

H₂S detection from near-IR to THz spectral regions via Quartz - Enhanced Photoacoustic Spectroscopy

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CBRNs and explosives typically have absorption signatures in the THz and Mid Infrared ranges of the spectrum (TERA-MIR). Quartz enhanced photoacoustic spectroscopy (QEPAS), being a technique exploiting gas absorption signatures, can be successfully employed for detection of explosives and several CBRN agents such as hydrogen cyanide, nitrogen dioxide, formaldehyde, hydrogen chloride, hydrogen sulfide (H₂S) etc., once dedicated laser sources are employed [1,2]. We select H₂S as CBRN agent and developed sensitive QEPAS sensors with the ultimate goal of realizing CBRNs detection with high sensitivity. H₂S is a toxic gas and is a threat to human health, since it is rapidly absorbed by the lungs. Exposure to H₂S at high concentration levels will cause unconsciousness and death, because of respiratory paralysis and asphyxiation. Thus, due to its toxicity, flammability, and corrosivity, it is extremely important to real time detect and monitoring its presence. We investigated all the TERA-MIR radiation range (from near IR to THz), targeting absorption bands related to different kinds of transitions (vibrational and rotational). With this aim, we employed different laser sources and different quartz tuning fork (QTF) resonators. In particular, we employed for the first time a new generation of QTFs, with custom geometry providing high sensing capability. The performance of four QEPAS sensors realized are summarized in the following table.

	Near-IR [3]	Near-IR [4]	Mid-IR [5]	THz [6]
Laser source & Power	Fiber amplified Laser Diode, 1500 mW	Laser Diode, 3 mW	External Cavity QCL, 45 mW	Fabry-Perot QCL, 0.24 mW
QTF	Custom QTF	Standard QTF	Standard QTF	Custom QTF
Wavelength (μm)	1.5	2.6	7.8	103 (2.91THz)
Line-strength (cm/mol)	$1.15 \cdot 10^{-23}$	$1.67 \cdot 10^{-21}$	$1.51 \cdot 10^{-21}$	$1.13 \cdot 10^{-22}$
NNEA (cm⁻¹·W/√Hz)	$1.3 \cdot 10^{-8}$	$2.4 \cdot 10^{-9}$	$7.3 \cdot 10^{-9}$	$3.6 \cdot 10^{-9}$
Detection sensitivity @ 30sec	30ppb	750 ppb	330 ppb	107 ppm

The best detection limit has been obtained in the near-IR range employing very powerful fiber amplified laser diodes. However, the NNEA value measured in the THz results several times lower than those observed in the near-IR and mid-IR ranges, confirming that the THz spectral range is the most suitable for the QEPAS technique. Moreover, in the THz range H₂S shows its strongest absorption lines, up to two orders of magnitude with respect to the mid-IR. Thus, a significant enhancement of the signal-to-noise ratio by more than two orders-of-magnitude and a detection limit of few tens of ppb is expected in the case of stronger absorbing H₂S.

References

- [1] M.F. Pereira, TERA-MIR Radiation: Materials, Generation, Detection and Applications II, Opt Quant Electron 47, 815–820 (2015).
- [2] M.F. Pereira, TERA-MIR radiation: materials, generation, detection and applications, Opt Quant Electron 46, pp. 491–493 (2014).
- [3] S. Viciani, et al., “A quartz-enhanced photoacoustic sensor for H₂S trace-gas detection at 2.6 μm” Appl. Phys. B, 119, 21–27 (2015).
- [4] H. Wu et al., “Quartz enhanced photoacoustic H₂S gas sensor based on a fiber-amplifier source and a custom tuning fork with large prong spacing”, Appl. Phys. Lett. 107, 111104 (2015).
- [5] M. Siciliani de Cumis et al., “Widely-tunable mid-infrared fiber-coupled quartz-enhanced photoacoustic sensor for environmental monitoring”, Opt. Express 22, 28222–28231 (2014).