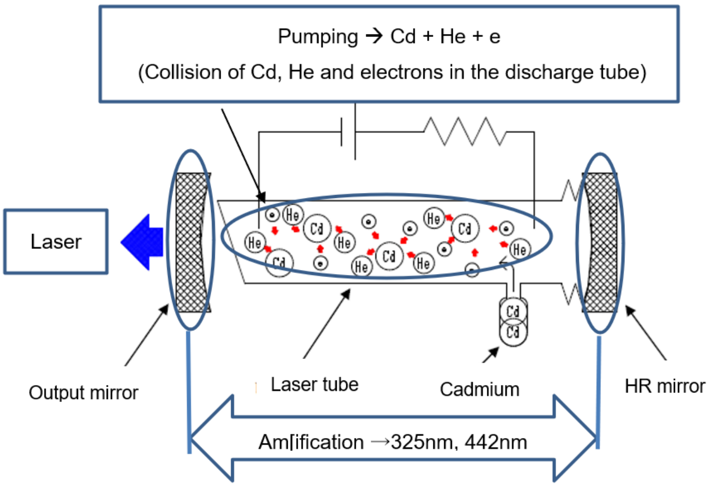

Figure 2: Schematic diagram of the He-Cd laser

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase and polymorphy, crystallinity and molecular interactions. It is based on the interaction of light with the chemical bonds within a material. Schematic diagram of a Raman spectrometer shows figure 3.

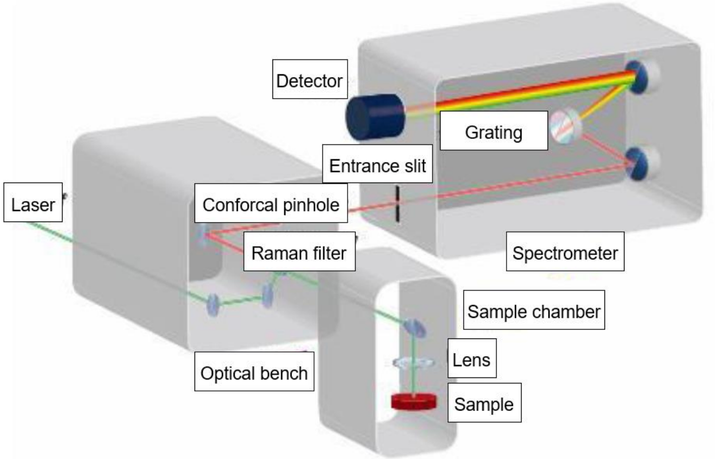

Figure 3: Schematic diagram of a Raman spectrometer

Raman is a light scattering technique, whereby a molecule scatters incident light from a high-intensity laser light source. Most of the scattered light is at the same wavelength (or colour) as the laser source and does not provide useful information – this is called Rayleigh Scatter. However, a small amount of light (typically 0.0000001 %) is scattered at different wavelengths (or colours), depending on the chemical structure of the analyte – this is called Raman Scatter.

Raman spectroscopy probes the chemical structure of a material and provides information about:

- Chemical structure and identity
- Phase and polymorphism
- Intrinsic stress/strain
- Contamination and impurity

Laser wavelengths ranging from ultra-violet through visible to near infra-red can be used for Raman spectroscopy. Typical examples include (but are not limited to):

- Ultra-violet: 244 nm, 266 nm, 325 nm
- Visible: 405 nm, 458 nm, 473 nm, 488 nm, 515 nm, 532 nm, 633 nm, 638 nm, 660 nm
- Near infra-red: 785 nm, 830 nm, 980 nm, 1064 nm

The choice of laser wavelength depends on the application

The He-Cd laser is used as a laser source.

The He-Cd laser can stably emit a wavelength of 325 nm.

The following benefits are provided by the He-Cd laser:

- Increased sensitivity can result from UV excitation, since Raman scattering efficiency is proportional to λ^{-4}, where λ is the laser wavelength. Thus, Raman scattering at 325 nm is a factor of 14 times more efficient than that at 633 nm.

