

Questionnaire 1 (Clarification) for Exemption IV-10 (PE et al.)

Current wording of the exemption IV-10

Table 1: Currently valid wording of exemption IV-10

No.	Current exemption wording	Current scope and dates of applicability
IV-10	Lead and cadmium in atomic absorption spectroscopy lamps	<p>Applies to categories 8 and 9.</p> <p>Expires on</p> <ul style="list-style-type: none"> - 21 July 2021 for category 8 other than in vitro diagnostic medical devices and for category 9 other than industrial monitoring and control instruments. - 21 July 2023 for category 8 in vitro diagnostic medical devices. - 21 July 2024 for category 9 industrial monitoring and control instruments.

Acronyms and Definitions

AAS	Atomic absorption spectrometry
Cat.	Category, referring to the categories of EEE specified in Annex I of the current RoHS Directive 2011/65/EU
Cd	Cadmium
COM	European Commission
CS-AAS	Continuum light source AAS
CS-AAS	Continuous spectrum AAS
CVG-AAS	Chemical vapour generation AAS
EDL	Electrodeless discharge lamp
EEA	European Economic Area (EU 27 + Iceland, Liechtenstein and Norway)
EEE	Electrical and electronic equipment
EU	European Union
F-AAS	Flame AAS
GF-AAS	Graphite furnace AAS
HCL	Hollow cathode lamp
Hg	Mercury
IMCI	Industrial monitoring and control instruments

LS-AAS	Line source AAS, umbrella term for other types of AAS like CVG-AAS, F-AAS, etc.
Pb	Lead
PE	Perkin Elmer
X-free	Not containing restricted substance X in the applications in scope of the exemption to be reviewed, i.e. X = cadmium and/or lead.

1. Background

Bio Innovation Service, UNITAR and Fraunhofer IZM have been appointed¹ by the European Commission through for the evaluation of applications for the review of requests for new exemptions and the renewal of exemptions currently listed in Annexes III and IV of the RoHS Directive 2011/65/EU.

Agilent Technologies, Perkin Elmer et al. submitted a request for the renewal of the above exemption as detailed in the below table.

Table 2: Requested exemption renewal

No.	Requested exemption	Requested scope and dates of applicability
IV-10	Lead, cadmium, <u>and mercury</u> in atomic absorption spectroscopy lamps	Applies to category 9 industrial monitoring and control instruments. Expires on 21 July 2031 (2024 +7 years)

Underlined phrases: Deviations from current wording

As result of a first review we identified that some information is missing. Against this background the questions below are intended to clarify some aspects concerning the request at hand.

We ask you to kindly answer the below questions until 2 October 2023 latest.

General remark:

We understand that some information is sensitive and therefore confidential. It is, however, important to highlight that the consultants cannot recommend granting exemptions based on confidential available information. Confidential information may provide helpful background for the consultants' understanding but applicants must make facts publicly available that are essential for the renewal of exemptions if they shall be used to substantiate an exemption request.

¹ Implemented through the specific contract 070201/2020/832829/ENV.B.3 under the Framework contract ENV.B.3/FRA/2019/0017



2. Questions

1. Could you please confirm that Table 2 correctly reflects the requested renewal of the exemption?

Yes, table 2 does.

2. You indicated the volumes of restricted substances put on the EU market as follows:

- *Lead: 99 kg*
- *Mercury: 10 g*
- *Cadmium: 45 kg*

- a. The above numbers are based on the sales and market shares of producers. Does this include all producers' or only the applicants' sales?

The above numbers are an estimate of the total expected volumes of the restricted substances being placed on the market under the renewed exemption. The estimate is based on extrapolating sales and market share data, made available by applicants.

- b. If the figures refer to the applicants only, what would be the total expected volumes of the restricted substances being placed on the EU market under the renewed exemption?

Please see response to 2a., these are the expected volumes for the entire market.

3. Are there other manufacturers of LS-AAS systems that can be used for the analysis of Cd, Hg and Pb in samples that are not represented in the group of applicants for this exemption renewal request? Please name at least five of them if viable.

Additional manufacturers of LS-AAS systems that were not represented in the group of applicants^[1] include the following (this is not a fully exhaustive list). The applicants are aware of the following companies (but it is noted that not all of these manufacturers will have representation or sales and service distribution within Western and Eastern Europe):

- Thermo Fisher Scientific
- Persee PG Scientific Inc.
- Buck Scientific, Inc.
- GBC Scientific Equipment

- Aurora Biomed Inc.
- Shanghai Spectrum Instruments co., LTD.
- Jiangsu Skyray Instrument Co., Ltd.
- Chongqing Drawell Instrument Co., Ltd.
- Nanbei Instrument Limited
- Macylab Instruments Inc.
- Zhengzhou Laboao Instrument Equipment Co., Ltd. (LABOAO)
- Anhui Wanyi Science and Technology Co., Ltd.
- Biobase Biodustry (Shandong) Co., Ltd.

