

Exemption Request Form

Date of submission: 18th January 2023

1. Name and contact details

1) Name and contact details of applicants:

Company: [PerkinElmer, Inc.](#) Tel.: [1-203-402-5378](#)
 Name: [Richard Covell](#) Email: Richard.Covell@PERKINELMER.com
 Function: [Global Compliance Engineering Manager](#) Address: [710 Bridgeport Ave., Shelton, CT 06484, USA](#)

Company: [Agilent Technologies, Inc.](#) Tel.: [1-800-227-9770](#)
 Name: [Eric Vanclay](#) Email: eric.vanclay@agilent.com
 Function: [Spectroscopy Supplies Product Manager](#) Address: [5301 Stevens Creek Blvd. Santa Clara, CA 95051 USA](#)

In addition to the named applicants above, the following companies / organizations have also contributed to and or expressed their support of this exemption renewal:

| | |
|---|--|
|  | <p>Japan Business Council in Europe (JBCE) Rue de la Loi 82 1040 Brussels – Belgium</p> |
|  | <p>Analytik Jena Analytik Jena GmbH, Konrad-Zuse-Str. 1, 07745 Jena / Germany</p> |
|  | <p>Heraeus Noblelight GmbH, Heraeusstr. 12-14, 63450 Hanau, Germany</p> |

2) Name and contact details of responsible person for this application (if different from above):

Company: N/A Tel.: _____
Name: _____ E-Mail: _____
Function: _____ Address: _____

2. Reason for application:

Please indicate where relevant:

- Request for new exemption in:
- Request for amendment of existing exemption in
- Request for extension of existing exemption in [Annex IV](#).
- Request for deletion of existing exemption in:
- Provision of information referring to an existing specific exemption in:
- Annex III Annex IV

No. of exemption in Annex III or IV where applicable: [Annex IV, no.10](#)

Proposed or existing wording:

Existing wording:

[Lead and cadmium in atomic absorption spectroscopy lamps.](#)

Proposed wording:

[Lead, cadmium, and mercury in atomic absorption spectroscopy lamps.](#)

Duration where applicable: [7 years](#)

Other: _____

3. Summary of the exemption request / revocation request

[Line Source Atomic Absorption Spectroscopy \(LS-AAS\) systems use lamps which contain lead, cadmium, or mercury. The substance is used as a reference material in the cathode of the Hollow Cathode Lamps \(HCL\) or in the bulb of the Electrodeless Discharge Lamp \(EDL\). For detecting a substance, a reference material of the same substance is required, for example to detect cadmium, a reference cathode of cadmium is required in the HCL or a bulb containing cadmium in an EDL. The primary requirement of the lamp in a LS-AAS system is to generate a narrow emission line of the substance which is being measured. The narrow spectral line width optimises the conditions for absorbance by any atoms matching the reference substance, in the sample under test. The transmitted light detected enables the accurate calculation of](#)

absorbance and therefore the determination of the concentration of the substance in the sample.

There are no alternatives for using the substance under analysis, as the reference material in HCL and EDL lamps. These are the only substances that produce the precise light spectra required in LS-AAS, for determining the concentration of the same substance in test samples.

The exemption wording has been amended to cover mercury. To date AAS lamps containing mercury have been covered under the Annex III 4(a)-I exemption – *Mercury in other low pressure non-phosphor coated discharge lamps, where the application requires the main range of the lamp-spectral output to be in the ultraviolet spectrum: up to 15 mg mercury may be used per lamp.* However, it is felt that due to the wide application scope of the Annex III 4(a)-I exemption and the use of mercury for the same technical rationale as outlined in this application, it would be preferable to limit it to AAS lamps under the Annex IV-10 exemption.

No technically viable alternatives to the use of these substances, in lamps in line source AAS systems, have been identified.

Analysis using LS-AAS has been an established methodology for over 50 years and is embedded in numerous European standards. The development of products to support these alternative methodologies and to qualify them for the wide range of established line source AAS applications is anticipated to take more than seven years and have significant implications on end users. Based on data from the Analytical Life Science & Diagnostic Association (ALDA) there is estimated to be an installed base of LS-AAS systems in Europe¹ of approximately 5000.

4. Technical description of the exemption request / revocation request

(A) Description of the concerned application:

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

Name of applications or products:

Line source atomic absorption spectroscopy lamps, incorporating lead, cadmium or mercury.

- a. List of relevant categories: (mark more than one where applicable)

¹ ALDA data covers: Western Europe, the UK, Scandinavia, Eastern Europe (Belarus, Bulgaria, Czechia, Hungary, Moldova, Poland, Romania, Russia, Slovakia and Ukraine), the Balkans (Cyprus, Greece and Turkey and the Baltics)

- | | |
|----------------------------|---------------------------------------|
| <input type="checkbox"/> 1 | <input type="checkbox"/> 7 |
| <input type="checkbox"/> 2 | <input type="checkbox"/> 8 |
| <input type="checkbox"/> 3 | <input checked="" type="checkbox"/> 9 |
| <input type="checkbox"/> 4 | <input type="checkbox"/> 10 |
| <input type="checkbox"/> 5 | <input type="checkbox"/> 11 |
| <input type="checkbox"/> 6 | |

b. Please specify if application is in use in other categories to which the exemption request does not refer: **N/A**

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:

Line source Atomic Absorption Spectroscopy (AAS) systems use lamps which contain lead, cadmium, or mercury. The substance is used as a reference material in the cathode of the Hollow Cathode Lamps (HCL) or in the bulb of the Electrodeless Discharge Lamp (EDL). For detecting a substance, a reference material of the same substance is required, for example to detect cadmium, a reference cathode of cadmium is required in the HCL, or a bulb containing cadmium in an EDL.

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

100% max.

