Exemption Request Form

Date of submission: 27.11.2019

1. Name and contact details

1) Name and contact details of applicant:

Company:	Spectaris e.V.	Tel.:	+49 30 41 40 21 25
Name:	Dr. Wenko Süptitz	E-Mail:	sueptitz@spectaris.de
Function:	Head of Photonics Division	Address:	Werderscher Markt 15, 10117 Berlin, Germany

---

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 III

☐ 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: 13b, 13b-I, 13b-II, 13b-III

Proposed or existing wording:

For categories 1 - 7 and 10

13b-I Lead in ion coloured optical filter glass types

13b-II Cadmium in striking optical filter glass types; excluding applications falling under point 39 of this Annex

13b-III Cadmium and lead in glazes used for reflectance standards

For categories 8, 9 and 11

13b Cadmium and lead in filter glasses and glasses used for reflectance standards

Duration where applicable: We apply for renewal of these exemptions for the categories marked in section 4 further below for the respective maximum validity periods foreseen in the RoHS2 Directive, as amended. For these categories, the validity of these exemptions may be required beyond those timeframes.

☐ Other: _____

3. Summary of the exemption request / revocation request

This exemption renewal request is for the use of cadmium and lead in optical filter glass that is used in electrical and electronic equipment. There are many types of optical filter glass whose batch contains cadmium, but only a few formulations whose batch contains lead with only one filter glass whose batch contains lead being regularly manufactured. These types of optical filters are used in a very wide variety of optical applications and in many different types of equipment. These materials are used because of their unique optical properties, such as "sharp cut-off" in the visible spectrum that is unaffected by viewing angle. They are also very stable in harsh environments. Most of the alternatives to glass with cadmium and/or lead in the batch do not exhibit such sharp wavelength "cut-offs". Interference filters can sometimes be used as they do have sharp cut offs but the wavelength at which this occurs is viewing angle dependent and so these are unsuitable for many applications. Most of the apparent alternatives are detrimentally affected by harsh environmental conditions such as heat, moisture, UV light, etc. which makes them unsuitable for many applications.

A special type of infrared interference filter is also used that contains lead for analysis of low concentrations of gas. These are a different design to the filters to the types used for visible light wavelengths.

---

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: Optical filter glass is used in very many types of EEE. The following is an indicative non-exhaustive list of types of EEE:

- Security, surveillance and medical applications, e.g. infrared illumination with filters that suppress visible light (category 3, 8 or 9).
- Airport runway lamps that indicate the runway location (category 5 or 9) – bright specific coloured light visible from all directions which should not change in colour with viewing direction which would occur with coated filters and interference filters.
- Laser eye protection goggles / glass (most types have no electrical function but any designs with an electrical function would be in category 9).
- Traffic monitoring - cameras to take pictures of drivers exceeding the speed limit and toll monitoring systems (category 9).
- Environmental monitoring equipment, e.g. used to monitor environmental pollutants, waste sorting, waste water analysis, exhaust gas analysis, airborne (from airplanes, satellites) environmental diagnosis photography, etc. (category 9).
- Analysis of ppm levels of gases in air or in flue gases (category 9).
- Colour channel separation for colour television (category 4).
- Spectral filters for photographic cameras (category 3).
- Attenuation or separation of undesired wavelengths in telecommunication by

separation of undesired wavelengths transmitted by coated filters (category 3).

- Light barriers for motion control in electrical machinery (category 6).
- Bar code readers (category 6 and IVD category 8 used for identification of samples for IVD analysis).
- Logistics automation equipment such as letter and parcel sorting machines (category 6 or 9).
- Industrial measurement as part of or used with machines used for manufacturing – many different applications (category 6 or 9).
- Industrial displays (category 6).
- Fluorescence microscope (categories 8 and 9); more details below.
- Spectrometers; for example, as stray light filters for UV and for near-IR spectrometers, requires high % transmission in the desired wavelength range and a steep cut-off with no transmission outside of the desired range (categories 8 and 9).
- Gas chromatograph detectors – use filters containing lead to detect the spectra of sulphur and phosphorous compounds (category 9).
- Flame photometric detectors used for process gas chromatography- The filters are needed to separate light of 394nm from other wavelengths which is used to measure intensity and calculate the concentration of sulphur compounds in the process gas. Blue filters containing lead are used for this application (category 9).
- Infrared cameras (category 9).
- Surveying instruments (category 9).
- Radiation thermometer – (category 9) uses filters containing cadmium to detect light of specific wavelengths without interference from other wavelengths. These determine temperature by measuring the light intensity at a specific wavelength so other wavelengths must be blocked. Cadmium provides the steep edge and lead provides fine adjustment of the transmission limit wavelength.
- Filter in medical fibre optic core temperature probes that are used to measure body temperature of patients while undergoing MRI scans (category 8). This filter is used in the optical head of the signal conditioner to reduce/eliminate the unwanted scattered light (noise) in the optical head. Only red cadmium filters give accurate body temperature measurements.
- Imaging luminance colorimeter – light measurement to simulate the human eye’s light responses. The colour response is simulated by 4 different “stacks” for the so called Xr, Xb, Y and Z response of the "standard observer" as defined by the "International commission of illumination, CIE". The filters are sequentially introduced into the beam path of a camera system. Calibrations and evaluation of the data result in a precise image of luminance and colour. The closest match can only be achieved with filters containing cadmium (category 9).
- Spectroradiometer- This type of device has a very high fidelity of colour measurements. The light of different colours (plus infrared and ultraviolet) is dispersed by an optical grating and then analysed by a charge-coupled device sensor. However, optical gratings diffract the so called 'higher orders' of light as well as the required wavelengths.

This means that light with half the wavelength will follow the same beam path (e.g. 360nm will appear as signal at 720nm). To eliminate these higher order wavelengths, optical filter glass are used. Optical filters containing cadmium have to be used in these measurement devices for light measurement (category 9).

- Ingredient meters and thickness meters – use filters containing both cadmium and lead. These devices function by measuring the amount of an ingredient in the test sample to determine either its concentration, or if this is known, it can be used to measure the sample's thickness by making use of the Lambert-Beers law. This is achieved by accurate measurement of transmitted light at a specific wavelength and filters are needed to remove other wavelengths (category 9).
- Infrared sensors – these filters contain an evaporated layer of lead compounds which transmit light of wavelengths between up to 15µm and has a high refractive index. This combination of properties cannot be achieved by any other materials or designs.
- Light meter for specific wavelength ranges (category 9).
- Industrial image processing for quality assurance as part of electrical machines (category 6).
- Detection of faked paintings, filters are used in controlled wavelength light sources (category 9).
- High quality scanners used to digitise colour images (category 3).
- High performance cameras, such as television broadcasting, cinematography, medical applications, etc. (category 4).
- Light filters for astronomy research (category 9).
- Short Wavelength Automated Perimetery (SWAP) using a Humphrey field analyser (HFA) is a medical technique used to detect eye conditions such as Glaucoma and optic neuritis (category 8, more details below).
- IVD analysers (category 8); IVD analysers automatically analyse a variety of materials and some tests use colour to measure concentrations (using optical absorption spectroscopy). The required colours are selected by blocking other wavelengths using optical filters including some that contain cadmium. These must have sharp-edges to the transmitted spectrum and be stable with no colour change or fading during the life of the equipment for accuracy to be maintained.
- Many types of lasers with fundamental wavelength in visible and near-Infrared wavelengths use optical filters containing cadmium (such as RG1000 filters). Sharp spectral filtering using cadmium-containing glass is required to achieve spectrally pure signals for power level setting, attenuation, and diagnostics. These filters are used, for example, to separate the fundamental NIR radiation from other wavelengths like pump sources with 808nm /880nm / 888nm and harmonics such as 523nm / 355nm /266nm. The filtered NIR is used for determination of power values for diagnostic reasons, but mainly for power level settings and attenuation by end users of the tool. Ultra-short pulsed laser sources are used in a growing market segment like e.g. micromachining

of glass, in the semiconductor industry and used to produce photovoltaics and display technologies (category 6, 8, 9 and 11).

- Lead containing green filter glass such as VG9 has many minor uses. It separates the different colour channels for colour TV cameras (category 4) and is used for medical colposcopes (more details below) (category 8).
- Optical filters are used with optical microscopes to remove unwanted wavelengths (category 8, 9).
- Cadmium and lead filter glass may also be used in many other types of equipment, such as lighting applications, leisure products, medical devices and automatic dispensers.

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:
The exemption renewal request covers all types of products that require these exemptions, but excludes information on cadmium and lead in glazes used for reflectance standards as the applicants are not expert in these products.

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: Lead and cadmium are added to optical glass batches used for the production of light filters where a well-defined slope in the absorption spectrum is required, such as a sharp cut-off within a narrow wavelength range. Both Pb and Cd are needed to ensure that there is a high

percentage of light transmission at wavelengths above the “cut off” and close to zero transmission below the cut off wavelength. These filters are used in many types of EEE (as well as non-electrical applications) and a selection of illustrative example applications is listed below.

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

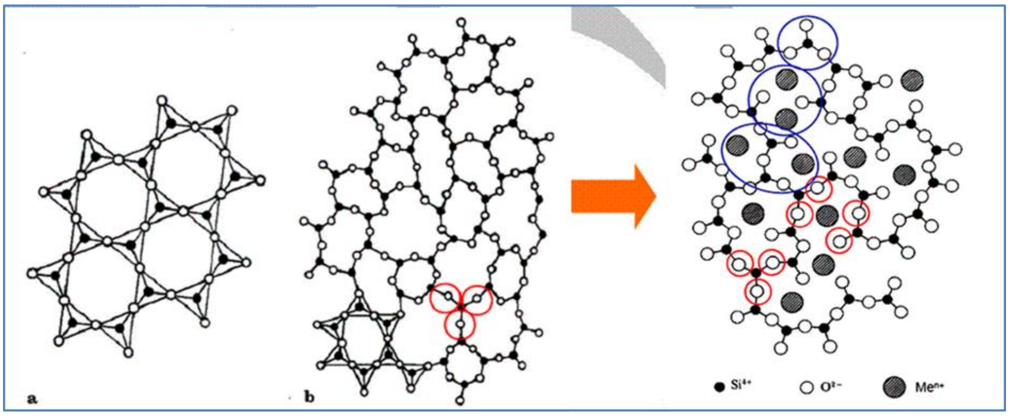
   Lead-based filter glass typically contains 10 – 15% by weight of lead calculated as oxide (range of 0.3 – 60%). With a derived average of 15% lead oxide, the lead content is about 13% wt.
   Cadmium-based filter glass contains typically about 0.4% and can be up to 1.8% by weight cadmium calculated as oxide (derived from the range of cadmium oxide content of 0.39 – 2.1% wt.).

5. Amount of substance entering the EU market annually through application for which the exemption is requested: 192 kg of cadmium and 46 kg of lead
   Please supply information and calculations to support stated figure.

   Cadmium/lead filter glass is made in Germany, Japan and China. The entire production is considered being stable over the years 2015-2019 based on company-specific information. The Japanese and German production is estimated to be about 60 tons p.a. of glass. No published Chinese data are available. The production is estimated to be around also 60 tons p.a. so that the total global production is 120 tons with approximately 40% being used in products placed on the EU market. With few exemptions (applications as satellites, military equipment, laser safety glass and large-scale stationary industrial tools) the majority is considered being in scope of RoHS. The total weight of Pb- and Cd-filter glass placed on the Global market is accordingly 120 tons p.a. and thereof approx. 40 tons placed on the EU market.
   The cadmium proportion of filters varies from 0.4 to 1.8% but on average it is closely to 0.4%. Thus based on the global consumption of cadmium filter glass used in EEE in scope of RoHS an amount of 480 kg Cd per year can be derived.
   The EU consumption of cadmium filter glass used in EEE in scope of RoHS is about 192 kg Cd per year.
   The lead proportion of filters varies from 0.3 to 60% and on average it is about 13%. Thus for those lead-based filter glass types the EU consumption of lead used in EEE in scope of RoHS is about SCHOTT data only 46 kg Pb per year (globally 115 kg).
   Filters coated with lead compounds for infrared analysis are used in small numbers in the EU with each filter containing only a few milligrams of lead (the coatings are typically 0.35µm thick) and so much less than 1 gram of lead is used for this application annually.