^[1] Please note amongst the applicants are JBCE which includes Hitachi High-Tech Corporation and Shimadzu as AAS system manufacturers.

4. You explain that EDL require by far less of the restricted substances (factor ~ 5,000 for lead) compared to HCL considering that the life time of the EDL is only around 50 % of the HCL life time. The use of EDL instead of HCL will thus considerably reduce the use of the restricted substances. You state that the shift from HCL to EDL would require a 10 year transition period since so far only one of the applicants offers a commercial EDL-based LS-AAS.
- a. Does the use of EDLs for AAS require more electrical and electronic circuitry compared to HCL?

Yes. This would require changes to items such as the power supply of the lamp as the operation of the EDL requires an RF field to be applied to the bulb to first ionize the inter gas fill, and then excite the vaporized analyte atoms inside the bulb. This requires a separate power supply to be incorporated into the AAS instrument.

- b. Since when are EDL bulbs commercially available for use in LS-AAS for detection of Cd, Hg and Pb?

The first use or description of EDLs specially designed for AAS is from 1973².

- c. We understand that a shift from HCL to EDL requires redesigns and adaptations of the platforms and thus time. The availability of a commercial EDL-based solution shows that the reduction of the restricted substances in LS-AAS lamps is not only scientifically and technically practicable but that it could be achieved in the available time until the expiry of exemption IV-10.

² Barnett, W.B.: At. Absorption Newslet. 12, 142 (1973).



Why should exemption IV-10 still be extended beyond 2024 without a restriction to the use of Cd, Hg and Pb in EDL lamps only?

Currently, there is only one applicant that offers instrumentation that can support or be used with the EDL lamps. While this is a major supplier, they do not have a dominant share in the market.

Users of AAS instrumentation from other manufacturers would then be forced to upgrade their instrumentation before it is at the end of its working life – or else, modify their existing instrumentation to enable the use of the EDL. This would require support and assistance from the manufacturer to provide/install the EDL driver (Radio Frequency (RF) power source) and the associated mechanical, electrical, firmware & software interfaces. There is no guarantee that this is technically feasible in every instance.

In addition, there is an associated risk that the instrument with the addition of the RF power source may no longer be CE compliant – and that the instrument is not able to be retro-fitted with appropriate connectors, shielding or other modifications required to enable it to satisfy both the radiated and conducted immunity test limits especially, to ensure that CE compliance was retained. This requires considerable expense to retrofit the older AAS systems with the upgrade – and especially to ensure the upgraded system remains CE compliant. Consequently, there is a high risk of premature retirement of stranded AAS instruments, which imposes a further potential recycling and waste issue.

5. Is CS-AAS considered a LS-AAS as well?

No CS- is 'continuum source' and uses a different type of light source and platform to LS- 'line source' technology.

The CS- technology requires a completely different spectrometer design to LS-. Due to these design differences (optically high resolving light profile and a comparatively low resolving spectrometer) LS-AAS is able to operate in a wider range of environments, including production areas, non air-conditioned environments and non-clean room conditions which are necessary for CS-AAS and ICP- OES.

6. You state that the exemption would be applied in LS-AAS.

a. Is AAS only practiced as LS-AAS, or are there other types of AAS?

There are, continuum light source and solid state light source AAS technologies, but as discussed in section 6 of the submission these are not considered a replacement for LS-AAS in all instances.

Laser Diode AAS has been used in research applications, but it is limited in the wavelength range that can be covered (generally in the range from 640–930 nm where laser diodes are commercially available – this excludes determinations of Cd, Pb and Hg). This restricts its commercial applicability.

- b. If so, do these types of AAS also depend on the use of Cd, Hg and Pb? If applicable, please explain which ones and whether they also require the lamps used in LS-AAS.

There are other light source technologies such as continuum and UV-LEDs which do not depend on the use of Cd, Hg and Pb, but as discussed in section 6 of the submission these are not considered a replacement for LS-AAS in all instances.

Could the scope of the renewed exemption be restricted to LS-AAS?

Lead, cadmium, and mercury in line source atomic absorption spectroscopy lamps

Yes

7. You state on page 17 of your renewal application: *“In some applications, line source AAS is still considered to be the optimal test method to CS-AAS.”*

What exactly does this statement want to express, and to which “some applications” does this statement apply?

Further details of these were shared in confidential submission 08 Confidential EU exemption IV-10 renewal. Unfortunately, this information cannot be publicly shared.

8. ICP-OES as potential alternative

- a. You explain why ICP-OES is no alternative to LS-AAS. On page 18 you explain the role of the plasma:

“The plasma ionises the elements of interest in the sample.”

Does this imply that elements can be ionised fully or partially selectively in a sample? Could, for example, Cd be ionised selectively in a sample containing other elements as well, or could at least some elements in the sample maintain their elemental form while others e.g. with a lower excitation energy than Cd would be ionised together with Cd (partially selective ionisation)?