- With certain samples, UV laser excitation can interact in ways not possible when using visible laser sources. For example, in semiconductor materials, the penetration depth of UV light is typically in the order of a few nanometres, and thus UV Raman can be used to selectively analyse a thin, surface layer (as is commonly found in silicon on insulator (SOI) materials). In another example, UV excitation can give rise to specific resonance enhancement with biological moieties, in particular protein, DNA and RNA structures. Specific analysis of these materials within tissue can be difficult using visible laser wavelengths.
- Resonance Raman on carbon materials is well documented in scientific literature at 325 nm and this is frequently used for material characterisation, a small shift in excitation even to 320 nm may invalidate the results presented in this literature. This represents over 20 years of active research worldwide.[1]
- Fluorescence suppression can often be assisted using UV lasers, by spectrally separating the Raman and fluorescence signatures. With visible lasers it frequently occurs that Raman and fluorescence are superimposed, and the incomparable strength of the fluorescence is what can perturb (or completely mask) the Raman spectrum. With UV excitation, the Raman spectrum lies close to the laser line, whereas the fluorescence is often slightly removed to higher wavelengths. Thus, they no longer overlap, and the fluorescence is no longer an issue.

The laser is used for photoluminescence (PL) measurement. The application field is semiconductor materials for defect measurement and energy state analysis.

- Photoluminescence spectroscopy, often referred to as PL, is when light energy, or photons, stimulate the emission of a photon from any matter. It is a non-contact, non-destructive method of probing materials. In essence, light is directed onto a sample, where it is absorbed and where a process called photo-excitation can occur. The photo-excitation causes the material to jump to a higher electronic state, where it will then release energy (photons) as it relaxes and returns back to a lower energy level. The emission of light or luminescence through this process is photoluminescence (PL).

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

The cadmium is heated to convert it into the gas phase. Collisions with He atoms which have been excited by electrical discharge then excite the Cd atoms into the laser-emitting excited state in the laser tube to generate light of specific wavelengths (325 nm and 442 nm), which is amplified by mirrors at both ends.

[1] Please see the link as an example of the research. Ferrari et.al (2004), Raman spectroscopy of amorphous, nanostructured, diamond–like carbon, and nanodiamond, Volume 362, Issue 1824, https://royalsocietypublishing.org/doi/10.1098/rsta.2004.1452 last accessed on December 2, 2022.

Without cadmium, it is not possible to achieve specific wavelengths (325 nm, 442 nm) as illustrated in figure 4 shows[2].

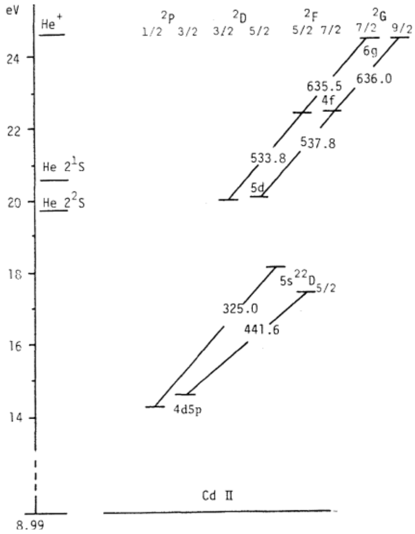

Figure 4: Energy levels of Cd II. Continuous Wave laser transitions are indicated by heavy lines. [wavelength in nm]

With certain samples, UV laser excitation can interact in ways not possible when using visible laser sources. For example, in semiconductor materials, the penetration depth of UV light is typically in the order of a few nanometres, and thus UV Raman can be used to selectively analyse a thin, surface layer (as is commonly found in silicon on insulator (SOI) materials). For example, the penetration depth is around 5 nm if a 320 nm laser is used. On the other hand, the penetration depth is around 450 nm if a 500 nm laser is used (e.g. Table 1 for a Si sample).

Table 1: The penetration depth of Si sample

Wavelength of lights [nm]	250	320	500	800	1000	1200
Penetration depth	2.72nm	3.91nm	450nm	5.88µm	78.1µm	227mm

325 nm laser is effectively used for the measurement of the surface of inorganic samples. For this application, the laser power required is generally more than 10 mW. This is because of the effect of increasing the efficiency of the Raman scattering, when the short wavelength laser is used.

When selecting a laser (wavelength) in Raman spectroscopy, a laser with a short wavelength (low wavenumber side) is suitable because the efficiency of Raman scattering is increased.