5. Amount of substance entering the EU market annually through application for which the exemption is requested:

| | |
|----------|----------|
| Lead: | 99 140 g |
| Mercury: | 10 g |
| Cadmium: | 44 646 g |

The quantities have been calculated based on average sales and estimated market share (rounded up to the nearest gram).

Please supply information and calculations to support stated figure.

This is provided separately as the calculation includes confidential market information.

Please refer to:

05 Confidential EU exemption IV-10 renewal.pdf

6. Name of material/component:

Hollow Cathode Lamp (HCL) Cathode:

- Lead reference cathode
- Cadmium reference cathode
- Mercury reference cathode

Electrodeless Discharge Lamps (EDL) Bulb:

- Lead reference bulb
- Cadmium reference bulb
- Mercury reference bulb

7. Environmental Assessment: Not applicable as there are no suitable substitutes that have been verified to meet the technical performance required from HCL or EDL lamps in line source AAS applications.

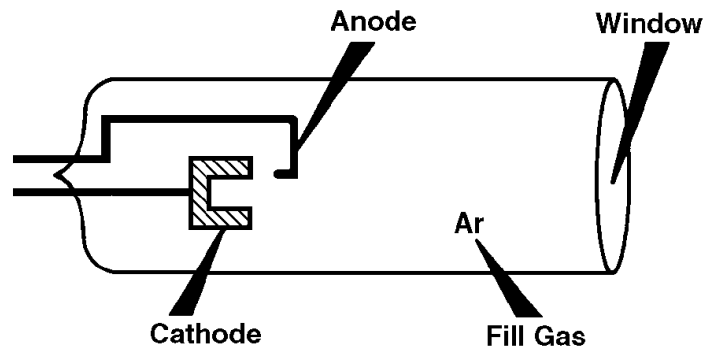
LCA: Yes
 No

(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 restricted substances (lead or cadmium or mercury) are used as a 'reference material' (substance matching that which is to be detected in the sample) in both Hollow Cathode Lamps (HCL) and Electrodeless Discharge Lamps (EDL). Both of

these lamps are types of light source used in line source atomic absorption spectroscopy (AAS) systems.

Figure 1 Hollow Cathode Lamp Schematic, cathode made of restricted substance

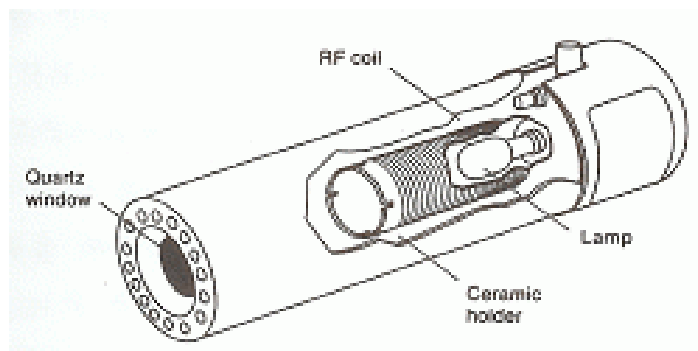


When an electrical potential is applied between the anode and cathode, some of the fill gas (typically argon or neon (shown in figure 1 as Ar), filling the inside of the lamp) atoms are ionized. The positively charged fill gas ions accelerate through the electrical field to collide with the negatively charged cathode and dislodge individual metal atoms in a process called “sputtering”. Sputtered metal atoms are then excited to an emission state. The emitted light is at a wavelength characteristic of the sputtered metal. For example, if the cathode is made from lead the emitted spectra will be characteristic of lead. Light with a specific wavelength characteristic is required for the next step in the AAS process.

When used as a reference material in an Electrodeless Discharge Lamp (EDL), the lamp contains a small quantity of the restricted substance of interest in the bulb e.g., Lead or cadmium or mercury (labelled ‘lamp’ in Figure 2). Instead of electrical

energy, an intense field of radio frequency (RF) radiation provides ionization and excitation of the metal to produce a spectrum.

Figure 2 Electrodeless Discharge Lamp schematic, with the restricted substance contained within the part labelled lamp