Ionization in a plasma depends on the plasma (electronic) temperature and the density of electrons/ ions in the plasma. It is generally accepted that the elements are fully ionized in the hottest or central channel of the plasma used in the ICP-OES technique.



The idea that some elements may maintain their elemental form to enable partially selective ionization is incorrect.

There may be ways to modify these parameters to some extent. However, this may not be possible and the big advantage of ICP-OES is its multielement capability, the physical and chemical conditions in a plasma may be compromised in such a situation. This could lead to a wanted ionization ratio for some elements and an unwanted one for other elements.

- b. If a (partially) selective ionisation is feasible, the “Complexity of use” which you describe on page 19 would be largely reduced, in particular steps a), c), and e), and ICP-OES would be more attractive as a potential alternative. Please kindly comment.

As described in a) the issue in most cases is spectral overlap and spectral interferences. Sophisticated plasma conditions may minimise that to some extent. But the technique is still competing against the spectrally interference-free AAS and therefore will always be inferior.

- c. You describe the various preparatory steps. We wonder whether step a) of your description (“crude analyses” and step b) “wavelength selection based on the result of step a)” are actually required for an analysis where the presence and content of Cd, Hg or Pb is to be assessed, i.e. the sample will be screened for these elements only. This task would in our understanding define the wavelengths to be selected. It seems that the steps you describe might be more applicable to a full analysis of an unknown sample rather than a dedicated analyses of Cd, Hg or Pb in a sample.

In case, please correct our view and kindly let us know why it is incorrect.

It was noted in the submission that these steps (step a) crude analysis and step b), wavelength selection) are essential steps in the method development process.

Even if you only want to analyse these few elements, there may be an impact of other (unknown and unwanted) elements to method development. Cd lines can be affected by Fe and As lines (soil analysis), Pb can be affected by Fe or Al.

Once a method has been developed for a specific sample type, in most cases, routine analyses can be completed without requiring those specific preparatory steps. However even then, the user needs to be aware of other potential issues that can occur, including higher concentration samples that may induce unexpected spectral interferences and/or memory effects, errors associated with sample preparation etc.

If the analysis for Cd, Hg or Pb is required on a different sample type, then the method development steps outlined in the submission will be required.

- d. We wonder whether step e) – and thus also step a) might not be required for LS-AAS as well. Or can it be excluded that any other substance in the sample may have absorption bands that are very close to Cd, Hg or Pb respectively?

Spectral interferences in AAS cannot be excluded completely but there are technical means (physical/technical working background correctors which completely compensate these spectral interferences). These instrumental means do not exist in ICP-OES.

9. You claim that *“The ICP-OES technique is in most cases not sensitive enough (% to ppb) to reach the detection limits of GF-AAS (ppm to ppt), especially for lead. So, this quantification technique is no alternative to GF-AAS and ICP-MS (ppm to ppt) for many applications.”*
 - a. Isn't the sensitivity and the sensitivity range of ICP-OES (% to ppb) not even higher and broader than that of GF-AAS (ppt to ppm)?

Yes, the sensitivity range of ICP-OES is broader than that of GF-AAS – but importantly, it does not have the same detection capability so the low end of the working range and the detection limits achieved with GF-AAS (from ppt levels) are generally an order of magnitude better (lower) than that achieved with the ICP-OES technique.

- b. Why is ICP-OES not only no alternative to GF-AAS but to ICP-MS neither? Could ICP-MS be used as an alternative to GF-AAS?

The sensitivity of ICP-MS rivals and even exceeds that of GF-AAS – so this can be an alternative to GF-AAS for some applications. However, it is not possible for ICP-MS to replace every application where GF-AAS is used.

GF-AAS still provides unique functionality which is not able to be replaced by ICP-MS where:

- The sample volume is limited. GF-AAS consumes just microlitres of sample for analysis at trace levels, which makes it ideal for handling samples where limited sample volume is available.
- The level of dissolved solids in the sample is high, as the generally accepted limit for ICP-MS is 2000 ppm Total Dissolved Solids (TDS), though this can vary depending on matrix type. Although a simple dilution with a dilute acid matrix can be used to bring the TDS level into range, this may not always be possible,



especially when measuring trace levels. This extra dilution may mean the elemental concentration in the diluted sample is now below the instrument detection limit – so the concentration is no longer quantifiable. By contrast, GF-AAS is a technique that can tolerate much higher levels of dissolved solids in the sample, so this limitation is removed.

- The number of elements and samples that are to be determined is low.

Please note that answers to these questions will be published as part of the evaluation of this exemption request. If your answers contain confidential information, please provide a version that can be made public along with a confidential version in which proprietary information is clearly marked.

We ask you to kindly provide the information in formats that allow copying text, figures and tables so that they can be included into the review report.