[2] Ohta, Sasaki, Oscillation Spectra in Metal Vapor Lasers, 1982 Volume 10, Issue 1, Pages 13-25, p.17 https://www.jstage.jst.go.jp/article/lsj1973/10/1/10_1_13/_article Last accessed on October 15, 2022

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.)

The excitation mechanism of He-Cd laser is as follows. First, in a laser discharge tube, electrons flow from the anode to the cathode, and constant current flows (direct current discharge). Cadmium heated and vaporized by the heater flows into the discharge path. Collisions of cadmium, helium, and electrons are repeated in the discharge tube. The Cadmium is then excited and emits laser light whilst transitioning to the ground level. Cadmium flows out of the cadmium reservoir into the discharge tube. It then moves from the anode side to the cathode side, adheres to the discharge tube wall and solidifies. When the cadmium in the cadmium pool has completely moved, the laser tube reaches the end of its useful life.
A laser manufacturer provides a service of replacing a waste laser tube that has reached the end of its life and recover the waste laser. The user returns the expired laser to the manufacturer, and the manufacturer replaces it with a new laser tube and returns it to the user.

There is a lower power limit for the laser used by the user. Manufacturers receive inquiries from users for replacing laser tubes. The waste laser is returned to the laser manufacturer's factory outside the EU, and in less than a month, the old laser tube is replaced with a new laser tube, adjusted, inspected and shipped back. Each laser tube is numbered and managed by recording the number, characteristics, etc. in the laser history document.

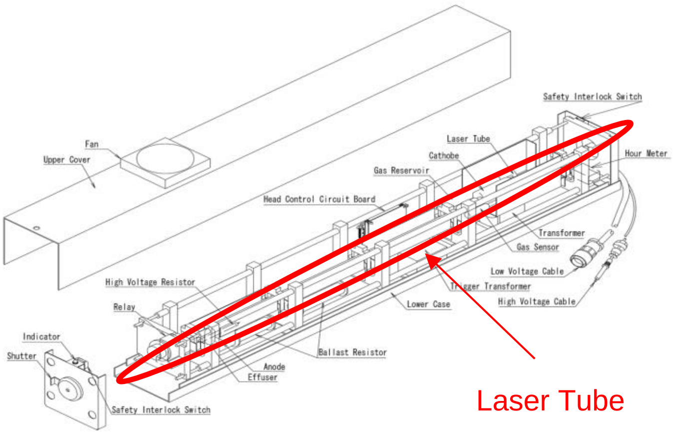

Figure 5: Diagram of the internal structure of a He-Cd laser

No cadmium from He-Cd lasers remains in the EU. Cadmium is enclosed in the laser tube, and work is being done to replace the laser tube shown above. Cadmium does not leak out of the laser tube (Figure 5).

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 See 4(A)5.
☐ In articles which are recycled _____
☐ In articles which are sent for energy return _____
☐ In articles which are landfilled _____

Japan Business Council in Europe

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

As mentioned in 4(C), specific wavelengths are produced due to the physical properties of Cd. Current flows from the anode to the cathode in the He-Cd laser tube. By vaporizing the cadmium contained, collisions of cadmium, helium and electrons are repeated in the discharge tube. This phenomenon is called pumping by pumping, electrons in the outermost nucleus of the cadmium atom gain energy (potential energy), thereby raising the energy level.

When the electron emits light, it returns from the excited state to the ground level. Each energy level is fixed (Bohr's theory), and the wavelength emitted by electrons is a fixed wavelength. For example, in the figure below, from the ground state it emits light at 325 nm when the electron transitions to $5_s{}^{22}D_{3/2}$ and returns to $5p^2P^0{}_{2/1}$ (Figure 6).

