PPTF Polish Tecnological Platform on Photonics

Ożarów Mazowiecki, 1st of September 2020

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Dear Dr. Billaud,
in response to the questionnaire regarding exemption request 1(c) "Lead, cadmium and mercury in infra-red light detectors", we would like to submit answers to the question you raised.

Your Sincerely,

Adam Piotrowski,
President of the Board

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Questions

1. **In the figure 3, what does mean 2TE and 4TE?**

TE is part of an acronym TEC, which stands for ThermoElectric Cooling of the detectors an alternative to liquid nitrogen cooling. The number before the acronym, xTE (where x is 2 or 4 in the question) denotes the number of stages of the thermoelectric cooler. Typical operating temperatures are ~230K and ~195K for two- (2TE) and four-(4TE) stage coolers.

2. **You request an exemption for cadmium and mercury for mi-infrared spectroscopy for the analysis of gases in medical applications. In which equipments can we find these types of detectors?**

MCT detectors are widely used in construction of breath analysis equipment, especially utilizing mid-IR laser spectroscopy. The list of equipments is of course very long and here we only enclose several examples:

- **FTIR (Fourier transform infrared) spectrometers** use double beam interference to modulate the signal from broadband source and scan throughout the infrared wavelength range

  https://www.bruker.com/products/infrared-near-infrared-and-raman-spectroscopy/ft-ir-routine-spectrometers/ftir-microscope-lumos-ii.html

- MCT detectors are used in **NDIR (non-dispersive infrared) spectrometers**, for example used to selectively detect isotopic variations of CO2, which takes advantage of difference between the spectra of CO2 with different C isotopes and therefore enables marking with other isotopes.

- Another equipment type are **CRDS systems (Cavity Ring-Down Spectroscopy)**. The principle is absorption spectroscopy, whose sensitivity is enhanced by utilizing an external cavity. Those systems are entering the commercial market and show great potential, as they are robust and compact, all while showing great detection capabilities. https://www.degruyter.com/downloadpdf/journals/oere/20/1/article-p26.xml

- Also utilizing absorption spectroscopy **are MUPASS systems (MultiPass Absorption Spectroscopy Systems).** They take advantage of using a specially designed cavity, which increases the optical path of infrared light in order to enhance sensitivity. Fully functioning MUPASS systems for detection of various gaseous species are emerging from research facilities and are expected to enter the commercialization phase in upcoming years. (https://www.osapublishing.org/oe/fulltext.cfm?uri=oe-25-11-12743&id=366985)

- **TDLAS (Tunable Diode Laser Absorption Spectroscopy)** is a high-resolution infrared spectroscopic technique applied for gaseous samples. It combines regular absorption spectroscopy with tunable diode laser, which allows it to focus on one specific, isolated absorption line of particular species of interest.

Light source is tunable laser diode (TDL), which can operate in broad spectral range (3 - 30 μm) and enables easy change of wavelength. Multi-pass cell and mirrors allow to increase optical path to hundreds of meters. Intensity of transmitted laser light is measured by a photodetector. https://www.osti.gov/servlets/purl/1435936

- **ICOS (Integrated Cavity Output Spectroscopy) or CEAS (Cavity Enhanced Absorption Spectroscopy)** – it is a laser spectroscopic technique, which uses a Fabry-Pérot external cavity, formed by two highly reflective mirrors, to increase path length. The laser beam in this technique is introduced to the cavity at a small angle (off-axis), which results in dense mode structure. Thanks to this system is less affected by instability of cavity and laser spectrum and also resonances of the cavity are avoided.

New methods are emerging as well, e.g. using optical frequency combs in mid-IR to perform spectroscopy at much broader spectrum. Broad spectral response of MCT detectors combined with high detectivity is a great advantage in such equipment. Time-resolved Fourier transform spectrometers with high speed lasers are also being developed using ultrafast MCT detectors.

Above list of techniques and equipment is far from exhaustive, but it shows great potential for gas analysis using IR light for easy and accessible diagnostic tools for medical use.