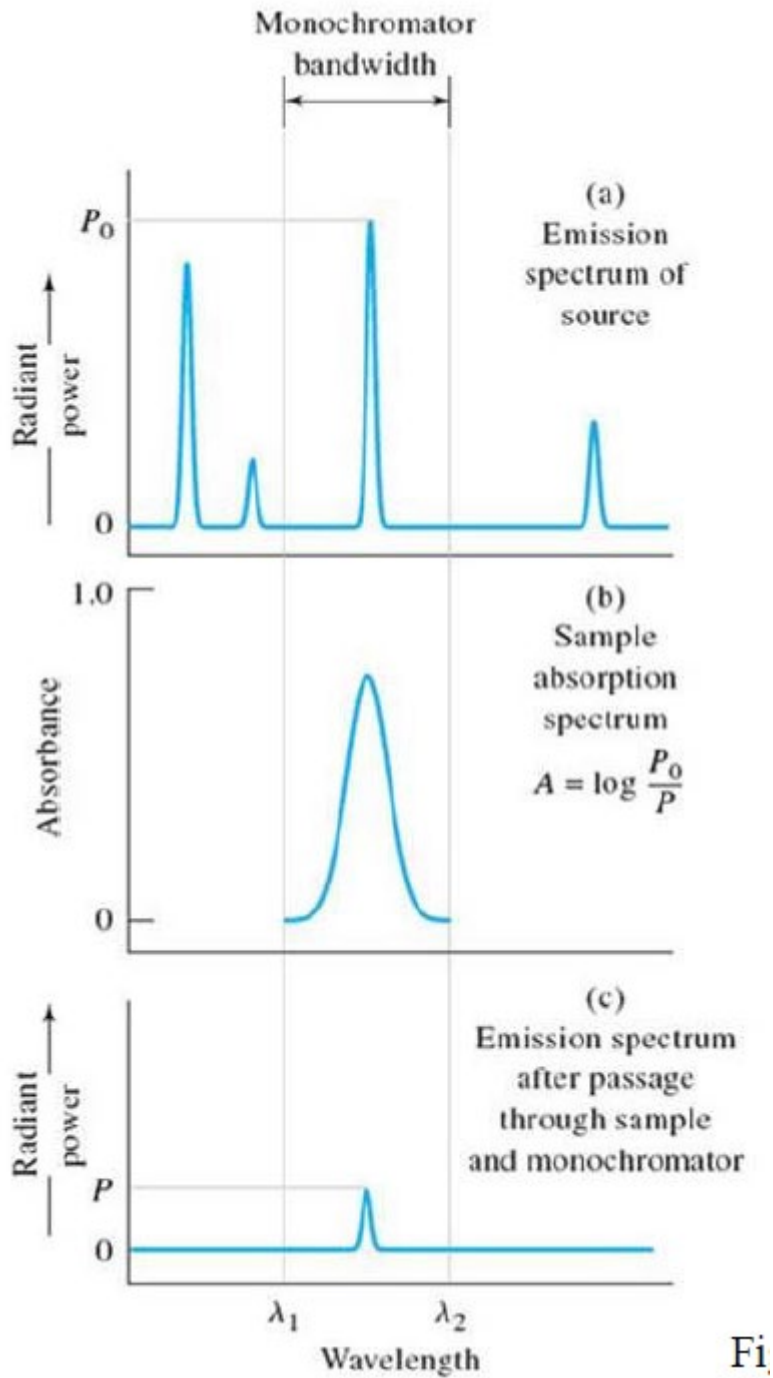


Line Source Atomic Absorption Spectroscopy:

The two lamps described above are used to produce the 'line source' (a narrow emission line of the element which is being measured) in AAS. Hollow cathode lamps establish a low pressure, ambient temperature discharge between a metal anode and a cathode containing the specific substance to be detected. The cathode material is evaporated in small amounts into the discharge by ion impact onto the cathode. By subsequent excitation in the discharge, it starts to emit the substance specific spectral lines. As a result of the low pressure and temperature in the hollow cathode lamp, the linewidth of the substance specific emission is very narrow in the order of the doppler-broadened linewidth of 10^{-3} to 10^{-4} nm. Due to the nature of the discharge conditions in a hollow cathode lamp the wavelength and the spectral linewidth of the element specific emission matches exactly or is even narrower than the spectral absorption characteristic of the specific substance to be detected in a sample. Therefore, the spectral sensitivity is high, and the signal-to-noise ratio is low, allowing the characterisation of samples when only containing very low levels of the substance (parts per quadrillion (ppq), for some applications).

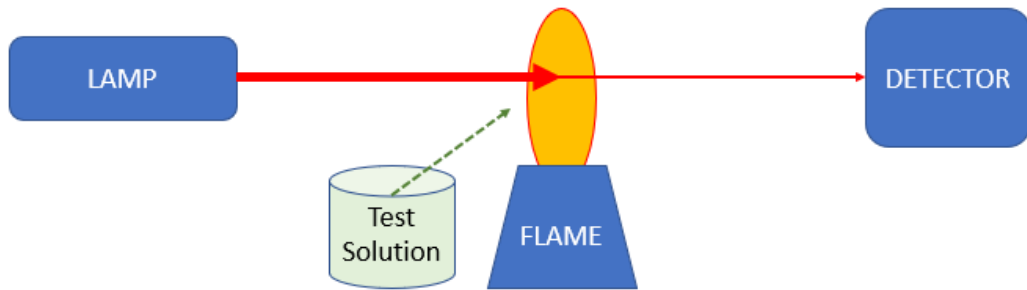
The first plot in Figure 3 shows the narrow bandwidth of the primary wavelength of light produced by the lamp. This is narrower than the absorption bandwidth (see second plot) of the sample under analysis and narrower than the bandwidth of the detector (monochromator).

Figure 3 Examples of Spectra



Line source atomic absorption spectroscopy (AAS) has been established for over 50 years as an analysis technique used to determine the concentrations of metals. It is widely used to analyse alloys, ceramics, plastics, and other materials.

Figure 4 - AAS system schematic



There are various procedures to prepare a sample for testing, so that it can be sprayed into a hot flame. Normally liquid samples or solid samples need to be digested in strong acid for the matrix to be broken down and then diluted and injected into the flame/furnace.

Only a small sample size is required, between μg and mg , depending on the sample introduction methodology.

The lamps (HCL or EDL) described above are used to generate a specific wavelength of light to detect lead or cadmium or mercury in the sample being analysed. For example, Pb hollow cathode lamps have their principal wavelength at 217.0 nm, Cd hollow cathode lamps at 228.8 nm and Hg lamps at 253.7 nm. Those wavelengths cannot be addressed by spectral lines of other elements in a discharge lamp as the emission wavelength is wholly dependent on the specific element. One strong line in the spectrum is chosen (one where any other metals present will not interfere) and this light passes through the flame where any vaporised atoms of the test metal will absorb light of the wavelength chosen. There is a logarithmic relationship between absorbance and the ratio of incident intensity and transmitted intensity (transmittance) as given below.

$$A = \log_{10} \frac{I_0}{I}$$
$$A = -\log_{10} T$$

A - Absorbance

I_0 – Incident intensity

I – Transmitted intensity

T - Transmittance

The light that has passed through the flame is measured using a monochromatic detector (an optical device that selects and transmits a specified wavelength) set at the required wavelength. The detector produces an electrical signal that is proportional to the intensity of light. The intensity value is compared with the known intensity of that emitted from the lamp, from which the absorbance can be calculated.