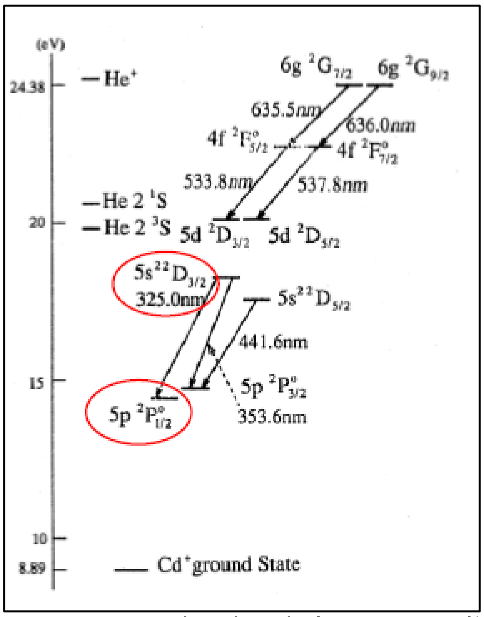

Figure 6: Energy levels relating to $He\text{-}Cd^+$ laser transitions

Although the excitation method is different depending on the laser, a similar energy transfer is achieved. Cd is the only substance that can achieve 325 nm wavelength light.

The status of the development of Diode Pump Solid State lasers (DPSS laser) with an oscillation wavelength band of 320 nm is described below. A He-Cd laser manufacturer has also been developing a DPSS 320 nm band laser that complies with the RoHS Directive. It is a laser that excites a fluoride-doped fibre with a semiconductor laser and converts red fundamental laser light into UV light with a wavelength conversion element. The laser has an oscillation wavelength of 318±1 nm and an output of 100 mW, which is similar to a He-Cd laser. As such, it is considered an alternative laser for many of the applications that use He-Cd lasers. Currently, they are verifying whether DPSS lasers can actually be used in many applications, including Raman spectroscopy. Today the specifications of this laser do not match what is required for Raman spectroscopy, so they are conducting various evaluations to improve the quality of the laser, and they plan to place it on the market in the near future.

Raman spectroscopy has the following requirements, which are stability of the wavelength value (better than 0.1 cm^{-1}, which is 0.001 nm for 325 nm excitation, when you are measuring stress in semiconductors) and the laser power (>20 mW).
Recently, semiconductor lasers operating with a 320 nm wavelength have been released by some laser manufactures. However, in these products the laser wavelength is generally unstable because the resonator length is impacted by the temperature of both the laser body and atmosphere. As a result, the wavelength value shifted by approximately 0.1 to 1 nm which inevitably affects the Raman measurement, making it impossible for correct spectral peak analysis (a Raman peak is typically 0.01 nm wide, and its position is expected at the same precision level). [3]The semiconductor laser is not still suitable as an alternative. Wavelength variations/instability also affect the Rayleigh filters, making it impossible to guarantee Raman spectra close to the laser line.

325nm He-Cd lasers for Raman spectroscopy typically offer the following advantages and disadvantages listed below;

- Advantages

- With certain samples, UV laser excitation can interact in different ways not possible when using visible laser sources. For example, in materials, such as Si, as mentioned above, the penetration depth of UV light is typically in the order of a few nanometres, and thus UV Raman can be used to selectively analyse a thin, surface layer, as is commonly found in biological moieties, in particular protein, DNA and RNA structures.
- Fluorescence suppression can often be assisted using UV lasers, by spectrally separating the Raman and fluorescence signatures. With visible lasers it frequently occurs that Raman and fluorescence are superimposed, and the incomparable strength of the fluorescence is what can perturb (or completely

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[3] Philippe de Bettignies, "Optics/instrumentation: Micro-Raman spectroscopy: theory and application" Physical Sciences Reviews, vol. 5, no. 1, 2020, pp. 20190027. https://doi.org/10.1515/psr-2019-0027

mask) the Raman spectrum. With UV excitation, the Raman spectrum lies close to the laser line, whereas the fluorescence is often shifted to higher wavelengths. Thus, they no longer overlap, and the fluorescence is no longer an issue.

- Disadvantages

- Cadmium is used, which is a restricted substance under the RoHS Directive.

Table 2 presents a comparison of the characteristics of a Raman spectrometer compared with other type of analysers that operate near UV wavelengths. Raman spectroscopy enable analysis of the physical properties of gases, liquids and solids, and has many different applications beyond metal material structure analysis in the ultraviolet, visible and infrared ranges.

A fluorescence meter measures the fluorescence or light emitted by different fluorescing objects. A fluorescence meter cannot be used for crystal analysis and stress analysis.

A spectrophotometer absorbs the lights of solutions and gases, and it measures concentrations, characteristics and molecule structures. A spectrophotometer cannot be used to analyse solids materials.