Using of MCT detectors will facilitate introduction of new diagnostics equipment, as it is a readily available and well-described technology, combining broad spectral response with high sensitivities. This is a great opportunity for engineering companies, as it enables rapid prototyping of equipment using readily available detector components, and also will play a role in fast coming of medical equipment to clinical trials, and later regular use.

3. **You mention the use of MCT for the analyses of exhaled breath as a diagnostic tool and CO2 is among the gases that can be detected. PbSe-based detectors are employed for the CO2 analysis in inhaled air and exhaled breath of patients (capnometers) thanks to their high sensitivity to CO2 wavelength. COCIR requested an exemption for Pb in capnometers stating that it is used as and with medical devices.**

    a. **Are capnometers an application of your request?**

    b. **If so, what are the differences in the applications in the scope of COCIR's and your requested exemption so that you do not require lead while COCIR does not request the exemption for mercury and cadmium?**

Capnometers understood as sensors for CO2 in exhaled breath are one of the applications of our request. They utilize PbSe-based detectors for their good sensitivity to CO2 and are a well-established technology.

However, CO2 is just one of numerous gases which remain in interest of medical applications. MCT-based detectors have tunable and much broader spectral sensitivity than PbSe detectors, which allows them to be used in applications which require analysis of other gaseous specimens. Exhaled breath contains some main components (O2, CO2 etc.) and more than thousand other substances in low concentrations (ppm/ppb/ppt). The concentration of some of them may depend on health status. Those substances are called biomarkers and they may be used to diagnose some diseases or pathological processes in the human body. Breath analysis is a promising screening test, because it is non-invasive, quick and painless. Due to low concentrations of breath biomarkers use of high-resolution measurement techniques and sensitive detectors is needed.

Some breath biomarkers detected by MCT detectors are presented in the table below.

Breath biomarker	Disease	Limit of detection, ppb	Norm, ppb	Spectral fingerprints, mm	Measurement technique
acetaldehyde CH3COH	after alcohol consumption, lung cancer	80	0-104	5.79 and 5.67	TDLAS (Tunable Diode Laser Absorption Spectroscopy)
ethane C2H6	oxidative stress, Alzheimer's disease	-	<10	3,33	TDLAS (Tunable Diode Laser Absorption Spectroscopy)
acetone C3H6O	type 1 diabetes	510	100-2700	8,2	QCL(Quantum Cascade Laser) -based infrared spectrometer
methane CH4	oxidative stress, cancer	48	<10000	3.3916 and 3.3920	HWG-TLAS (Hollow WaveGuide-Tunable Laser Absorption Spectroscopy)
nitrogen monoxide NO	asthma, chronic bronchitis, allergic rhinitis	5	< 50 (adults)	5.26296	ICOS (Integrated Cavity Output Spectroscopy)
ammonia NH3	renal diseases, asthma	3 or 4	250-400 (morning)	10.341	pulsed QCL (Quantum Cascase Laser) based spectrometer
formaldehyde CH2O	lung and breast cancer	< 100	<1500	3.530	ICOS (Integrated Cavity Output Spectroscopy)
hydrogen cyanide HCN	cystic fibrosis	8	<14	1.538	ICOS (Integrated Cavity Output Spectroscopy)

Breath biomarker	Disease	Limit of detection, ppb	Norm, ppb	Spectral fingerprints, mm	Measurement technique
methanethiol CH3SH	halitosis, cirrhosis, hepatic encephalopathy and coma	13	< 150 (overall value of all sulfur compounds)	3.3565	WMS-TDLAS (Wavelength Modulation Spectroscopy-Tunable Diode Laser Absorption Spectroscopy)
ethylene C2H4	lipid peroxidation, ultraviolet radiation damage of skin	5 or 7	-	10.309	pulsed QCL (Quantum Cascade Laser) based spectrometer
carbonyl sulfide OCS	hepatic failure, cystic fibrosis, rejected lung transplant	1.2	3-30	4.86	TDLAS (Tunable Diode Laser Absorption Spectroscopy)

The broad range of detected wavelengths may also be beneficial in equipment designed to analyze many gaseous species at once, as only one MCT detector can be therefore used. Analysis of other gaseous species is vital to the development of novel diagnostics methods.