Applying the Beer-Lambert Law (Beer's Law), which defines the linear relationship between absorbance, concentration, the molar absorption coefficient, and the optical coefficient of a solution it is then possible to determine the concentration of the test substance (lead / cadmium / mercury) in the test solution:

$$A = \epsilon cl$$

| | | |
|------------|------------------------------|----------------------------------|
| <i>A</i> | Absorbance | |
| ϵ | Molar absorption coefficient | M ⁻¹ cm ⁻¹ |
| <i>C</i> | Molar concentration | M |
| <i>l</i> | optical path length | cm |

There are a number of different types of line source AAS, including:

- FAAS – Flame AAS, as described above.
- GFAAS – Graphite Furnace AAS
- CVG-AAS – Chemical Vapour Generation AAS

They all use the line source lamps described above, the differences are related to the sample introduction and atomisation of the sample.

End Use Applications:

The detection and monitoring of toxic and eco-toxic elements such as lead, cadmium and mercury is essential to prevent the exposure to humans and the environment with these toxic elements.

End use applications include:

- Environmental testing for contaminants or pollutants,
 - For example, the mining and metal processing industry can add pollution to the air in the form of dust, to the water in the form of 'washings' from ore processing and the land in the form of waste heaps.
 - Another example of a critical application would be for the analysis of drinking water for harmful contaminants.²
- Pharmaceuticals (manufactured pharmaceuticals),
 - For example, in the quality control process to ensure a pharmaceutical product is free from heavy metals such as cadmium, mercury & lead.^{3,4}
- Food (contaminants),
 - Heavy metals like arsenic, cadmium, mercury, and lead can enter the food chain through the water, air, and soil. Although usually present at trace levels, the toxicity of heavy metals, even at low levels, requires very sensitive analysis of metals in foods to ensure safe levels that meet regulatory requirements.⁵
- Industrial (raw materials, finished goods) and
- Clinical testing (for research purposes rather than diagnostic purposes).
 - For example, for detecting lead levels in blood.⁶

The use of line source AAS for detecting lead, cadmium and mercury is well established in a number of application areas, this is further demonstrated by its adoption by a large number of European Standards. Across the various application sectors, appropriate analytical methods are prescribed by standards. Numerous standards require the use of AAS, explicitly by means of Hollow Cathode Lamps (HCL). A non-exhaustive list of these standards is outlined in Table 1, all of which mandate the use of AAS as a methodology.

Table 1 - Standards adopting AAS for the detection of lead, cadmium and/or mercury

| Standard | | Title |
|----------|-----|---|
| DIN EN | 237 | Liquid petroleum products - Petrol - Determination of low lead concentrations by atomic absorption spectrometry |

²C.Radulescu.Determination of heavy metal levels in water and Therapeutic mud by atomic absorption spectrometry. Romanian Journal of Physics 59(9-10):1057–1066,October2014.

| Standard | | Title |
|-------------------|---------|---|
| DIN EN ISO | 5961 | Water Quality; Determination of cadmium by atomic absorption spectrometry; (ISO 5961:1994) |
| EN | 10181 | Steels - Determination of lead content - Flame atomic absorption spectrometric method (FAAS) |
| DIN ISO | 11047 | Soil Quality - Determination of cadmium , chromium, cobalt, copper, lead , manganese, nickel, and zinc in aqua regia extracts of soil - Flame and electrothermal atomic absorption spectrometric methods (ISO 11047:1998) |
| EN ISO | 12193 | Animal and vegetable fats and oils - Determination of lead by direct graphite furnace atomic absorption spectroscopy |
| CEN EN | 14082 | Foodstuffs - Determination of lead, cadmium , zinc, copper, iron, and chromium by atomic absorption spectrometry (AAS) after dry ashing |
| CEN EN | 14083 | Foodstuffs - Determination of trace elements - Determination of lead, cadmium , chromium, and molybdenum by graphite furnace atomic absorption spectrometry (GFAAS) after pressure digestion |
| CEN EN | 14084 | Foodstuffs - Determination of trace elements - Determination of lead, cadmium , zinc, copper, and iron by atomic absorption spectrometry (AAS) after microwave digestion |
| CEN EN | 15550 | Animal feeding stuffs: Methods of sampling and analysis - Determination of cadmium and lead by graphite furnace atomic absorption spectrometry (GF-AAS) after pressure digestion |
| CEN EN | 16277 | Animal feeding stuffs - Determination of mercury by cold-vapour atomic absorption spectrometry (CVAAS) after microwave pressure digestion |
| CEN EN ISO | 11212-2 | Starch and Derived Products - Heavy Metals Content - Part 2: Determination of Mercury Content by Atomic Absorption Spectrometry |
| CEN EN ISO | 11212-3 | Starch and derived products - Heavy metals content - Part 3: Determination of lead content by atomic absorption spectrometry with electrothermal atomization |
| CEN EN ISO | 11212-4 | Starch and Derived Products - Heavy Metals Content - Part 4: Determination of Cadmium Content by Atomic Absorption Spectrometry with Electrothermal Atomization - Incorporating Corrigendum September 1997 |
| CEN EN ISO | 12846 | Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment (ISO 12846:2012) |

³ Nessa F, Khan SA, Abu Shawish KY. Lead, Cadmium and Nickel Contents of Some Medicinal Agents. Indian J Pharm Sci. 2016 Jan-Feb;78(1):111-9. doi: 10.4103/0250-474X.180260. PMID: 27168689; PMCID: PMC4852560.

⁴ Nancy S. Lewen, Martha M. Schenkenberger, Atomic Spectroscopy, Pharmaceutical Applications, Pages 107-114, Encyclopedia of Spectroscopy and Spectrometry (Third Edition), ISBN 9780128032244.

⁵ Flame Atomic Absorption Spectrophotometry Analysis of Heavy Metals in Some Food Additives Available in Baghdad Markets, Iraq. Indian Journal of Forensic Medicine and Toxicology, October 2020. Abdulwahid, Dawood, Mohammed, Jamur.

