

# Recent Advances in quartz enhanced photoacoustic sensing

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Trace gas detection has long played an important role in developing photonics sensing technology. Scientists have proposed several types of sensors for different applications. Many of these target health and safety monitoring purposes. Furthermore, hazardous toxic gases and air pollutants such as methane and other hydrocarbons, which are deemed to be environmentally threatening exist in the atmosphere at ppm levels. Environmental assessment and control have become the global issues to which new technologies can introduce ways to resolve rapidly growing environmental issues.

Techniques based on laser absorption spectroscopy for trace gas sensing, compared to other techniques, provide fast response times of  $<1$  s, offer high gas specificity and sensitivity and permit real time in-situ measurements.

One of the most robust and sensitive trace-gas optical detection techniques is quartz-enhanced photoacoustic spectroscopy (QEPAS), an alternative approach to standard photoacoustic detection of trace gas, utilizing a quartz tuning fork (QTF) to detect weak photoacoustic excitation and allowing the use of extremely small volumes. The QEPAS technique exploits the enhancement of acoustic energy density provided by the QTF, which acts as a high quality-factor piezoelectric acoustic transducer [1,2].

QEPAS measurements are usually performed at a detection frequency of about 32 kHz and are more sensitive to the V-T relaxation rate compared to the conventional PAS which is commonly performed at  $f_0 < 4$  kHz. In case of slow V-T relaxation, with respect to the modulation frequency, the thermal waves in the gas cannot follow fast changes of the laser induced molecular vibration excitation. Thus, the generated photoacoustic wave is weaker than it would be in case of fast V-T energy equilibration. With the aim to reduce the QTF resonance frequencies and identify the optimal design for optoacoustic gas sensing, we realized custom QTFs by varying their geometry in terms of spacing between the prongs, their length, width and thickness [3].

The successful implementation of this custom QTFs in QEPAS sensors opens the way to new approaches in terms of acoustic micro-resonator (AmR) system geometry and to the exploitation of the first overtone flexural mode for gas sensing. Recent advances of the QEPAS sensing, achieved using custom QTFs and novel AmR systems will be reported.

The acoustic micro-resonator (AmR) tube for sound wave enhancement is an important component that is acoustically coupled with the QTF to strongly enhance the sound wave intensity. In the standard configuration, a stainless-steel tube is cut into two pieces and the QTF is inserted between them [2]. The possibility to operate with QTFs with space between the prongs up to 1 mm allowed the realization of a novel micro-resonator configuration in which a single tube is inserted between the prongs of the QTF (single-tube AmR) [4].

Single-tube AmR configurations provide increased sensitivity enhancement factors and a reduction of the required AmR length. For a 7.2 kHz custom QTF, an AmR length of 38 mm an sensitivity enhancement factor of  $\sim 100$  was achieved, with respect to that obtained using a bare custom QTF [4]. However, the 38-mm AmR length still remains  $\sim 4$  times larger than the AmR used for the commercial 32 kHz QTF.

Lowering the QTF fundamental resonance frequency reduces also the overtone frequencies, opening the way to their implementation in QEPAS sensor systems. By optimizing the QTF prongs sizes, overtone modes can provide higher QEPAS sensor performances with respect to using the fundamental mode [5, 6]. Since the 1<sup>st</sup> overtone frequency is  $\sim 6.2$  higher than the fundamental one, the AmR optical length can be significantly reduced. Optimal AmR length of 14.5 mm, only 5 mm longer than that employed so far with a commercial 32 kHz QTF and sensitivity enhancement factor of  $\sim 380$  with respect to a QTF operating on the fundamental resonance mode has been demonstrated [7]. The implementation of a dual tube AmR system, exciting simultaneously the two antinodes of the 1<sup>st</sup> overtone flexural mode leads to sensitivity enhancement factor of  $\sim 500$  [8]. A comparison of the performances obtained with different QEPAS configurations is depicted in Fig.1

Furthermore, we developed a dual-gas QEPAS sensor system based on a frequency division multiplexing technique of a quartz tuning fork (QTF). Two beams from two independently lasers focused at two different positions along between the QTF prongs allow exciting both the QTF fundamental and 1<sup>st</sup> overtone flexural modes simultaneously. The resonant resonance frequency difference between two flexural modes ensures that the correlated photoacoustic signals generated by different target gases do not interfere with each other, thereby allowing a continuous real-time dual-gas monitoring [9]. The results obtained using a dual-gas QEPAS methodology will be also discussed.

QTF	configuration	OD (mm)	ID (mm)	L <sub>s</sub> (mm)	Gain factor	NNEA
Custom	bare QTF				1	1.59*10 <sup>-6</sup>
	two-tubes	1.5	1.3	46	40	4.0*10 <sup>-8</sup>
	single-tube	0.9	0.65	38	128	1.21*10 <sup>-8</sup>
	Single-tube+overtone	0.98	0.62	14.5	380	2.76*10 <sup>-9</sup>
	Double antinode + overtone	1.58	1.3	19	500	1.73*10 <sup>-9</sup>
Standard	bare QTF				1	3.7*10 <sup>-7</sup>
	on-beam	1.24	0.8	10.0	30	1.8*10 <sup>-8</sup>

**Fig. 1.** Comparison between the performance of QEPAS systems based on different AmR configurations.

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