Moreover, MCT-based detectors have much higher detectivities than other detectors, which should allow to detect much smaller concentrations of gaseous species. This again can contribute immensely to development of novel diagnostics methods. Also capnometer design could benefit from higher detectivities of MCT detectors, to increase sensitivity and accuracy of CO2 detection.

4. **Hamamatsu offers a technology based on InAs/GaSb that is commercially available since September 2019. (https://www.hamamatsu.com/eu/en/news/featured-products_technologies/2019/20190828000000.html). It can detect mid-infrared light up to 14.3µm. Can you mention applications for which this alternative technology would be suitable, and why it is not suitable to cover at least parts or your applications in the scope of the requested exemption?**

According to spectral response characteristics presented by Hamamatsu the actual detectivity level at 12 µm is approx. $2{,}5*10^9$ cm·$Hz^{1/2}$/W (which is 16x lower than the MCT detector offered by Infrared Associates – see table below) and at 14 µm is approx. $4*10^8$ cm·$Hz^{1/2}$/W (which is 75x lower than the MCT detector). Its spectral response characteristics makes this detector unfeasible for most applications in the

LWIR (>8 µm) spectrum, as the level of detectivity is significantly lower than in case of other equivalent MCT detectors cooled with LN2. In fact its detectivity levels are similar to MCT detectors cooled with more efficient thermoelectric coolers (~195K).

The above-mentioned Hamamatsu detector indeed can detect IR radiation up to 14,3 µm. However it requires liquid cooling and as such is not feasible to be used in most of the measurement devices. Access to liquid nitrogen is usually restricted and inconvenient. Besides, liquid nitrogen cooling requires additional care and maintenance, and this may provoke problems in medical applications. In contrast, HgCdTe devices can operate at ambient temperature or at temperature achievable with simple, low cost and reliable thermoelectric coolers and their spectral response can be easily tailored for various medical applications.

Manufacturer	Hamamatsu	InfraRed Associates	InfraRed Associates
Symbol	P15409-901	FTIR-16-1.00	MCT-13-1.00
Active element material	type II superlattice (InAs and GaSb)	HgCdTe (MCT)	HgCdTe (MCT)
Cooling	LN2 (-196°C)	LN2 (-196°C)	LN2 (-196°C)
Peak wavelength λpeak, µm	5.4	14.0	12.0
Cut off wavelength λcut-off, µm	14.3*)	≥16.6**)	≥13.0**)
Detectivity D*, cm·Hz1/2/W	1.6×10^{10}(λpeak)***)	3.0×10^{10}(λpeak)	4.0×10^{10}(λpeak)
Active area	Ø1mm	1×1mm2	1×1mm2

*) The wavelength at which the detectivity becomes 10% of the value at the peak wavelength.

**) The wavelength at which the detectivity becomes 20% of the value at the peak wavelength.

5. You state that the concentration of cadmium in articles (infrared detectors) is below 0,1 % w/w. Does this apply to the homogeneous material, or to the entire detector?

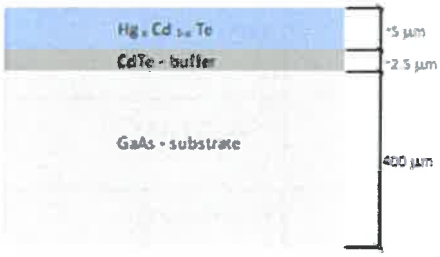
The values referred to in our application apply to the weight of the detector chip, not to the entire detector. The detector chip is based on MCT (HgCdTe) epi-layer grown by Metal-Organic Vapor Phase Epitaxy on CdTe-buffered GaAs substrate, whereas

the entire detector is a detector chip mounted typically on a sapphire pad, wirebonded to a thermoelectric cooler and encapsulated in a standard package.

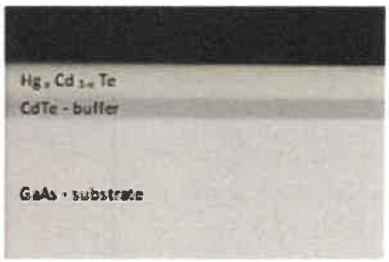
Since the MCT semiconductor layer (together with CdTe buffer) is grown directly on the substrate it is not possible to disjoint the detector chip into a separate MCT layer and GaAs substrate.