⁶ [Determination of lead in blood by graphite furnace atomic absorption spectrometry with Zeeman background correction: Improving a well-established method to support a lower blood lead reference value for children - ScienceDirect](#)

| Standard | | Title |
|-------------------|---------|---|
| CEN EN | 13094-2 | Lead and cadmium in metallic items in contact with the body - Part 2: Flame atom absorption spectrometry (F-AAS) after acidic extraction |
| CEN EN | 13806 | Foodstuffs - Determination of trace elements - Determination of mercury by cold-vapour atomic absorption spectrometry. (CVAAS) after pressure digestion |
| CEN EN ISO | 14902 | Ambient air quality – Standard method for the measurement of Pb, Cd , As and Ni in the PM10 fraction of suspended particulate matter |
| CEN EN | 15411 | Solid recovered fuels – Methods for the determination of the content of trace elements (As, Ba, Be, Cd , Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb , Sb, Se, Tl, V and Zn) |
| CEN EN ISO | 15774 | Animal and vegetable fats and oils - Determination of cadmium content by direct graphite furnace atomic absorption spectrometry |
| DIN EN | 15841 | Ambient air quality – Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition |
| CEN EN | 16175-1 | Sludge, treated biowaste and soil - Determination of mercury - Part 1: Cold-vapour atomic absorption spectrometry (CV-AAS) |
| DIN | 38406-6 | German standard methods for the examination of water, waste water and sludge - Cations (group E) - Determination of lead by atomic absorption spectrometry (AAS) (E6) |
| DIN | 54605 | Testing of pulp, paper and board; atomic absorption spectrometric determination of the cadmium content |
| CENELEC EN | 62321-4 | Determination of certain substances in electrotechnical products - Part 4: Mercury in polymers, metals, and electronics by CV-AAS, CV-AFS, ICP-OES and ICP-MS - Incorporates Amendment A1: 2017 |
| CENELEC EN | 62321-5 | Determination of certain substances in electrotechnical products - Part 5: Cadmium, lead and chromium in polymers and electronics and cadmium and lead in metals by AAS, AFS, ICP-OES and ICP-MS |

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.)

A closed loop system does exist.

2) Please indicate where relevant:

Article is collected and sent without dismantling for recycling (complete AAS system containing lamps & lamps that have reached end of life)

Article is collected and completely refurbished for reuse

Article is collected and dismantled: (complete AAS system containing lamps & lamps that have reached end of life)

The following parts are refurbished for use as spare parts: _____

The following parts are subsequently recycled: AAS lamps and reference cathode materials.

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 _____

In articles which are recycled

It is assumed that the lamps recycled will approximately equate to lamps purchased so the quantities given in section 4(A), 5, will apply here also.

In articles which are sent for energy return _____

In articles which are landfilled _____

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

Line Source Lamp Alternatives

There are no alternatives for using the substances under analysis, as the reference material in HCL and EDL lamps. These are the only substances that produce the precise light spectra

required in line source AAS for determining the concentration of the same substance in test samples.

It is notable that the EDL utilises less of the restricted substance in comparison with HCL, for example for lead, the EDL contains less than 1mg of lead compared with HCL, which contains 8-12 g lead. So, although it would not eliminate the use of lead, cadmium, or mercury in line source AAS lamps, a change to solely EDL lamps would result in a reduction in the use of the restricted substances. In order for EDL lamps to be used in place of HCL lamps in line source AAS systems, modification to the systems would be required, including but not limited to the addition of an EDL driver (High Frequency (HF) power source), mechanical, electrical, firmware & software interfaces. Currently only one of the applicants has explored this option and have a commercial solution. The development time for the other applicants would be similar to the development of a new platform as detailed in section 7B (around 10 years). This option would not eliminate the use of the substances but would result in a 99% reduction of the quantities of restricted substances involved.

Eliminating lead, cadmium & mercury from HCL & EDL would result in the removal from the market of the option of line source AAS for detecting these substances.

Alternative light sources

Solid state light sources, like UV LEDs do not utilise any of the restricted substances but offer the flexibility to adjust their peak wavelength by adjusting the design and composition of the active region of the semiconductor. However, UV LED devices with peak wavelength <250 nm are currently not commercially available and therefore would not be able to undertake testing for lead and cadmium which are at 217.0 nm and 228.8 nm respectively.

Another challenge with using a different light source of the same wavelength, but different spectral line width is that it would reduce the sensitivity drastically. UV-LEDs for example are adjustable in wavelength but have a typical spectral linewidth of around 10 nm. As a result, >99.9% of the light will not be absorbed by the absorption line of Cd, Pb or Hg in the sample but would still arrive at the detector. This increases the background signal by a factor >1000 and reduces the signal to noise-ratio correspondingly. Although the peak wavelength of alternative light sources may be the same, this is not a viable approach for detection of low levels of specific trace elements in AAS. The perfect match of emission and absorption characteristic of the spectral line can only be achieved by using the substance to be detected in the sample as the light emitting reference substance in the lamp.

Continuum Light Source

An alternative to HCL or EDL lamps is a continuum light source (CS) e.g. Xenon lamp, rather than a line source. A continuum light source emits radiation over a broad range of wavelengths. A continuum light source could not be used in the existing platform for an HCL/EDL based AAS. This is because the monochromators in these systems would provide too large a spectral bandwidth resulting in poor sensitivity and specificity, non-linear calibration curves and greater susceptibility to spectral interferences. In addition, the intensity of most CS decreases dramatically below 280 nm, to levels not detectable by a line source

monochromator; consequently, the use of a CS for AAS requires re-design of the whole instrument⁸.