Name of material/component: “Glass” whose batch contains cadmium, lead, silicon, sodium and other elements as a variety of complex mixed oxide compositions.

Glass is characterized by their non-regularly ordered amorphous atomic structure



crystalline SiO_2 amorphous SiO_2 multi-component glass

Figure 1. Atomic structures of silica and multi-component glass

Glass is produced from different constitutional components:

1. Glass formers form glass network

- SiO_2	silicon oxide
- B_2O_3	boron oxide
- P_2O_5	phosphorus oxide

2. Network modifiers break up the network

alkaline oxides:

- Li_2O	Lithium oxide
- Na_2O	sodium oxide
- K_2O	potassium oxide

Alkaline earth oxides such as CaO

Rare earths elements

Etc.

3. Intermediate elements added as oxides may also be bound into the network

- Al_2O_3	aluminium oxide
- MgO	magnesium oxide

4. Additional agents introducing special properties

- Colouring ions
  Fe, Mn, Cr, V, Co, Cu, Cd, Se
- Laser active ions
  Nd^{3+}, Yb^{3+}, Er^{3+}, …
- Ionizing radiation stabilization compounds
  - CeO_2
- etc.

A crystalline structure with composition well defined by chemical formula
e.g. silicon dioxide: quartz, is:

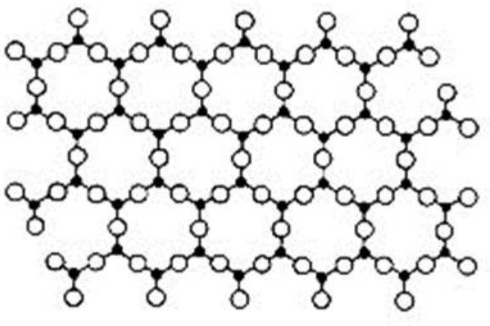


Figure 2. Atomic structure of crystalline silica

An amorphous structure still having a well-defined composition and precise chemical formula, e.g.: amorphous silicon dioxide: fused silica

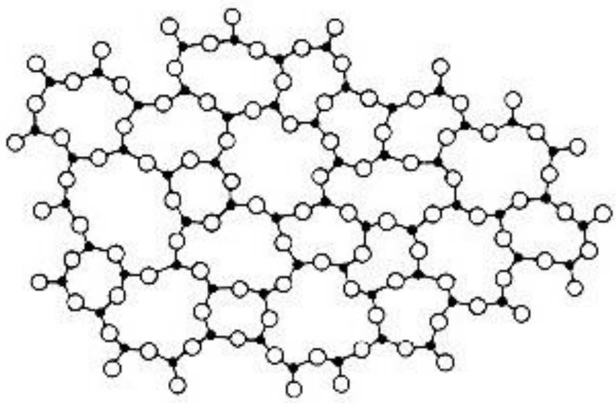


Figure 3. Atomic structure of amorphous silica

An amorphous structure produced on the basis of a defined recipe, but without composition that can be well defined by a chemical formula, e.g. sodium - lime glass with a broad range of possible contents of sodium and potassium. In the figure below, only sodium ions are shown for simplicity.

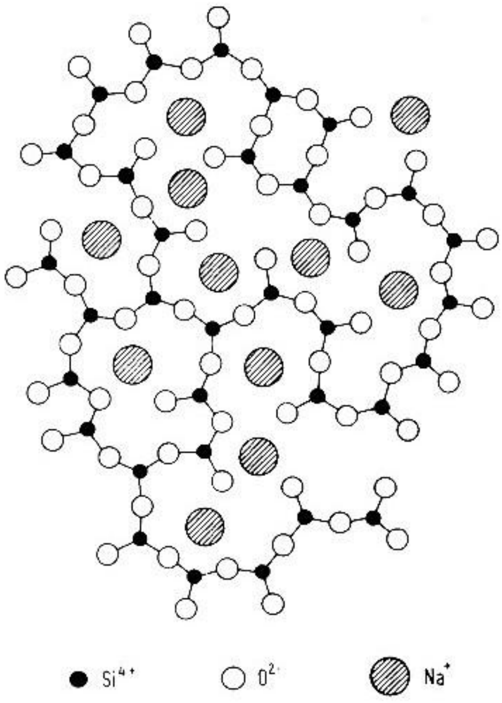


Figure 4. Atomic structure of a soda-lime glass (showing only Si, O and Na)

The infrared filters used for gas analysis have a different composition, as these are "interference" filters that utilise a thin coating of a lead compound deposited on an infrared transparent substrate. The coating material composition and thickness are chosen to achieve a high percentage of transmission in the desired narrow wavelength range in which infrared light transmission occurs. Various lead compounds are used for different gases being analysed including the oxide, sulphide, selenide, telluride and fluoride, with the compound choice dependent on the ability to transmit infrared light in the wavelength range required for the gases being analysed.

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?

Optical filter glass

Optical filter glass serves for separation or selection of light wavelength ranges in a wide variety of applications in research and industry. Ideally separation occurs at a given wavelength with 100% transmission on one side and 0% at the other side with an infinitely steep slope. Real filters show residual absorption in the transmittance range and residual transmittance in the blocking range with transition ranges of differently steep slopes. In production of filters it is important to come as close as possible to the desired ideal filter characteristics.

Striking filter glass provide uniquely steep slopes and an extremely high blocking effect but due to their single edge only with a long pass characteristic. Band pass or band blocking filters require ion coloured glass, which have two edges. However, these edges are smooth rendering only a moderate separation capability.

Striking optical filter glass

Striking optical filter glass is made by adding about 1% of cadmium compounds to molten glass. In the first stage they are colourless clear glass types. By precisely controlled heat treatment (the so-called striking process) cadmium chalcogenide microcrystals are grown. Their semiconductor band gap renders the desired long pass filter characteristic with a very steep slope and high blocking of the short wavelengths. By changing the heat treatment parameters temperature and time it is possible to control the crystals' size and thus the cut-off wavelength.

The cadmium containing filter glass allows highly selective separation of wavelength ranges. Their high blocking effect for unwanted light wavelengths makes them indispensable for safety applications such as laser goggles.

Ion coloured optical filter glass

Ion coloured optical filter glass makes use of the light absorption of ions of special elements such as iron, manganese, chromium, vanadium, cobalt and copper. The special absorption characteristic of a given ion in a well-defined glass composition depends not only on the metal ion itself but also on its environment of other ions to which it is bonded in the glass matrix. The environment is given by the base glass composition in the first instance. Secondly it varies considerably due to the amorphous character of glass, which contrary to crystals provides many different bonding distances and angles for the same type of ions. This variable environment causes absorption bands to broaden and hence leads to inferior filter properties with much less steep slopes.

In order to obtain the best filter characteristics the best environmental glass and the optimum ion content has to be found. A further remaining optimization possibility is to use more than one colouring ion as e.g. in the green filter glass VG9, where Cu^{1+}/Cu^{2+} and Cr^{3+} ions are used. This, however, puts even more stringent requirements on the base glass composition.

Function of cadmium in striking glass

Cadmium must be used to obtain the sharp cut-off required and plastic filters with organic pigments will degrade when exposed to sunlight by photochemically induced decomposition processes.

Optical filter glass types are clear transparent non-crystalline materials with a variety of compositions. Traditionally “glass” has been understood to consist of complex inorganic silicates based on a variety of ingredients such as sodium, barium, calcium, potassium, boron, arsenic, antimony and lead but there are many diverse compositions of materials that meet the definition of “glass”. The essential characteristics that cadmium give to glass optical filters is as follows:

The function of cadmium in optical glass is to absorb light at wavelengths shorter than a specified value and to allow all light of longer wavelengths to be transmitted through the filter. When added to glass, the cadmium compound initially appears to disperse to give a colourless clear glass. This is then heated to nucleate and crystallise very small (sub-micron), coloured cadmium chalcogenide particles that are dispersed in a colourless matrix.

The steep slope effect is based on the semiconductor electron band gap characteristic of the microcrystals formed by the cadmium compounds, as shown below.

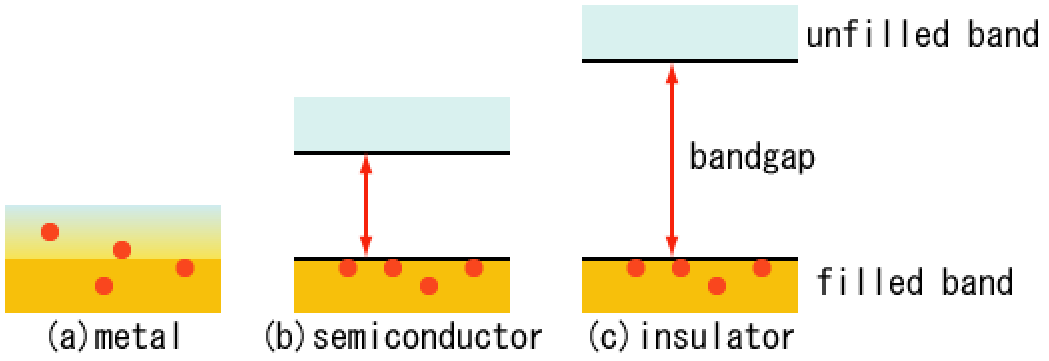


Figure 5. Difference in electronic structure of metals, semiconductors and insulators

In order to cross the bandgap, electrons must have energy that is higher than the threshold value given by the bandgap’s width. For the glass type GG495 e.g. this energy lies at 2.5 eV. All light with higher energy will be strongly absorbed. Just below this energy electrons cannot surpass the bandgap and so light will be fully transmitted. This is because the energy of visible light radiation is dependent on its wavelength as shown below in Figure 6.

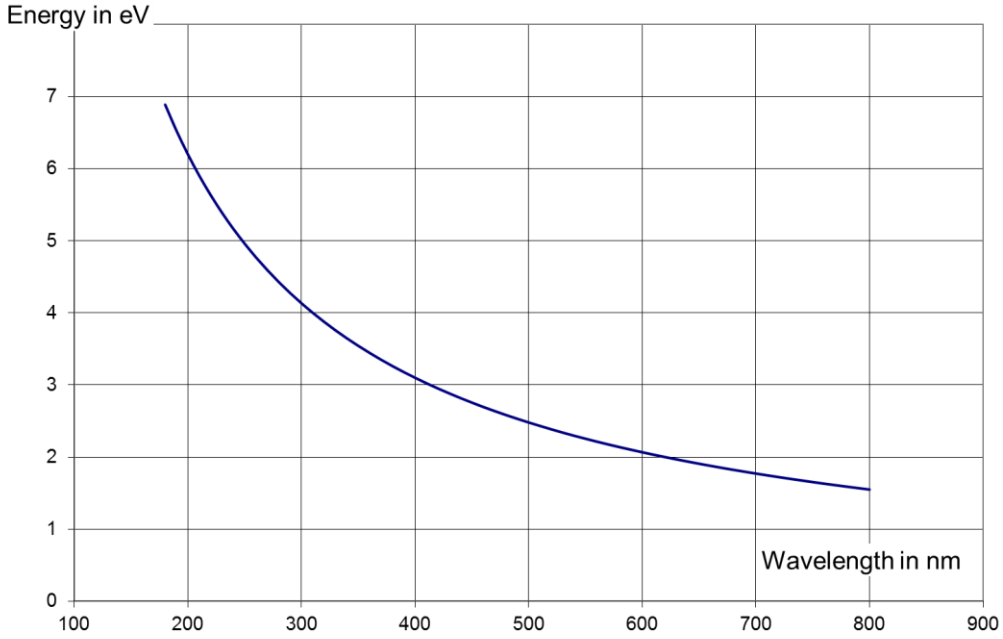


Figure 6. Relationship between the energy of light and its wavelength

The cadmium chalcogenide semiconductor is unique in having the required bandgap energy and bandgap width to achieve the absorption edge wavelengths that are required (in the red/orange range) for the filter. Also, the precise absorption edge wavelength is adjusted by the temper (heat treatment) process that has been found to be unique in that it grows the cadmium chalcogenide particles to the desired particle size and this controls the cut-off wavelength of the filter. No other compounds have been found that perform this function.