Structure of detector chips varies depending on detector type. Figure below shows an exemplary cross-section of the detector active element (a) picture of its structure taken under a microscope (b) and SEM (c). Typical size of the detector chip is 1mm x 1mm.

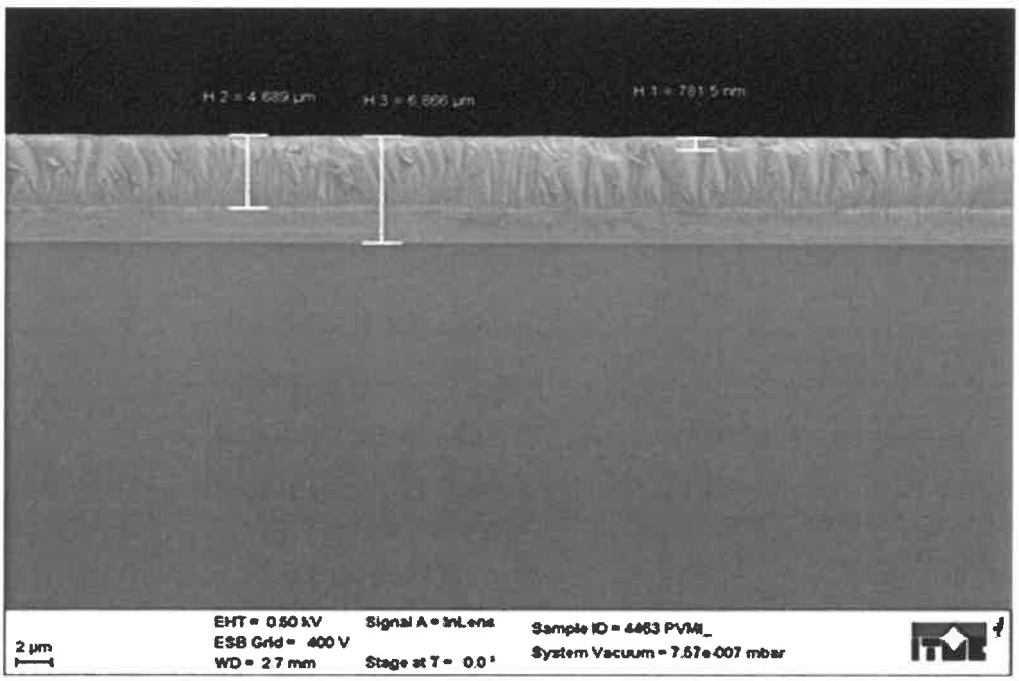
(a)



(b)



(c)



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Referring only to the very thin CdTe/HgCdTe layer (without the substrate) the concentration of mercury and cadmium would be as follows (in a typical 1mmx1mm detector chip):

- mercury ~31%
- cadmium ~23%

6. **You explain that there are alternative detectors without cadmium and mercury (and lead). Why can such detectors not cover at least parts of the (less demanding) applications in the exemption scope?**

Yes, there are potential alternative technologies of detectors based on non-RoHS restricted III-V semiconductor compounds and they may cover some applications. However it is very difficult to precisely distinguish applications that may be covered by III-V detectors. It depends very much on the actual wavelength of analysed biomarkers.

For the most demanding applications there is usually the need to use cryocooled detectors (with LN2). As it was shown in the answer to Question 4, MCT detectors are still much better than III-V detectors, and for some applications they are the only choice, as the detectivity level of III-V detectors is outside of the useful scope.

For other, less demanding applications, not requiring cryocooling, MCT detectors are currently also the only choice, as there are no commercially available III-V detectors with adequate detectivity levels for the LWIR spectrum (>8 µm), working at 195K (temperature reached with the use of simple, low cost thermoelectric coolers).

We expect that the steady progress in the technology will eventually allow to replace completely the use of the RoHS restricted materials but this requires time as described in the application.