There is only one known example of a commercially available AAS system, using a continuum source, (HR-CS AAS), launched in 2011 and manufactured by Analytik Jena. This system provides simultaneous multi element analysis. Whilst it can perform the analysis carried out by traditional (HCL & EDL based) AAS systems, it is considered overly complex in terms of hardware and software for applications where single element analysis is required or where sequential multi element analysis is not required. This is reflected by the fact that Analytik Jena continue to market their traditional AAS systems. Having been launched in 2011 it is still relatively new to market compared with line source AAS systems which have been around for over 50 years. Consequently, the adoption of this technology and qualification of testing on different sample types/applications is still relatively low, there are no known standards prescribing the use of this technology. In some applications, line source AAS is still considered to be the optimal test method to CS-AAS. Further details of these are shared in confidential submission 08 Confidential EU exemption IV-10 renewal. Section 7B details the steps that manufacturer's (other than Analytik Jena) would need to take in developing a new system platform based on a continuum source. The total time to market for an equipment manufacturer to develop such a technology is estimated to be around 10 years. This is before the conversion / qualification of established test methods to the new platform. (See below for further detail)

Inductively Coupled Plasma (ICP) Systems

There are two other alternative processes to line source AAS that should be commented on, these are Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)⁹ and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Inductively Coupled Plasma – Optical Emission Spectroscopy:

ICP-OES is an optical emission spectrometry method, as opposed to absorption.

⁸ [High-resolution continuum-source atomic absorption spectrometry: what can we expect?](#) -Welz, Becker-Ross, Florek, Heitmann, Vale.

⁹ Also referred to as Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

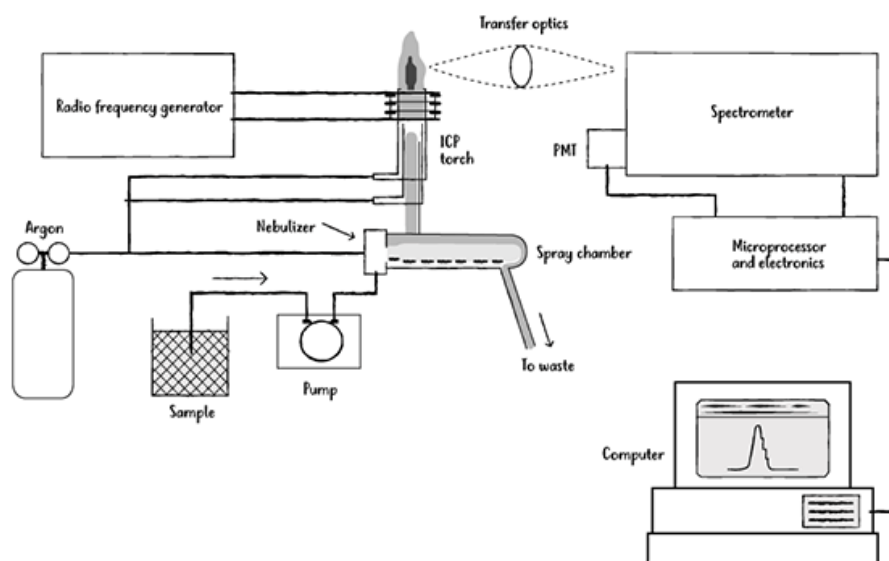


Figure 5 - ICP-OES system schematic

The following describes one of the methods of sample introduction into an ICP OES system and the analysis method. The sample to be analysed is dissolved in acid and water. Nitric acid is the most common acid used as most elements form water soluble nitrates. The water solution is then pumped into the instrument nebulizer, which turns the sample into a spray that is subsequently fed into the plasma. This plasma is most commonly composed of argon, although nitrogen gas and mixed gas compositions may also be used. The plasma is generated through the use of a high-power radio frequency signal or through microwave irradiation, which causes the gas to ionize to form electrons and other charged species within the plasma matrix. The plasma ionises the elements of interest in the sample. The ionised elements recombine with free electrons available in the plasma source, emitting specific spectral lines that are picked up by a detector. The detector converts the light signal emitted from the elements into an electrical signal producing a response that is proportional to the concentration of the element.

Inductively coupled plasma mass spectrometry (ICP-MS)

As with ICP-OES a fine aerosol of a sample is introduced into a hot (6000–10,000 K) argon plasma of sufficient energy to dry the aerosol and form analyte atoms, which are

simultaneously ionized. The ions are then sorted and quantified based on their mass-to-charge (m/z) ratio in the mass analyser.

Some disadvantages of ICP-OES & ICP-MS compared with AAS include:

Complexity of use:

AAS is much simpler to operate than ICP-OES or ICP-MS enabling its use by a lower skilled operator. This is reflected in the training courses offered, the ICP-OES course being twice the duration of that for AAS. Method development using ICP techniques can be a time-consuming process, as it necessarily involves multiple steps:

- (a) doing crude analysis to obtain a basic idea of the elements present in the sample;
- (b) wavelength selection based on that initial knowledge;
- (c) optimisation of separation so that signals from the various wavelengths have limited overlap;
- (d) comparison with an internal standard to validate the method and system performance; and
- (e) analysis for spectral interferences and ways to eliminate those from the read-out without eliminating target signals.

Due to the above the upfront time investment is greater for ICP-OES/MS than AAS, in situations where a fast turnaround for results is required, this is a limiting factor for ICP-OES/MS. One example is the fast and immediate determination of oil in tankers before they are unloaded. Pb and Cd are elements determined with ET-AAS before the ship is unloaded. With ET-AAS, the procedure can be run night or day without the need for an analytical chemist.

Sensitivity:

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.

Sample Dilution:

In applications where high salt concentrations are present GF-AAS is often technically favored as it requires minimal or no dilution of the sample compared with ICP-MS which requires dilution factors between 1:100 to 1:1000).