By adjusting the quantities of other constituents (S, Se and Te), as well as the temper process conditions, red, orange and yellow filters are produced and the wavelength separation should occur at well-defined wavelengths, ideally as shown below.

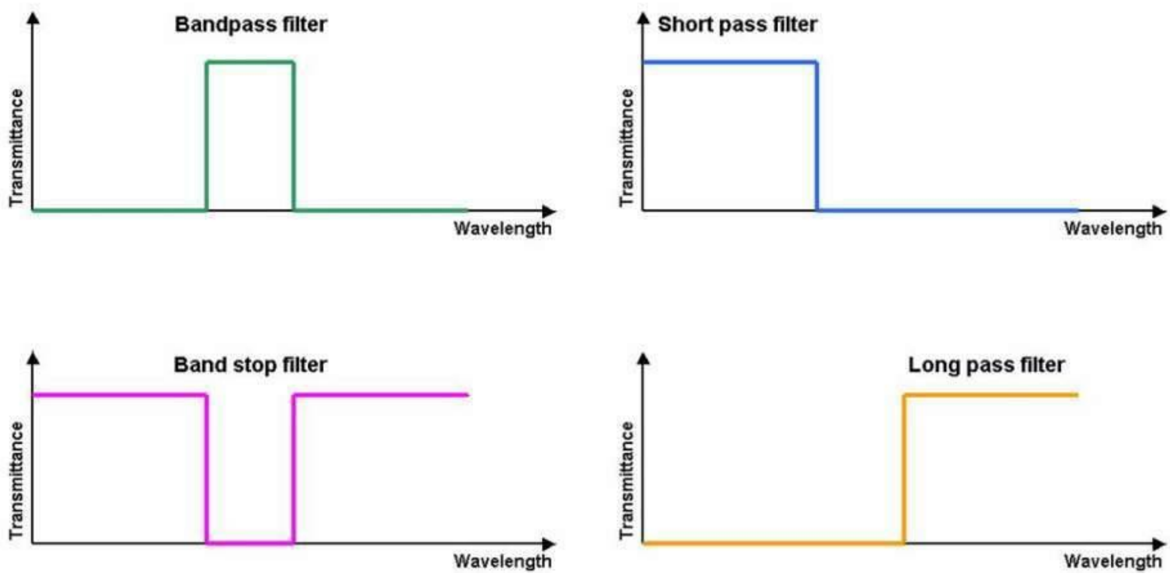


Figure 7. Idealised shapes of transmission / wavelength curves for light passing through optical filters

Filter glass produced with cadmium are used to absorb wavelengths from ca. 400nm. For example:

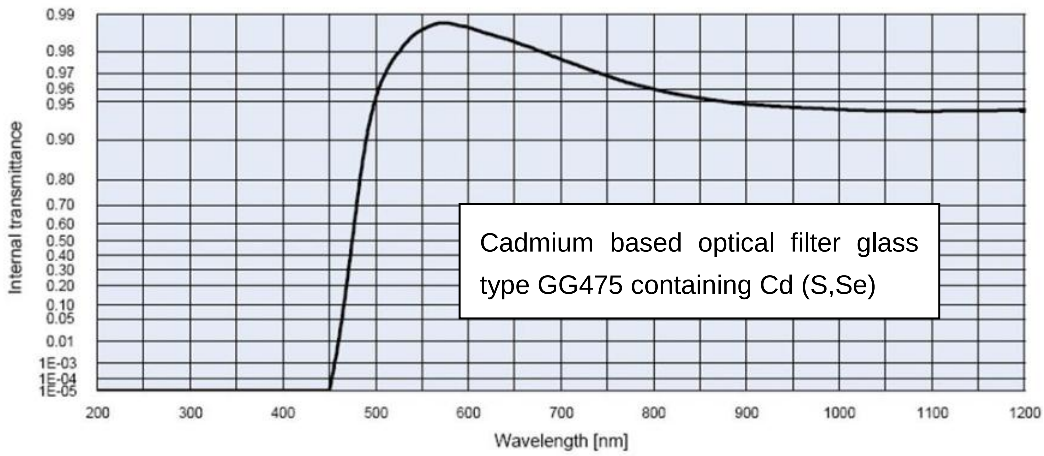


Figure 8. Real optical striking glass filter. Please note the strongly nonlinear y-axis scale is used for a better view of residual absorption and transmittance by stretching the extreme parts of the transmission scale

A red filter allows only red light to pass whereas an orange filter allows red and orange light to pass. An important characteristic of cadmium-based optical filters is the difference in optical filtering above and below the cut-off wavelength. Cadmium filters can be designed to absorb almost 100% of light having wavelengths shorter than the cut-off value and transmit better than 95% of light with longer wavelengths. Furthermore, the range of wavelengths between 95% transmission and <1% transmission can be designed to be relatively small, so that these filters are classified as “steep-edge” filters. Spectra obtained from optical filters that contain cadmium, manufactured by SCHOTT (Germany) are shown in Figure 9.

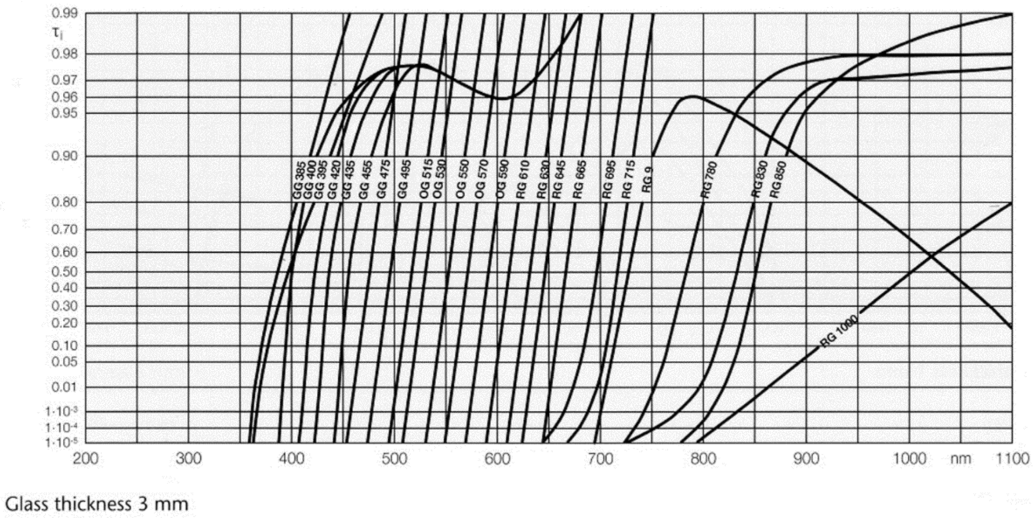


Figure 9. Optical transmission spectra of cadmium-based glass filters

Optical filters with cadmium proportion can be designed to have sharp cut-offs at most wavelength values by control of the cadmium compound composition and the heat treatment conditions of the glass. A few of the curves above in Figure 9 have different shapes to achieve specific absorption profiles which are achieved by adjusting the ingredients in the filter glass.

As will be explained in answer to Q6, coloured filter glass is obtained by a variety of metallic additives, but a steep cut-off as shown in this section, can be obtained only by the use of cadmium compounds. These types of optical filter are also called "striking" glass and are made by adding the cadmium compounds to molten glass based on K_2O, ZnO and SiO_2[1]. The cadmium compound initially appears to disperse to give a colourless clear glass. This glass is then heated to nucleate and crystallise very small (sub-micron), coloured cadmium chalcogenide particles that are dispersed and firmly bound in a colourless matrix. The heat treatment temperature, time and cooling rate all are used to control the particle size which in turn affects the cut off wavelength and the steepness of the cut off. Research has shown that some zinc is present in the cadmium chalcogenide particles and some cadmium remains in the glass matrix, the amounts depending on the cooling rate.

Striking glass types with cadmium are not colloidal dispersions and so the colour of the individual particles is important for the optical characteristics. A steep edge cannot be obtained by colloidal dispersions that are red in appearance and research has shown that the steepness of the absorption edge increases during heat treatment and the steepness is a characteristic of the cadmium chalcogenide particles. Alternative sulphides such as antimony, lead, copper,

[1] W. Vogel, “Glass Chemistry”, Springer-Verlag, 2nd edition 1994. ISBN 3-540-57572-3

etc. can give ruby red glass, but these all form dispersions of colloidal particles and the glass does not exhibit the steep edge obtained only by cadmium compounds. 3d metals[2] such as Fe, Mn, Ni, etc., when added to glass dissolve in the glass to form ionic complexes within the matrix. The colour depending on both the metal ion and the structure to which it is bonded. These all however have shallow absorption edges unlike cadmium filters.

As well as giving a steep edge, cadmium compounds give very low transmission at wavelengths shorter than the steep edge and very high % transmission at longer wavelengths. This is important for many applications as this prevents image distortion effects such as “flare” (stray light) and “ghosting” (a second feint image).

Lead in filter glass

The classical way to colour glass is by adding colouring ions to a glass matrix. These are usually metal ions such as iron, copper, nickel, cobalt and chromium. The colour achieved depends on the valence of the metal ion and on its surrounding glass matrix ions. So, there is not much freedom for choice of a metal ion / glass matrix combination for best performing glass filters. The green glass filter VG9 is the last remaining regularly manufactured type of a family of VG glass coloured with chromium III and copper II ions in a lead silicate glass matrix. The lead content of VG9 is 15% lead oxide. It is the only green filter glass type in a portfolio of 58 glass types. Its usage is with about 400 kg / year (very low). Chromium III and copper I ions added to lead-free glass matrices do not give the same light filtering properties so are not suitable replacements. One application of lead-based optical filters is in fluorescence microscopes to transmit only the desired wavelengths. This needs to be independent of viewing angle. Although only one type of filter (VG9) is made as a standard product at present, it is conceivable that a use may arise from an equipment manufacturer who has no alternative to using a type of lead glass filter that is not currently produced as a standard product and so this material will need to be covered by this exemption 13b.

Just like all optical filters, lead-based band pass filters, such as VG9, should have very steep edges for the separation of the desired transmitted light from the undesired light which is to be strongly blocked.

---

[2] Regions of the periodic table are given letters and numbers, 3d being the transition metals.

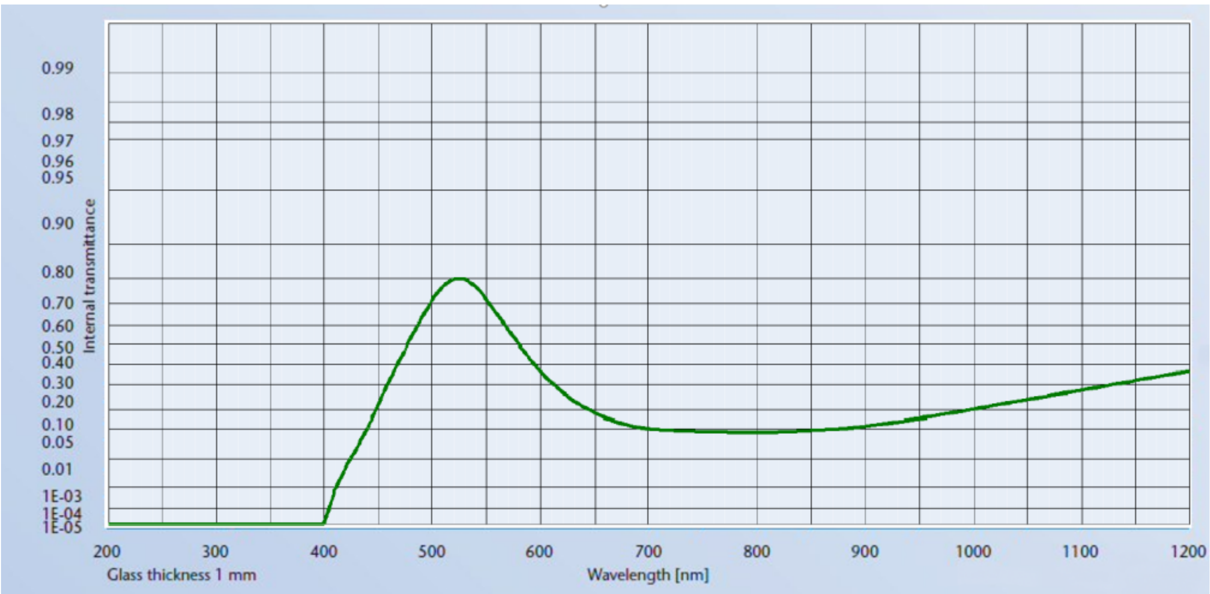


Figure 10. Light transmission / wavelength curve for VG9 optical filters

With metrology applications, false light coming from wavelength ranges, which should be blocked off but still have some residual intensity due to the smooth edges will reduce signal to noise ratio and thus give inferior accuracy and poor image quality. The task in developing such glass is to find compositions leading to the steepest possible slopes and the highest light transmission. Mineral filter glass consists of a base glass and colouring chemical elements. However, one is not free to choose combinations of elements arbitrarily as only a few elements have the required light absorption bands. In the case of VG9, only copper II and chromium III in combination give the required performance. In different base glass the absorption bands of these colouring agents will shift in position and vary in width. For VG9 the optimized base glass is a silicate glass with 15% lead oxide in its composition. Other variants will decrease the quality of the filter characteristics.