Table 2: Comparison of analytical methods for detecting ultraviolet spectrum

		Analytical methods for detecting ultraviolet spectrum		
		Raman Spectrometer	Fluorescence meter	Spectro-photometer
Wavelengths range	γ-ray	Unable	Unable	Unable
	X-ray	Unable	Unable	Unable
	UV	Able	Able	Able
	Visible	Able	Able	Able
	Infrared	Able	Able	Unable
	Micro	Unable	Unable	Unable
	Electric/wave	Unable	Unable	Unable
Sample type of analysis	Gas	Able	Able	Able
	Liquid	Able	Able	Able
	Solid	Able	Able	Unable
Applications of the scope	Metal material structure analysis	Unable	Unable	Unable
	Inorganic compounds material structure analysis	Able	Able	Unable
	Organic compounds material structure analysis	Able	Able	Able
	Crystal analysis	Able	Unable	Unable
	Stress analysis	Able	Unable	Unable

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

As discussed in 6(A), no substitution is possible.

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.

Cadmium-free lasers have been developed as described above in section 6 (A).

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

No substitutions are currently possible as described in section 6.
The substitute lasers are being developed, but at present there are no substitutes with satisfactory characteristics.
When the laser characteristics have been improved, the equipment manufacturer will conduct functional evaluations. The equipment manufacturer will conduct a detailed performance and stability evaluation. At the same time, the system for procurement, manufacturing and service will be improved.
ERA Technology (2006) stated: "The new product development time for many Category 8 and 9 products is over 4 years and can be 7 years or longer." [4]
It is therefore estimated that it will take 4-7 years to develop the equipment after the characteristics of the substitute laser are improved.

Note that equipment manufacturers sometimes change electronic circuits and mechanical designs in order to adopt substitute lasers, and it is therefore not appropriate to describe the equipment manufacturer's schedule in general.

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[4] ERA Technology (2006) , Review of Directive 2002/95/EC (RoHS) Categories 8 and 9 – Final Report, 2006 , p.29 https://ec.europa.eu/environment/waste/weee/pdf/era_study_final_report.pdf

8. Justification according to Article 5(1)(a):

(A) Links to REACH: (substance + substitute)

1) Do any of the following provisions apply to the application described under (A) and (C)?

☒ Authorisation

☒ SVHC
☒ Candidate list
☐ Proposal inclusion Annex XIV
☐ Annex XIV

☒ Restriction

☒ Annex XVII
☐ Registry of intentions

☐ Registration

2) Provide REACH-relevant information received through the supply chain.
Name of document: Not available.

(B) Elimination/substitution:

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

☐ Yes. Consequences? ______

☒ No. Justification: As described in this document, cadmium-free lasers cannot be substituted due to their inferior performance.

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

☐ Yes.

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

☒ No.

Justification: Please see Section 6(B).

3. Give details on the reliability of substitutes (technical data + information): Substitutions do not exist.
4. Describe environmental assessment of substance from 4(A)1 and possible substitutes with regard to
   1) Environmental impacts: As described in section 5, waste lasers are returned to a laser supplier outside the EU, and refurbished by the supplier. There is no cadmium which originates from the He-Cd lasers that remains in the EU.
   2) Health impacts: Not applicable.
   3) Consumer safety impacts: Not applicable.

⇨ Do impacts of substitution outweigh benefits thereof?
Please provide third-party verified assessment on this: Not available.

(C) Availability of substitutes:

a) Describe supply sources for substitutes: Not applicable. Please see Section 6(B).

b) Have you encountered problems with the availability? Describe: Not applicable. Please see Section 6(B).

c) Do you consider the price of the substitute to be a problem for the availability?

☐ Yes ☐ No Not applicable.

d) What conditions need to be fulfilled to ensure the availability? Not applicable. Please see Section 6(B).

(D) Socio-economic impact of substitution:

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

☐ Increase in direct production costs

☐ Increase in fixed costs

☐ Increase in overhead

☒ Possible social impacts within the EU

☐ Possible social impacts external to the EU

☐ Other: ______

⇨ Provide sufficient evidence (third-party verified) to support your statement: Not applicable. Please see Section 6 (B).

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9. Other relevant information

Please provide additional relevant information to further establish the necessity of your request:

None.

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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:

None.