Isobaric Interferences:

Isobaric interferences refer to different elements whose isotopes share a common mass, which causes an issue in analysis techniques reliant on mass spectrometry such as ICP-MS. Isobaric interferences occur in the quantification of cadmium by ICP-MS for molybdenum oxides, which leads to incorrect results if the molybdenum concentration is dominant. Tin is another element forming isobaric interferences regarding cadmium. As a result, low cadmium concentrations in molybdenum or tin content in components or chemicals, can yield poor results when using ICP-MS, this does not arise with AAS techniques.

Complexity of instrument architecture:

More infrastructure and consumables are required for an ICP-OES/MS system than AAS system.

An AAS system typically requires the following consumable items and utilities: Compressed air source, ethylene, lamps, reagents, standards and power. An ICP system requires argon gas (typically 25-20 L/min¹⁰ required), quartz torches, reagents and standards, pump tubing, power and cooling water. ET-AAS & CVG-AAS, require argon, but at a consumption rate of 20x less than ICP. This means, flame AAS can operate at remote sites (specifically for mining or chemical hygiene) where it would be near impossible to run an ICP-OES/MS. ICP-OES/MS requires costly instrumentation for plasma generation, sample aerosolising, and signal analysis. The complexity of the instrument architecture results in a larger equipment footprint (as indicated by table 2) and initial capital cost¹¹. There may be instances where this larger footprint prohibits the use of the larger systems in some laboratory spaces. It is also possible that a laboratory would want to retain the AAS for the detection of substances other than lead, mercury and cadmium. The ICP systems also usually require an ultra-clean, thermostatically controlled environment.

Table 2 AA/ICP/ICP-MS footprint Summary (based on actual systems)

| System Type | | Width /m | Depth /m | Footprint/m ² | Height /m | Weight /Kg |
|----------------------------|---------------------|----------|----------|--------------------------|-----------|------------|
| Line source AA | Single flame | 0.67 | 0.63 | 0.42 | 0.64 | 57 |
| | Flame & GF combined | 0.95 | 0.68 | 0.65 | 0.73 | 133 |
| Continuum source AA | Single flame | 0.787 | 0.751 | 0.59 | 0.64 | 90 |
| | Flame & GF combined | 0.78 | 0.775 | 0.61 | 0.625 | 170 |
| ICP | Middle end | 0.65 | 0.76 | 0.49 | 0.81 | 99 |
| | High end | 0.76 | 0.84 | 0.64 | 0.87 | 163 |
| ICP-MS | Middle end | 0.81 | 0.69 | 0.56 | 0.75 | 150 |
| | High end | 1.15 | 0.85 | 0.98 | 0.75 | 205 |

Established Methods:

As supported by the table of standards in section 4, the use of AAS is embedded in a number of prescribed procedures. Many applications have methods which have been developed and validated for years. Although these methods could be adapted and converted into a method to enable the analysis using one of the other atomic spectroscopy techniques (such as ICP-OES or ICP-MS), this is not an easy or quick undertaking. This is best illustrated by the following example from one of the applicants referred to here as “Applicant X”.

¹⁰ <https://oliver.chemistry.ucsc.edu/122/Lab5%20Handout.pdf>

¹¹ ICP-OES is typically twice the cost of AAS and ICP-MS in the region of five times the cost of AAS.

Applicant X has recently worked with ASTM and an international collaboration task group consisting of 12 independent laboratories around the world, to develop and validate two new test methods for determination of elements in biodiesel and biodiesel blends by Microwave Plasma Atomic Emission Spectrometry (MP-AES) and determination of metals and other elements in residual fuel and crude oil by Microwave Plasma Atomic Emission Spectrometry (MP-AES). The goal was to streamline this elemental analysis by allowing the use of a single technique. Measuring the same elements previously required using multiple ASTM methods and multiple techniques: Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Flame Atomic Absorption Spectrometry (Flame AAS), and X-ray spectrometry.

Initially, this required Applicant X to develop a method for determination of the target elements in Biofuels, residual fuel and crude oil using a MP-AES method. This was completed and a draft standard test method was prepared in December 2014. It was then necessary to “recruit” 12 laboratories who were either routinely completing this analysis already – or had the expertise to participate. Applicant X equipped these laboratories with the MP-AES instrumentation, the analytical standards and other consumables required to complete the analysis and provided on-site training for each of the laboratories. The goal was to generate data demonstrating the achieved performance, especially interlaboratory reproducibility, for the ASTM committee. As part of this collaboration, the laboratories involved in the study also compared the results for metals content in the biodiesel, residual fuel and crude oil samples using the techniques of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Microwave Plasma Atomic Emission Spectroscopy (MP-AES).

The ASTM D8322-20 method for determination of metals and other elements in residual fuel and crude oil using the Microwave Plasma Atomic Emission Spectrometry (MP-AES) technique (ASTM D8322-20 Standard Test Method for Determination of Elements in Residual Fuels and Crude Oils (V, Ni, Ca, Na, Al, Si, Zn, P, and S for residual fuel oil and Fe, V, Ni, Ca, Na, K, and S for crude oils) by Microwave Plasma Atomic Emission Spectroscopy (MP-AES) was finally released in July 2020.

The ASTM D8351-22 method for determination of trace elements (calcium (Ca), magnesium (Mg), phosphorus (P), potassium (K), and sodium (Na)) in Biodiesel and Biodiesel Blends using the Microwave Plasma Atomic Emission Spectrometry (MP-AES) technique (ASTM D8351-22 - Standard Test Method for Determination of Trace Elements in Biodiesel and Biodiesel Blends by Microwave Plasma Atomic Emission Spectrometry (MP-AES)) was finally released in May 2022.

The scope of this method development is similar to what would be expected for any of the European (EU) methods using atomic absorption to either an ICP-OES or an ICP-MS method. As noted in the above example where new ASTM methods were developed, the elapsed time was 6 – 8 years for EACH method.

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

There is no known substitute for lead, cadmium, or mercury as a reference material in line source AAS lamps used for detecting these substances. Eliminating lead, cadmium and mercury from HCL & EDL lamps would result in the removal from the market of the option of line source AAS for detecting these substances.