Interference filters with lead compound coatings

Filters made from an infrared transparent material with thin coatings of lead compounds are used in instruments for accurate chemical analysis of trace concentrations (sub-ppm to 100%) of gases such as SO_2, NO, CO, CH_4 and N_2O in air or in flue gases. These instruments analyse flue gases from boilers crematoria and from industrial processes to ensure that the concentrations of toxic gases (such as CO) are as low as possible and this data is used to control the combustion process conditions in real-time. These analysers are also used to analyse gases for trace impurities such as in compressed oxygen that is used for hospital patients. This type of analysis is difficult because analysis results obtained with most methods are affected by the presence other gases that also respond to the analysis technique, so that the wrong composition information is obtained. For example, analysis of a few parts per million (ppm) of carbon monoxide in a gas containing many percent of carbon dioxide requires a technique that can accurately discriminate between the absorption wavelengths of these two gases. Infrared spectroscopic analysis of gases is described below, which relies upon the use of lead containing interference filters.

The analyser can selectively analyse single compounds in a gas mixture by selecting an appropriate wavelength using infrared filters which block other wavelengths.

Example uses of filter glass

More detailed descriptions of some of the uses (as listed above) of cadmium optical filters are described below.

Colour image recording: Several of the above examples which record colour images (colour TV) require steep edge filters to split the visible spectrum into several colour channels each of which are recorded separately. This requires that the filters have the steepest edge possible and that they are not affected by viewing angle. This combination of properties is achievable only by optical glass filters based on cadmium and lead.

Fluorescence spectroscopy is an analytical technique that is used for analysis of some types of organic substances, molecular biology (e.g. cell and tissue analysis), medical research, cancer detection and other medical diagnostic procedures and industrial applications such as semiconductor analysis. All fluorescence techniques require optical glass with high percentage transmission at short wavelengths and fluorescence microscopes require many high-quality lenses that contain lead as well as optical filters that are independent of viewing angle. Fluorescence spectroscopy operates by exposing the sample to light of a preselected wavelength which can be ultraviolet or visible light. Some materials absorb this light and then emit light of a longer wavelength by fluorescence in all directions. The emitted fluorescence is detected for quantitative analysis, imaging or mapping, depending on the type of instrument used. Medical diagnostics, for example often use near Ultra Violet (UV) or blue/violet light to cause fluorescence and so a high percentage transmission of light at short wavelengths is essential.

Fluorescence microscopes can be used to create images in which light is scattered by the object and so the optical filters must have a steep edge and be independent of viewing angle. Images are often made by staining materials with fluorescent dyes. The wavelength of light used to illuminate samples will have a different wavelength to the fluorescent light emitted by the dyes, but these two wavelengths are usually similar. If a white light source is used, steep-edge cut off filters are needed to remove light of wavelengths that are not required for inducing fluorescence and filters are also used to remove the input excitation light from the output fluorescent light. Examples of tests carried out with fluorescent dyes shows the small differences in wavelengths that need to be separated, for example, an orange-red dye is excited at 553nm to fluoresce at 569nm. Only cadmium-based filters have sufficiently steep edge filter properties at all viewing angles to separate these wavelengths.

Some fluorescence spectrometers use diffraction monochromators to select the wavelengths required to induce fluorescence and to separate out fluorescent wavelengths from light of other wavelengths. Diffraction gratings always however emit 2nd, 3rd, 4th etc. order diffracted wavelengths and these must be separated from the 1st order light that is required and this is achieved by steep-edge filters. Thin film diffraction filters are “steep-edge” but transmit side-bands of undesirable wavelengths so are not suitable without the addition of optical glass filters. Thin film filters also suffer from other disadvantages, as described below in answer to Q6A. Diffraction gratings and interference filters are unsuitable for imaging due to their dependency on incident and viewing angle and so only steep edge filters can be used.

Humphrey field analyser (HFA) SWAP: The patient’s retina is illuminated with light of specific wavelengths to determine their response to coloured light. This technique uses two types of optical glass filters that contains cadmium (SCHOTT OG530 and RG850). The OG530 is a yellow filter that provides yellow background illumination. The HFA uses normative databases that are used to compare patient’s visual field test results to an age-matched population. To use these databases, the optical spectrum from the optical filters must not change. Figure 11 below shows how the yellow filter is used.

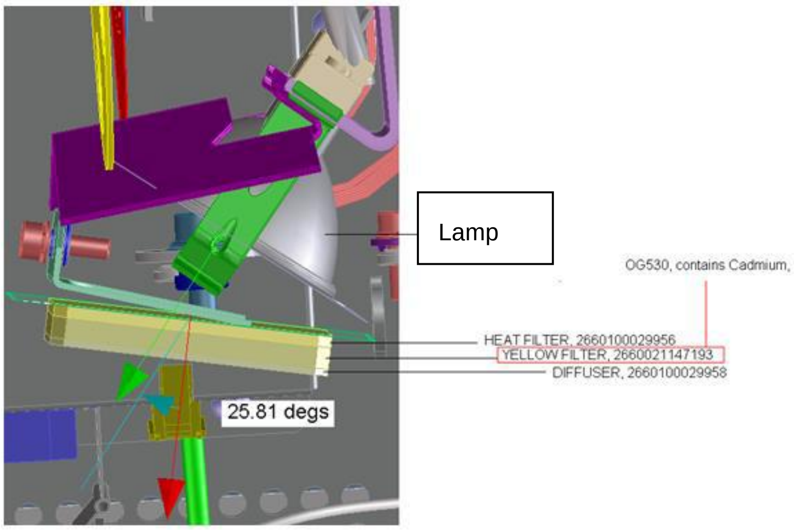


Figure 11. Position of lamp and yellow filter in Humphrey Field Analyser

A cadmium-based optical filter is used so that the spectrum is the same irrespective of the angle between the lamp and the patient’s eye.

The RG850 optical glass filter is used to pass near infrared light from an 880nm light emitting diode (LED) and to block visible light. The purpose of the LED is to generate a reflex from the cornea and to illuminate the pupil to track the gaze of the patient. This filter is critical because it blocks the emission from the LED in the red part of the spectrum that would be visible to the patient and possibly could be mistaken for a stimulus. Cadmium-free dichroic filters cannot be used to reject visible light by reflection, because it would appear as a bright spot in the bowl instead of a dark spot, which could also confuse the patient into thinking a stimulus was presented, when it was not.

Colposcopes are used to examine inside the cervix to look for abnormalities. The instrument is essentially a low power binocular microscope but the illumination light is filtered to use in particular a green colour. This enables blood vessels and any abnormalities to be visualised. Lead glass filters (such as VG9) need to be used to ensure that the transmitted green light wavelengths are stable. Lead has a dual function of providing the required optical properties and of lowering the glass melting point so that the added green pigments are stable.

Light filter domes for solar radiation measurement: An example is shown below:

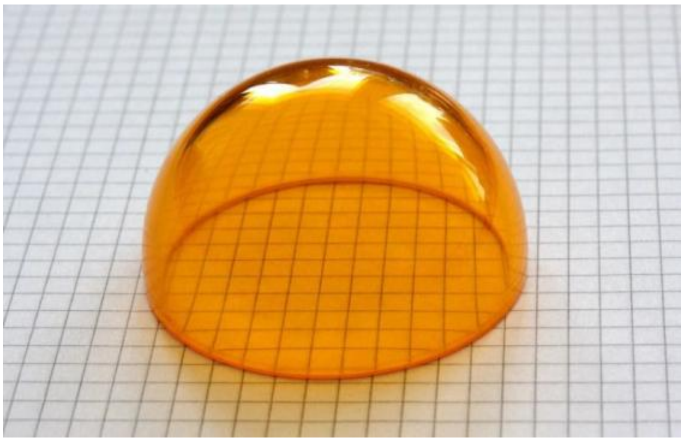


Figure 12. Light filter dome

The light detector of the measuring device is located in the centre of the sphere, and all sunlight rays that reach the detector, hit the filter surfaces with normal incidence and all rays have the same path-length through the filter material as shown below:

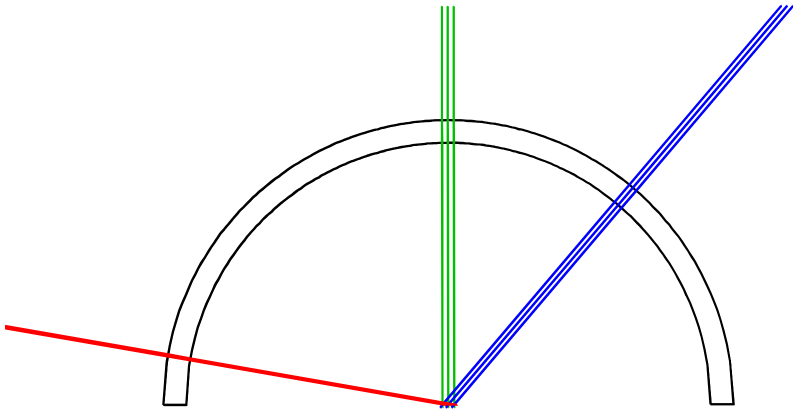


Figure 13. Measurement principle in a light filter dome

The filter characteristics must be independent of the direction of the detected rays and so cannot be replaced by planar dielectric filters as their optical properties are dependent on angle of incidence. If a planar substrate were used, the incident angle varies with the light ray's direction and the incident angle changes the dielectric filter's characteristic. If a curved substrate is used to avoid this effect, then the dielectric filter layers change their thickness due to the changing inclination angle during the filter production, which also shifts the spectral properties of the filter.

Infrared spectroscopic analysis of gases.

This analysis method can selectively analyse single compounds in a gas mixture by selecting an appropriate wavelength using infrared filters which block other wavelengths. Figure 14 shows a typical layout of the analyser.

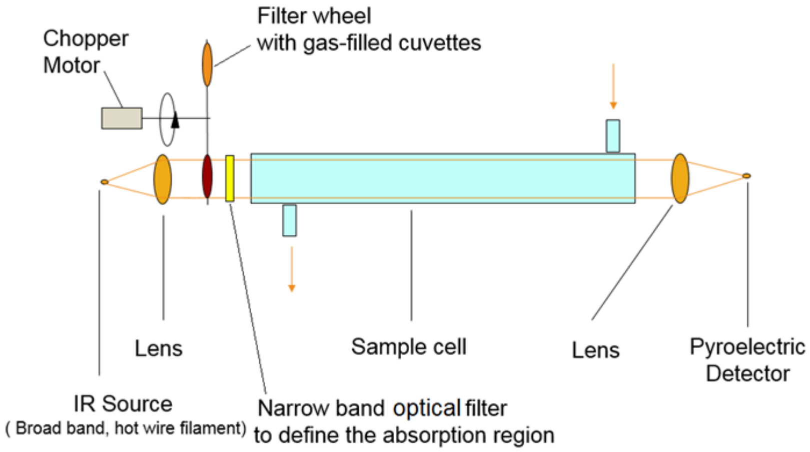


Figure 14. Infrared gas analysis using lead-containing optical filters

The filters consist of a thin coating of a lead compound deposited onto an infrared transparent material (e.g. optical glass, silica, calcium fluoride, etc.). The choice of lead compound, substrate and the coating thickness determine the wavelengths where infrared light has a high percentage of transmission and different wavelengths are selected for each gas being analysed. As each gas absorbs infrared light at specific wavelengths, it is possible to design filters that are specific for analysis of one gas in a mixture and the analysis results are not affected by different gases that absorb at different wavelengths. Typically, these filters are designed to function in the 4 to 14µm wavelength range.