If alternative lamps, such as CS AAS were utilised, some tests would no longer be able to be supported at this point, as discussed above and in the confidential submission. In addition to this there is no backward compatibility with current systems on the market which would mean the premature disposal of a large number of systems already on the market as they could no longer source AAS lamps for these substances.

There are alternative technologies available for detecting these substances, as discussed above, in section 6(A). These are not lamp replacements but whole system replacements. They are continuum source AAS and ICP based systems. It is unlikely these options will be suitable as a replacement for all the applications of line source AAS, due to the physical size, complexity and therefore user competency requirements and utilities requirements of the systems.

In the absence of lead, cadmium and mercury line source lamps, line source AAS systems will become obsolete in the EU for the analysis of these substances. The typical life of a line source AAS is in excess of 10 years, so where the system is being used solely for the detection of one or more of these substances (lead, mercury, or cadmium) the whole system would become obsolete before end of life.

The data required to qualify the use of a different system for a particular application is very much dependent on the application and whether its use is defined in established standards or not. An example of the typical timeframes for qualifying a new procedure covered by a recognised standards body are given in section 6(A) and could extend to 10 years.

The change to using alternative systems could be supported by the system manufacturers but the burden would be placed on the end users, to source a new system and on the standardisation organisations to drive a change in the requirements.

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.

HCL to EDL

Changing from HC to all ED lamps in line source AAS is an option. The EDL utilises less material than HCL, for example for lead the EDL contains less than 1mg of lead compared with HCL, which contains 8-12 g lead. So, although it would not eliminate the use of lead, cadmium, or mercury in AAS lamps, a change to solely EDL lamps would result in a reduction in the use of these substances.

Changing to ED lamps would require modifications to the existing AAS platforms, this is platform design / manufacturer specific, it is anticipated this would be similar to the new product development timescales detailed in section 7(B) of in the region of 10 years. It is estimated that the majority (> 95%) of the atomic absorption spectrometers that have already been installed and are in operation incorporate HCLs.

In addition, EDL has the following disadvantages:

- High heat generation during operation
- Short lifetime of the lamps. Less than half that of HCL.

Change to Continuum Source AAS

Changing to a continuum source AAS platform is currently only feasible for one (system manufacturer) applicant. For the others to take this approach would require just under a 10-year new product development cycle (for further details of steps involved refer to section 7(B)).

Change to ICP based System

All the applicants that manufacture line source AAS systems, also market ICP solutions. Whilst this technology could perform the function of the line source AAS, for the reasons outlined in section 6 a blanket change to this technology would require an extensive feasibility study involving end users and standardisation bodies.

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

Development of a Continuum Source AAS

The following is provided as an example of the steps and timeframes involved for the development of a continuum AAS system, effectively a new product development for all but one of the applicants for this exemption.

Pre-concept stage: requirements specification and technical feasibility ~12 months.

Concept stage: develop concept ideas and some proof of concepts to verify if they are achievable **~18 months**.

Planning Stage: generate the baseline of schedule, cost, and quality, and define SRS (system requirements specs) **~12 months**.

Development phase: generate detailed designs & drawings, build prototypes, and run prototype verification (typically two prototype runs are required) **~48 months**.

Validation & commercialisation stage: prepare materials and build pilot run instruments in the manufacturing plant, run instrument validation tests, to make sure instruments accord with URS¹². This stage is also used to verify the design is ready for mass production and train service engineer **~24 months**.

In total this is 114 months or around 10 years.

Change to ICP based system

See section 6(A) example of developing and qualifying new methodology for standardisation. Total duration of 10 years. This excludes the manufacture (typically 4-8 weeks), transit to (variable) and installation (typically 1-2 days) of ICP systems at end user facilities.

Conversion of existing HCL source systems to EDL sources

The steps involved will be equivalent to a new product development and could take an equivalent timeframe, around 10 years. This excludes the program required to replace or retrofit installed units. This solution does not result in the elimination of the substances.

¹² User Requirement Specifications

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 [Lead Registration Dossier - ECHA \(europa.eu\)](#), [Cadmium Registration Dossier - ECHA \(europa.eu\)](#) and [Mercury Registration Dossier - ECHA \(europa.eu\)](#)

2) Provide REACH-relevant information received through the supply chain.

Name of document: _____

(B) Elimination/substitution:

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

Yes. Consequences?

No. Justification: [Reference should be made to Section 6](#)

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

Yes.

Design changes:

Other materials:

Other substance:

No. Justification:

[Refer to section 6 for further detail.](#)

[Only lead, cadmium and mercury can generate the required spectra for line source AAS.](#)

3. Give details on the reliability of substitutes (technical data + information): _____

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to

1) Environmental impacts: _____

2) Health impacts: _____

3) Consumer safety impacts: _____

⇒ Do impacts of substitution outweigh benefits thereof?

Please provide third-party verified assessment on this: [Not applicable](#)

(C) Availability of substitutes: Not applicable

- a) Describe supply sources for substitutes:
- b) Have you encountered problems with the availability? Describe: _____
- c) Do you consider the price of the substitute to be a problem for the availability?
 Yes No
- d) What conditions need to be fulfilled to ensure the availability? _____

(D) Socio-economic impact of substitution: Not applicable

- ⇒ 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: _____

9. Other relevant information

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

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:

Q4(a). 5. Calculation of quantity of cadmium and lead placed on the EU market annually for this application

Confidential market data has been used to calculate the quantity of restricted substance entering the EU market annually. This information has been submitted separately. Please refer to: 05 Confidential EU exemption IV-10 renewal.pdf

Q6(A) CS-AAS as an alternative to line source AAS

In some applications, line source AAS is still considered to be the optimal test method to CS-AAS. Further details of these are shared in confidential submission 08 Confidential EU exemption IV-10 renewal.pdf.