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

All of the following are required:

- Optical filters are required to block light of certain wavelengths and transmit light of other wavelengths. Ideally 100% of the desired wavelengths are transmitted and 0% of undesirable wavelengths are blocked. Also, the wavelength range between 100% and 0% transmission should be as small as possible.
- The function of optical filters needs to be independent of viewing angle.
- Optical filters should be robust and not easily damaged, such as by scratching, abrasion, heat or moisture.
- Precise control of light wavelength control is essential.

---

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.)

No, this is not possible.

2) Please indicate where relevant:

☒ Article is collected and sent without dismantling for recycling:

Based on WEEE EUROSTAT data for categories 8 and 9 (the categories that have most uses for this exemption), data for Germany indicates about 86% of collected WEEE is recycled.

☒ Article is collected and completely refurbished for reuse:

Eurostat data[3] is available for only a few EU States and only for a few WEEE categories. Based on categories 8 and 9 data for France and Germany, reuse is typically 0.1 to 1%.

☐ Article is collected and dismantled:

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

[3] Via links from https://ec.europa.eu/eurostat/web/waste/key-waste-streams/weee

☐ The following parts are subsequently recycled:

☒ Article cannot be recycled and is therefore:

☒ Sent for energy return: Based on WEEE EUROSTAT data for categories 8 and 9 (the categories that have most uses for this exemption), data for Germany indicates about 11% of collected WEEE is incinerated.

☒ Landfilled: Based on WEEE EUROSTAT data for categories 8 and 9 (the categories that have most uses for this exemption), data for Germany indicates about 2% is not recovered (6 – 8% France), so is probably landfilled, but this does not included unreported WEEE.

3) Please provide information concerning the amount (weight) of RoHS substance present in EEE waste accumulates per annum:

The quantities of cadmium and lead filter glass used annually is fairly stable so although the precise quantities in waste are not measured or known, these are likely to be similar to the amounts placed on the EU market annually.

☐ In articles which are refurbished ______
☐ In articles which are recycled ______
☐ 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

Potential cadmium substitutes.

There are three alternative types of optical filters that are used for some applications, but these cannot replace cadmium-based optical filter glass where the essential characteristics of cadmium filters are required. These substitutes are (i) alternative additives in glass, (ii) coatings on glass and (iii) coloured "plastic" filters. These are discussed here:

i. **Alternative additives to the glass** – Cadmium plus sulphur, selenium and tellurium are added to glass to make a material that contains microparticles of cadmium as mixed sulphide, selenide and telluride (as $CdS_xSe_yTe_z$ where x, y and z range from 0 to 1 and x+y+z =1) in the glass matrix. The cut off wavelength is regulated by the ratio of these elements as well as by the heat treatment conditions. The exact form of the cadmium compound is unclear but can be seen as very small particles in a colourless matrix, so it is not a colloidal dispersion. To obtain the same optical properties, alternative inorganic compounds would be needed that are thermally stable at the melting temperature of the types of glass used (therefore all organic pigments cannot be used) and gives the same optical spectrum with the same steep edge. Research has been carried out for many decades to look for alternatives to cadmium, but with no success. The range of elements and their combinations that are suitable is limited as explained here:

- Industry is limited to the ca. 90 naturally occurring non-radioactive elements of the periodic table. The additive must be a compound with two or more elements which must be at least one metal and to match the performance of cadmium, also at least one non-metal.
- The compound must be coloured which eliminates many metallic elements. Many of the transition metals and rare earth metals will colour glass but none give the same optical characteristics (all combinations have been tested, see also section 7A).
- Non-metals could be O, N, S, Se, Te, P, As or Sb. Halides are unsuitable as they are either water soluble or too unstable and so cannot be combined with molten silicate glass.
- The compounds that are suitable must disperse in molten glass without causing crystallisation of the glass (this would destroy the optical properties) and form clear transparent glassy materials. The coloured phase particles that are firmly bound within the glass matrix must be so small (much smaller than 1 micron particle diameter) that the glass is clear and transparent.
- Research has found that a few compounds can be used as coloured glass additives which are either combinations of group II metals with group VI non-metals (i.e. II-VI compounds such as CdS) or group III metals with group V non-metals (i.e. III-V compounds such as GaAs). However, very few of these compounds are yellow, orange or bright red with sharp wavelength cut-offs.
- Most coloured compounds that can be added to glass give different colours to cadmium. For example, nickel compounds are green, cobalt compounds are blue, iron are dull red or brown, mercury (as sulphide) is pink, etc. Compounds with three or more elements have also been evaluated such as CuInSe (a II-III-VI compound), but these also do not give the required steep edge cut-off, as shown below in Figure 15. A recent patented quaternary glass is described in section 7 (A).

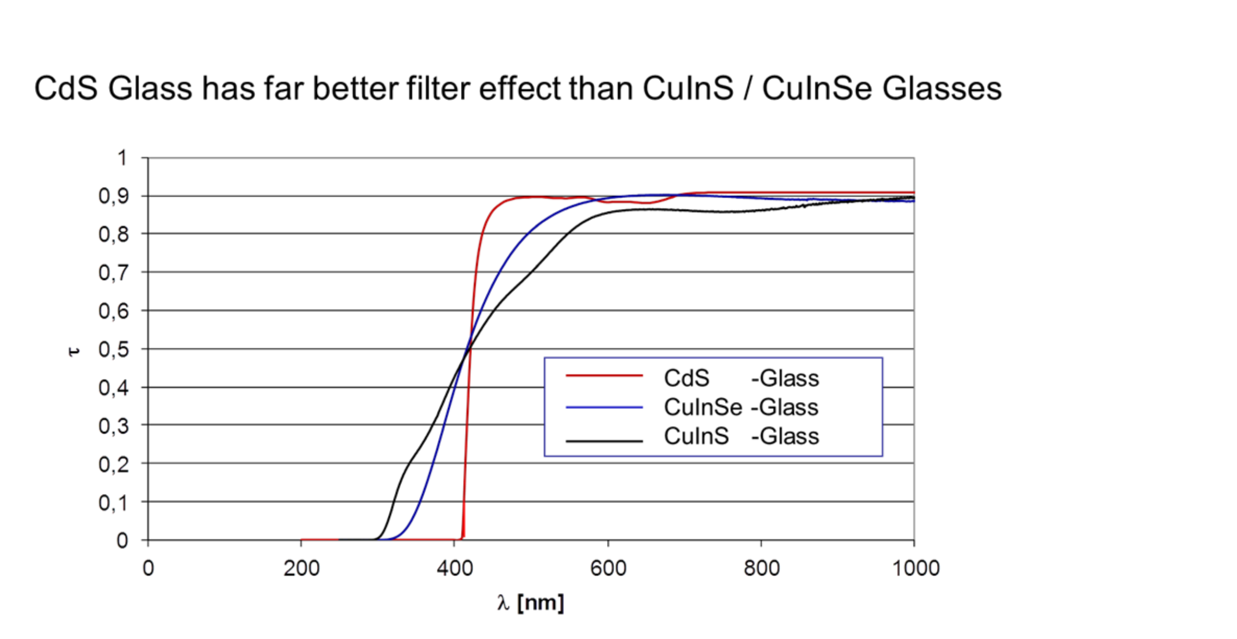


Figure 15. Optical transmission spectra of coloured filter glass (25 mm thickness) comparing slope shapes of CdS with CuInS and CuInSe.

The version of Figure 15 shown above is reproduced below to show the difference in wavelength range between 10% and 90% transmission.

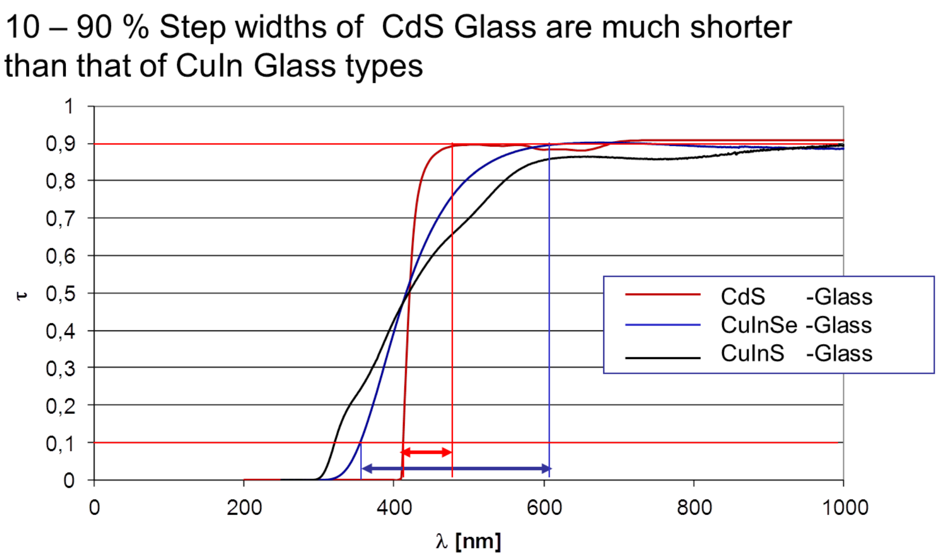


Figure 16. Comparison of cadmium glass filters with cadmium-free substitutes to show difference in slope

Metal ion coloured glass – This is another alternative type of coloured glass filter where metal ions (usually transition metals) are inserted into the glass matrix to colour the glass. In the typical example shown below, Cu^{+}/Cu^{2+} and Cr^{3+} ions are added to the glass, but the spectra are very different to those of cadmium steep edge filters:

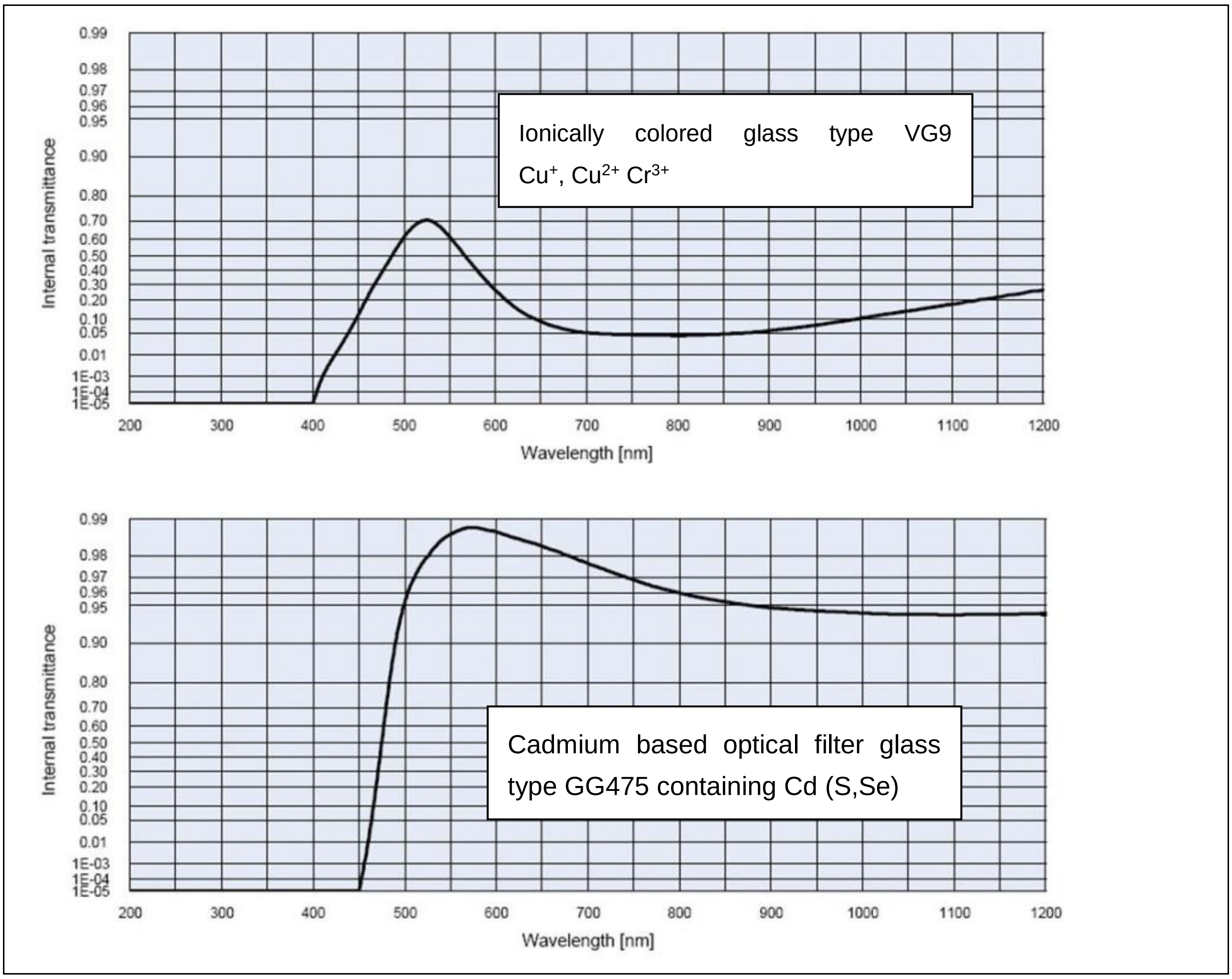


Figure 17. Spectra of ionically coloured glass (above) compared with cadmium glass (below)

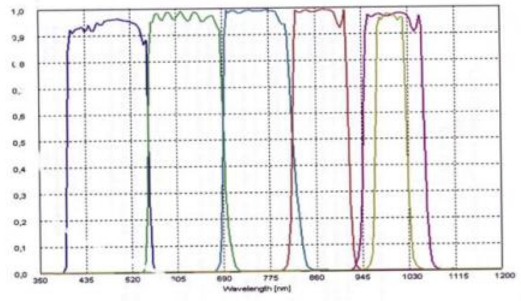
Figure 17 shows that ionically coloured glass types have different shaped spectra to cadmium based glass with lower % light transmission at longer wavelengths and the slope of the curve of the metal ion coloured glass is shallower than the steeper slope of the cadmium filter.

Colloidal dispersions: Coloured glass including ruby red colours can be obtained by adding substances to glass which form colloidal dispersions. The colloid's particle size controls the colour by light diffraction, but colloids do not however give sharp wavelength cut-offs, so are not suitable alternatives to cadmium compounds. Colloids are produced by several metal sulphides such as Pb, Sb, Cu, etc. and also by metals such as gold and silver.

ii. **Thin film coatings on transparent substrates**:

A. Interference filters - Interference, or dichroic filters, are quite widely used for certain applications but their properties are very different to glass filters based on cadmium compounds. Their main characteristic is that they absorb light within a specific but rather narrow wavelength range with sharp cut-offs at both ends of this wavelength range. Spectra of light that has passed through this type of filter are quite different to spectra obtained with cadmium glass filters as shown below.

Spectra of five types of interference coated filters



Spectra of coloured glass filters, the two at the right contain cadmium (RG9 and RG850)

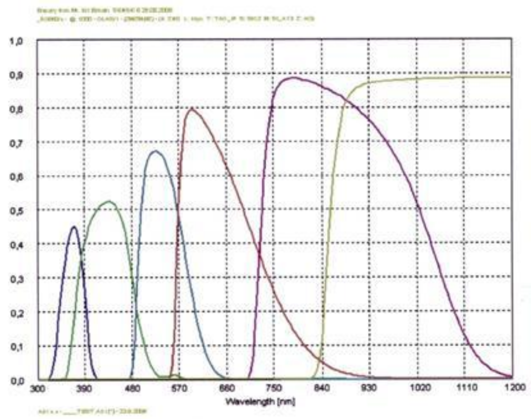


Figure 18. Spectra of interference coated filters with coloured glass filters

Interference filters are also viewing angle dependent and can give "ghost" images. The images below show how viewing angle affects the transmission spectra from glass filters and interference coated filters.

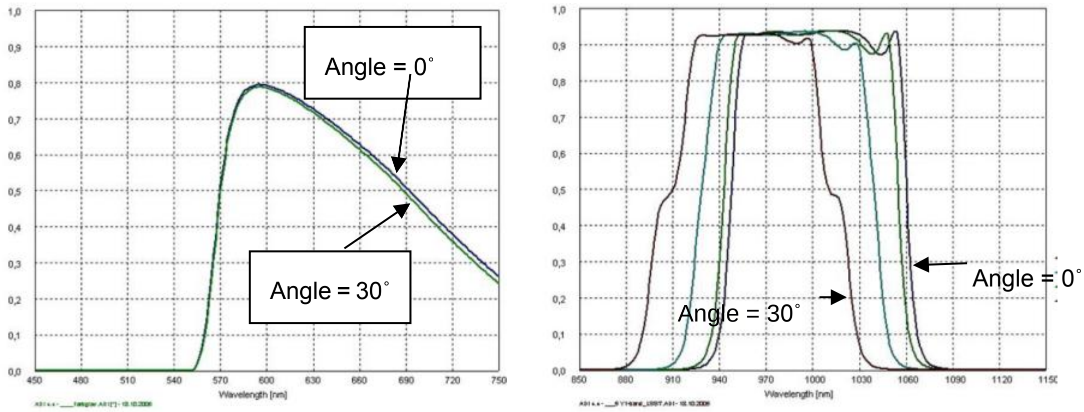


Figure 19. Spectra of light from coloured glass filter (left) and interference coated filter (right)

Interference filters may transmit light in one main band but also in unwanted side-bands at lower intensity.

One example that illustrates why dichroic filters cannot always replace optical filters containing cadmium is discussed in the answer to Q4 (B) where HFA SWAP is described. This technique uses two types of cadmium-based filters. Dichroic filters cannot be used instead of the yellow filter because changes in viewing angle affect the transmitted spectrum and any change means that the normative databases cannot be used to determine if the patient is suffering from early stages of glaucoma or other conditions. The light source used is a halogen lamp which gives light with a range of incident angles, as shown in Figure 20.

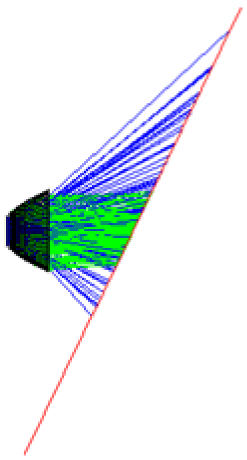


Figure 20. Range of incident angles from the lighting source in a HFA SWAP

The light spectrum transmitted through a cadmium-based optical filter will always be the same, whereas spectra of light transmitted through dichroic filters varies with angle of incidence. This will be the same if the filter is placed parallel with the lamp's face as the angle of incidence will span 20˚. Dichroic filters cannot be used as alternatives to the RG850 filter to reject visible light by reflection because it would appear to the patient as a bright spot instead of a dark spot, which could confuse the patient into thinking a stimulus was presented when it was not and give erroneous results.

A1. Interference filters for infrared gas analysis – Interference filters with thin lead compound coatings are used because the lead compounds have one of the highest refractive index of coating materials and also give very good blocking properties outside of the transmission wavelength range. This means that they allow only a relatively narrow wavelength range to pass and block higher and lower wavelengths. Using a coating material having a high refractive index gives the steep cut-off that is required to avoid interference from other gases. Also, this can be achieved by using one coating layer on the substrate. The use of multiple layers has been considered, but this introduces defects such as marks, splits and scratches which reduce transmission and result in poor yields as sub-standard filters become waste. Also, each filter typically allows through 70 – 80% of light in the required wavelength range and so if more than one filter is used, this significantly reduces the percentage of light passing which reduces the sensitivity and accuracy. An undesirable property of interference filters is that they also transmit light at wavelengths other than the main transmission wavelength and these are called "sidebands". Ideally the sidebands should be as far away from the main transmission peak as possible because they need to be blocked by other filters. As all filters typically give a "bell-shape" curve, if the sidebands are close to the main peak, the filters can also block some of the required wavelengths, thereby reducing sensitivity. The small signals obtained by spectroscopic analysis methods always experience some signal noise and so it is important that the signal from the transmission wavelengths is as strong as possible, despite the very low gas concentrations being detected. Any change that reduces signal strength will reduce performance because it decreases the signal to noise ratio. Research with lead-free coatings, such as germanium, shows that these sidebands are at wavelengths that are much closer to the desired transmission wavelength than with lead compounds. An example is shown in Figure 21.

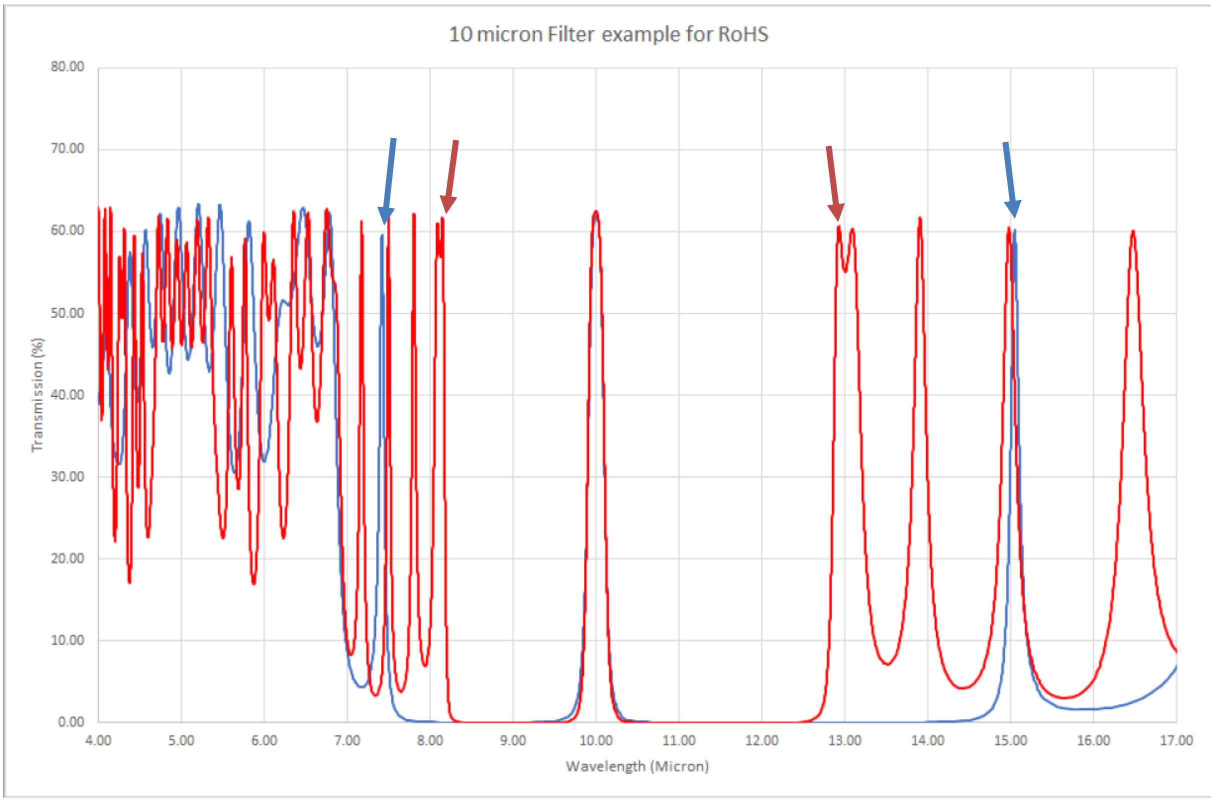


Figure 21. Transmission spectra of lead telluride interference filter (blue line) and a germanium transmission filter (red line). The arrows indicate the closest primary sidebands to the main transmission wavelength

The wavelengths of the closest sidebands are listed in Table 1 where a larger gap is desirable, as well as the refractive index, where a higher value is also desirable.

Table 1 Wavelengths of sidebands

	Lead telluride coating		**Germanium coating**	
Refractive index at 10µm	5.6		4.25	
First Order Sideband wavelengths	7.4µm	15µm	8.25µm	13µm
Δ from 10µm	2.6µm	5.0µm	1.75µm	3.0µm

Manufacturers have carried out extensive research to obtain the highest sensitivity and accuracy because these analysers are used to detect trace concentrations of toxic gases so that emissions of these can be prevented. Alternative coatings and changes to the analyser design have been considered. Research has found that lead compounds have the highest refractive index of the materials that transmit at the required infrared wavelengths and so because of the sideband issue described above, they give the best sensitivity and can detect lower gas concentrations than other filter materials.

One design option that has been considered to enable lead interference filters to be designed out is to increase the path length so that the infrared light passes through a longer tube of gas that is being analysed and so passes through more of the gas being analysed. This however has two disadvantages: A longer path length means that the response time is reduced. Typically, gas, such as from a flue, is pumped through the analyser tube, but the longer the tube is, the longer timescale before a change in composition is detected. This could mean, for example that more toxic gas is emitted from the flue before it is detected and corrective action can be taken. A second disadvantage is that with a longer path-length, more of the infrared light is scattered and lost so that sensitivity is not increased. Therefore, for each application, there is an optimum path-length for maximum sensitivity and this cannot be changed to allow the use of different filter materials.

B. Coloured coatings - If inorganic compounds are used as coatings onto glass, unless the coatings are based on cadmium compounds, the steep edge properties described above cannot be achieved. Organic pigment coatings are inferior because they fade when exposed to ultraviolet light and all thin coatings are easily lost by abrasion.

iii. **Transparent plastics with organic pigments** are used as optical filters and have advantages and disadvantages, but these disadvantages make them unsuitable for many applications. The addition of organic dyes and organic pigments to molten glass is impossible as all are thermally unstable at glass melting temperatures. Only heat stable inorganic compounds such as the cadmium chalcogenides (e.g. CdS/Se) can be used.

Coloured organic compounds can, however, be added to a few types of transparent non-crystalline plastics such as acrylics, to give clear coloured transparent plastics without decomposition of the coloured substance. Achieving optical clarity is however not possible for all combinations of coloured compounds and polymers. Most polymers are available only as opaque materials and most pigments will not dissolve so give opaque dispersions. Optical transparency requires that the pigment either dissolves in the polymer, so is present as discrete molecules, or that the particle size is sub-micron and smaller than the wavelength of visible light, so that they are not visible to the human eye. Coloured transparent plastics are however used for low-end optics (e.g. children’s toys) where high performance is not required. The main disadvantages are:

- Plastics are easily scratched.
- They are affected by humidity as all plastics absorb water from humid air.
- They are affected by high temperatures (distort, degrade, change colour). Optical filters are used with lamps that can become very hot as well as with laser light sources that heat the filter. Apart from heat transmitted by the lamps, most filters function by adsorbing light of certain wavelengths and transferring the absorbed energy into heat.

- Organic pigments fade when exposed to ultraviolet light and polymers are also affected causing colour changes. Brittle fracture may also occur when exposed to UV light.
- Image quality tends to be poor as the surfaces of plastic filters are easily warped, so are not optically flat.
- Some polymer filters with organic pigments have relatively poor maximum transmission percentages at wavelengths of light that should pass through the filter.
- Some polymer filters transmit light at wavelengths where light needs to be blocked.

An example of the spectra of four commercial cadmium-free plastic filters is illustrated below[4] showing that the slop

e is not as steep as Cd-containing filter glass and transmission is significantly lower.

[4] Source, downloaded May 2019, https://www.eventtechnik3000.ch/VARYTEC-Farbfolie-gelb-101

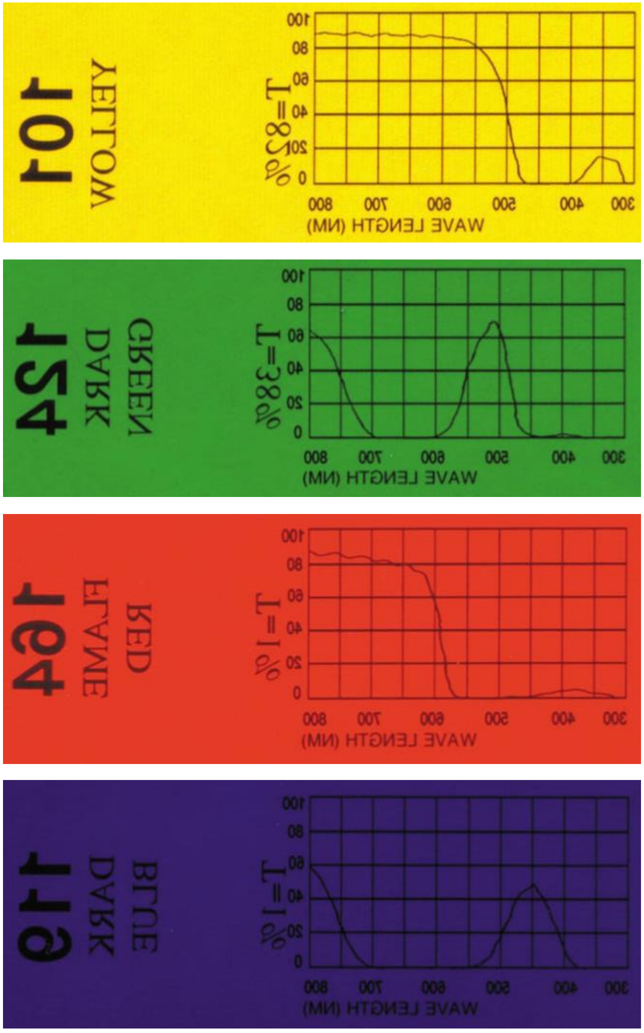


Figure 22. Spectra of light transmission for commercial plastic filters

In the red spectrum of Figure 22, the slope is much less steep than with cadmium based optical glass filters as shown in the Table 2.

Table 2 Comparison of yellow 101 plastic filter with SCHOTT glass filter GG495 filter (data from Figure 9 above)

Transmission %	Yellow plastic (nm)	SCHOTT GG495 (nm)
20	489.6	490
40	500	495
60	510.4	499
80	541.7	505
20 to 80% range	Over a range of 52.1 nm	Over a range of 15nm

Several types of “gel filters” are used for photography and other applications. These include polyester gel filters and the Kodak Wratten range of coloured filters. These are made of gelatine with organic dyes so will fade in sunlight, they will readily absorb moisture (and distort) at high ambient humidity and as gelatine is a protein, they will be affected by a wide variety of chemicals such as oils, fingerprints, etc. and are prone to degradation by micro-organisms. Gel filters are also heat sensitive so cannot be used with hot lamps or at high ambient temperature and being relatively soft, they are easily damaged.

The properties of optical glass and optical polymer filters are compared in Table 3.

Table 3. Comparison of glass and plastic materials for filters

Property	Glass filters	Plastic filters
Tolerance (i.e. variation in characteristics of commercial lenses)	Low (±0.0001) can be achieved, so variation is very small	Estimated at ±0.001
Abbe number	Broader range (20 to >80) especially to low dispersion values	23 – 58 is possible
Transmittance of unfiltered light (through 3mm)	>99% achievable	85 – 91% typically
Density	Lead-based are ca. 5 g/cm^3. This offers advantages and disadvantages	1 – 1.2
Water absorption	Zero (so moisture has no effect on performance)	All plastics absorb water causing changes to properties (as they swell) and potentially degradation can occur. From 0.01% to 0.3%
Thermal expansion	CTE(-30°C; +70°C) = 5.1 - 11.9 x 10^{-6} /K	Range is 47 to 80 x 10^{-6}/K. This causes optical changes with temperature and thermal degradation
Refractive index thermal dependence	Smaller range of - 0.7 to + 1.2 x10^{-5}/˚C	-8 to -14 x 10^{-5}/˚C
Resistance to damage	Relatively hard so not easily damaged	Soft so easily scratched
Exposure to UV light	No effect	Organic pigments fade and plastic discolours and degrades
Heat	Resistant to temperatures created by lamps and laser light sources	Lamps and lasers can easily cause deformation or even make holes

The methods usually used to measure the hardness of glass and plastic materials are not the same and so comparative data is not published. However, Spectaris has arranged for three plastics that are used for plastic lenses to be measured for “Knoop hardness” (0.1kg weight and 20 sec indentation, 5 measurements per sample), which is the standard method used for brittle materials such as optical glass. These measured values are compared with the values for glass published by SCHOTT in Table 4.

Table 4. Comparison of measured Knoop hardness of selected plastics and types of optical glass used to make optical filters

Material	Knoop hardness (Pascals)
Polycarbonate	Measured at 13.2 ± 0.2
PMMA	Measured at 22.4 ± 0.1
Polydithiourethane (used for spectacle lenses)	Measured at 14.0 ± 0.1
Lead-based glass SF57	350
Lead-based glass SF11	450

It is clear from these results that plastic filters will be much more easily scratched than glass filters. Scratches will cause light scattering which has a detrimental effect on most of the uses of cadmium-optical filters.

Lead

Only one type of filter glass is currently produced that contains lead and is used because of its unique combination of properties. Research has not identified an alternative material with the same combination of essential properties. Filter VG9 shows Chromium III and copper I ions dissolved in a lead silicate glass. The same ions in lead-free glass give completely different properties and performance showing that the interaction between the coloured metal ions and lead atoms in the glass matrix is what gives the required performance. Glass filter manufacturers have evaluated many other combinations of ions in lead-free glass, but none gives the required properties.

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

Reliability is not an issue for these exemptions, which is required because no alternatives provide all of the essential characteristics

---

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.

Research has been carried out for many decades and alternatives to cadmium and lead are already used where these are suitable, as discussed in this document. A Spectaris member has carried out a keyword literature search of optical glass filter materials. Since the last renewal request, there were no publications referring to substitution. Specific for the application of traffic lights, there was one publication with a suitable filter glass types, however this is based on lead containing glass and/or with an unusually high level of arsenic – thus overcompensating the benefit of cadmium-free filter glass types and also not achieving the high percent transmission.

As discussed in section 6A, glass manufacturers have in the last 30 years considered the entire periodic table to determine whether substitutes exist:

- Alkali and alkaline earth metals – give colourless glass.
- Transition metals (except zinc, cadmium and mercury, see below) and rare earth metals, - if these dissolve to form a glass, they result in coloured or colourless glass, but this depends on the valency state. If the valency changes, the colour also changes. Often, especially at higher concentrations, these metals ions cause crystallisation so that an opaque material is produced. Two transition metal ions are used in VG9 glass but this unique material has the required performance only with lead silicate glass. A recent patent[5] describes red coloured glass that contains copper and neodymium oxides. Figure 2 of this patent shows that this does not give sharp cut-off as provided by cadmium chalcogenides.
- Zinc, cadmium and mercury form chalcogenides with sulphur, selenium and tellurium. Only cadmium chalcogenides give red/orange/yellow coloured striking glass filters with steep edges (and requires small amounts of zinc to be present).
- Most transition metals (e.g. aluminium, indium, tin, bismuth) either do not form glass (so ceramics result) or if they do form glass, these metals dissolve without forming the fine semiconducting particles that give steep edge filtering that is achieved with cadmium chalcogenides. Lead oxide for example completely dissolves to form clear transparent glass and gallium arsenide is also colourless. Ternary chalcogenide glass types have also been investigated as described above in Section 6. Quaternary glass formulations are also being investigated and one recent patent[6] describes $Cu_2ZnSnSe_4$ in silicate glass. This glass appears to be an effective sharp cut-off filter in the as-annealed condition, but the cut-off wavelength is in the ultraviolet region and so is not a substitute for cadmium chalcogenides.
- Non-metals – these include sulphur, selenium and tellurium which are used in combination with cadmium. Phosphorous is used in colourless phosphate glass. Phosphides, antimonides and arsenides do not form transparent glass and react with acids to emit very toxic gaseous hydrides. The halogens tend to give materials that are water soluble and are usually colourless.
- Gaseous elements: Hydrogen – occurs in hydroxides, these are water sensitive and usually crystalline, oxygen is used in most optical glass, nitrogen occurs as nitrides but these are usually not transparent and the noble gases are unreactive and do not form

[5] US 9,061,939 B2, June 2015, „Red-dyed glass and method for producing same".

[6] US 9,650,287 B2, May 2017, "Visible light and infrared light transmitting optical colored glass, composition thereof, and preparing method thereof".

glass.

This list only leaves the radioactive elements which are unsuitable.

Combinations of all the elements in the periodic table have been evaluated and only cadmium gives **all** of the essential characteristics for the applications where these filters are currently used. The cadmium compounds used are semiconductors present as specific size particles. The semiconductor properties, such as band-gap, etc. cannot be matched by different semiconductors, and the ability to form dispersions of the correct particle size in glass is difficult to achieve as most materials either dissolve or remain as colloids. Therefore, it has not been possible to replace cadmium compounds in striking glass with cadmium-free alternatives.

At this time, the mechanism by which cadmium compounds create the steep edge in glass is not fully understood which makes the development of substitute materials difficult[7]. Ruby red glass can be made using cadmium-sulphide-selenide (chalcogenide glasses) or with colloidal dispersions of many substances with suitable particle size, but only chalcogenides gives the optical steep edge effect. Research has shown that the sharp edge of cadmium filter glasses is due to electronic excitation of electrons in cadmium chalcogenide crystals within the glass and that the edge can be steepened by heat treatment which enhances this effect. Simple light scattering by colloids does not do this. Steep edge light filtration by cadmium chalcogenides therefore depends on the energy levels of the valence and conduction bands of the atoms in the molecule as well as the bandgap. Research with alternatives to cadmium that give similar red colours also does not give steep edges and this appears to be because these are colloidal (their colour is dependent on particle size as this affects light scattering and diffraction). Colloidal substitutes do not form the necessary small semiconducting crystals that are formed by heat treating cadmium chalcogenides in glass. Therefore, so far it has not been possible to identify a substitute to cadmium that has the same steep edge property and this may never be possible as no alternative metals have the needed combination of energy levels and ability to form the correct size crystals dispersed in a transparent glass.

An example substitution option considered in the past is dichroic filters. These have been used by equipment manufacturers to replace cadmium filters in those applications where this has been technically possible and viewing angle is not an issue. There is a financial incentive for equipment manufacturers to replace cadmium filters with dichroic filters (or coloured glass and plastics) where this is possible because dichroic filters and coloured glass and plastic are cheaper that cadmium filters. However, for the reasons explained in Section 6, this is not always an option.

The only other possible alternatives in these applications would be completely different designs of optical equipment but, so far, alternatives have not been developed for the applications described in this renewal request and other applications that require cadmium and lead filter glass. It is also not possible to envisage alternative designs of equipment that would provide the same function and performance without these filters, so research timescales cannot be

[7] Glass Chemistry, by Werner Vogel, 2nd edition, Springer-Verlag, 1994

planned. Therefore, no substitutes are likely to be developed in the foreseeable future and so at least the maximum validity period is required for this exemption.

Coated filters are also cheaper than coloured glass filters and cadmium glass filters and they can be used in applications where transmissive sidebands and the angular dependence of coated filters are acceptable.

Plastic filters are also much cheaper than coloured filter glasses and are used when filter function tolerances are not stringent and visual colour perception is a more important aspect than strict wavelength separation. Plastic and coated filters can block unwanted light only to residual transmission of about 1%. If this is acceptable they may be used instead of cadmium filter glasses, which block unwanted light to 0.000001% and below. This very high blocking is needed in applications where safety and reliability is essential. An example where substitution has occurred is for amateur photographic camera filters where it can be expected that image processing software can imitate a filter's effect so that amateur photographers may have bought less yellow orange and red optical glass filters in recent years than previously. However, professional users with higher image quality requirements, this trend may not be the same because if an image is distorted because the cut-off-edge was not sharp enough, digital processing software will not achieve the image quality that would be achieved with cadmium (or lead) optical filters. Cheaper substitutes will already be used where this is possible and so cadmium filters are used only when substitution is not technically possible.

Since RoHS took effect in 2006, no cadmium (or lead) free steep-slope filter glass has been discovered, even though the search for a cadmium-free and lead-free replacement with the same filter properties was started at least around 1990. The application of these glasses was always restricted to niche uses with especially high-performance requirements. Manufacturers do not publish the quantities of cadmium / lead filter glass produced annually, so it is not possible to determine whether any decrease has occurred with any accuracy. If there has been an influence by RoHS1 on quantities produced, this has not been observable separately from year-to-year fluctuations.

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

During the last 30+ years, research into how striking glass filters function and substitutes for cadmium has been carried out as described above in section 7(A). Substitution by cheaper dichroic filters or coloured glass and plastics has already been carried out where this is possible by equipment manufacturers. Therefore, the current situation is that there do not appear to be any further combinations of elements from the periodic table to evaluate. A variety of alternative composition and production methods have been evaluated by one Spectaris member, but none produced a filter with the essential performance properties achieved by cadmium filter glass. It is therefore very difficult to estimate timescales for substitution. Based on current knowledge, substitutes will not be identified in the next 10 – 20 years.

---

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 – Although cadmium sulphide is an SVHC, the cadmium compounds present in optical filter glass are in the form of very small dispersed particles in the glass matrix. The exact composition of the dispersed particles is currently unknown as chemical analysis of these very small particles is extremely difficult. However, there is evidence that these particles are non-stoichiometric compounds that contain cadmium, sulphur and zinc from the glass matrix. To achieve a "steep edge", the dispersed particles are most likely to be a type of semiconductor and as such will not have an exact stoichiometric chemical formula, such as of "CdS or $CdZnS_2$". The same holds true for Pb compounds contained in batches for filter glass where it will be present as a complex multi-element mixed oxide in the new substance glass (CAS 65997-17-3) after the melting process.

☐ Candidate list

☐ Proposal inclusion Annex XIV

☐ Annex XIV

☐ Restriction

REACH restrictions on cadmium do not apply to its use in optical glass.

☐ Annex XVII

☐ Registry of intentions

☐ Registration

2) Provide REACH-relevant information received through the supply chain.
Name of document: _____

Based on the current status of Annexes XIV and XVII of the REACH Regulation, the requested exemptions would not weaken the environmental and health protection afforded by the REACH Regulation. The requested exemptions are therefore justified as other criteria of Art. 5(1)(a) apply

(B) Elimination/substitution:

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

   ☐ Yes. Consequences? _____

   ☐ No. Justification: _____

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

   ☐ Yes.

   ☐ Design changes:

   ☐ Other materials:

   ☐ Other substance:

   ☒ No.

   Justification: Not possible for all current uses. Substitution has already been carried out using cheaper filters where this is possible, as described above.

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

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

   1) Environmental impacts: Not applicable

   2) Health impacts: Not applicable

   3) Consumer safety impacts: Not applicable

⇨ Do impacts of substitution outweigh benefits thereof?

This is not applicable as these are not reasons for needing these exemptions. However, not allowing these exemptions would negatively affect all three, for example:

1) Environmental impacts: Unable to analyse for environmental pollutants. Gas analysers that use lead compound coated interference filters will be less sensitive if they are not permitted by these exemptions. This would result in higher emissions of toxic gases.

2) Health impacts: Medical research would be much more difficult or impossible without fluorescence microscopes, HFAs and other instruments that use these filters.

3) Consumer safety impacts: Facility security survey at night time without dazzling observer (by use of near infrared imaging). Some types of speed enforcement cameras use these filters.

Please provide third-party verified assessment on this: _____

(C) Availability of substitutes:

a) Describe supply sources for substitutes: Coloured glass and coated filters are widely available but have different performance characteristics so cannot be regarded as substitutes.

b) Have you encountered problems with the availability? Describe: Not applicable

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

☐ Yes ☒ No – cadmium and lead filters are more expensive than other types of filter.

d) What conditions need to be fulfilled to ensure the availability? Need to identify new composition.

(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 See below

☐ Possible social impacts external to the EU

☐ Other: _____

Filter glass and optical equipment manufacturers have already phased out filter glass types with cadmium and lead proportion wherever this has been possible, as most equipment manufacturers have already attempted to switch to cadmium and lead-free filter glass wherever possible because cadmium and lead-free substitutes have lower prices.

There would be a competitive disadvantage to EU filter glass manufacturers that manufacture cadmium and lead-based optical filter glass if these exemptions were not renewed because only a very few global manufacturers produce these types of filters as well as cadmium and lead-free alternatives. Several EU filter glass manufacturers stopped making cadmium and lead-based glass due to the declining market size resulting partly from the restrictions on cadmium and lead by RoHS as well as due to consumer demand.

In the EU, there is no real disadvantage to EU manufacturers of cadmium and lead-based filter glass as all manufacturers and importers must comply with RoHS in the EU. However, EU manufacturers may be at a disadvantage when competing outside of the EU with non-EU competitors that do not operate within the EU. This would not only be applicable to cadmium and lead-filter glass manufacturers, but also manufacturers of products made with glass if the EU versions were to have inferior performance. EU filter manufacturers are subject to the EU

Industrial Emissions Directive (IED), and therefore emissions are strictly controlled in the EU, however this Directive is only relevant to manufacturing sites located in the EU.

In the EU, there is only one cadmium and lead-based optical filter glass manufacturer left. Emissions from cadmium and lead containing filter glass types are very small and controlled. In Japan, almost all glass manufacturers have stopped production of cadmium and lead containing filter glass since consumer optics, which is the by far largest market, does not require the special performance of these filters. Due to cost reasons Japanese filter glass manufacturers shifted a large proportion of production to China many years ago. China is the only country with a significant production of filter glass but on a lower quality level. Details about Chinese production are not published.

There are an estimated 5,000 manufacturers in the EU that rely on optical glass and many of these use filter glass (most are SMEs), worth €69Bn per annum (not including end users such as the medical sector, aerospace, etc.). The European Photonics industry has a 50% global market share for production technology, 35% global market share for Optical Measurement & Image Processing and a 32% global market share for Optical Components and Systems[8]. The European Photonics Production Growth rate is more than 3.5 higher than the EU's GDP growth rate and has grown with an average CAGR of 5% since 2005.

If exemption 13b were not renewed, this would have a devastating impact on EU industry affecting up to 5,000 companies in the photonic sector alone with many billions of lost income to the EU and many lost jobs. 300,000 people work directly in the EU photonics sector, but many more in EU industries that rely on photonic equipment. If exemption 13b is not renewed, this would mean that many types of products could not be sold in the EU, making EU industries such as film production and R&D uncompetitive or impossible and the health of EU patients would be negatively affected as equipment that relies on these filters could not be obtained by EU hospitals and clinics.

Without this exemption, hospitals could not replace optical instruments such as "Short Wavelength Automated Perimetery", Fluorescence microscopes and IVD analysers and this would severely harm many thousands of EU patients per year. Also, EU manufacturers of a very wide variety of products ranging from aerospace, automotive, engineering, etc. could not buy the optical instruments they rely on so that many industries would not be able to continue operating in the EU. EU researchers in research establishments would become uncompetitive or be unable to continue in many fields without high performance optical instruments. Many manufacturers and researchers rely on equipment that needs exemption 13b to remain highly competitive.

The EU is continuing to fund research in the photonics sector (€85 million awarded in 2018) with the HORIZON 2020 Framework program which has funded research into optics technology for many years. Recently the European Commission confirmed the importance of this sector to the EU by announcing that this will continue as Horizon Europe (2021-2027),

[8] From Optech Consulting, data at https://www.photonics21.org/ppp-services/photonics-downloads.php

once the current Horizon 2020 period is completed. This funding will encourage research into new optical solutions as substitute materials for cadmium lead are unlikely to be successful. This funding would support the long-term EU aim to stay ahead of other competing economies, which currently do not have the same substance prohibitions as EU industry without these exemptions.

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:
