

White Paper

Carbon dioxide (CO₂) measurement using Non-Dispersive Infrared (NDIR) Spectroscopy with lead selenide (PbSe) photodetectors

May 26, 2020 – Ludwigshafen, Germany – In today’s world, carbon dioxide (CO₂) concentration measurement has become important, if not vital, in a wide range of applications. These include capnography for medical diagnosis, environmental (indoor/outdoor) pollution monitoring, heating, ventilation and air conditioning (HVAC) as well as industrial safety and monitoring.

This white paper outlines a non-dispersive way to measure CO₂ concentration along with its radiometric and mathematical background. The presented theory may be further used to calculate the detection limit for any other non-dispersive infrared gas detection system. Additionally, a comparison of trinamiX lead selenide (PbSe) detectors and state-of-the-art pyroelectric sensors is made regarding their performance as sensing elements. An example of use in capnography is presented to show how trinamiX bare chip PbSe detectors provide flexibility in optical design due to the small footprint of the bare chip devices, as well as high detectivity and frequency response.

Non-Dispersive Infrared (NDIR) Spectroscopy

Non-Dispersive Infrared (NDIR) spectroscopy is a measurement technique used to non-invasively detect gas concentrations. Depending on their molecular composition, polyatomic gases possess the ability to absorb electromagnetic radiation at specific wavelengths in the infrared region. NDIR spectroscopy utilizes this ability to determine the measured gas concentration.

Since the amount of absorbed radiation through a medium is proportional to the concentration of the absorbing molecules, the concentration of a gas can be determined by comparing the measured absorbance with the absorbance of a known standard, as expressed by the Beer-Lambert Law in Equation 1.

$$A = \log_e \left(\frac{I_0}{I} \right) = \epsilon l c , \quad \text{Equation 1}$$

where

A is the absorbance defined as a natural logarithm of the ratio of transmitted radiant power through the medium I [W] to the initial radiant power I_0 [W],

ϵ [$\text{cm}^{-1} \text{ppm}^{-1}$] or [$\text{mol}^{-1} \text{cm}^2$] is the molar extinction coefficient,

l [cm] is the optical path length of the medium through which the radiation propagates and

c [ppm] or [mol cm^{-3}] is the concentration of the absorbers in the medium.

The absorbance of a known standard is typically measured at a wavelength where the measured gas molecules do not absorb any radiation, which in turn is used to calculate the initial radiant power I_0 .

An NDIR system is comprised of three main parts. These are an infrared radiation source, an optical cavity and a photosensitive element. More specifically, it utilizes at least two infrared detectors, with one acting as a measurement detector, while the other serves as a reference detector. The radiation is optically filtered using narrow bandpass filters to transmit specific wavelengths onto the detectors.

Compared to electrochemical alternatives, NDIR systems are much more robust (even in harsh chemical environments), show no deterioration and require much less (or even zero) calibration over time. This makes NDIR systems attractive for many applications.

Using NDIR spectroscopy for CO₂ measurements

The concentration of CO₂ gas can be effectively measured using the NDIR spectroscopic technique, thanks to its strong absorption bands in the mid infrared region (MIR) corresponding to fundamental vibrational and rotational molecular energy transitions. In addition to their strength, the fundamental absorption bands of polyatomic gases in MIR are less congested compared to their much weaker overtones in visible (VIS) and near infrared regions (NIR), thus increasing the selectivity by reducing cross sensitivities.

The wavelength dependent extinction coefficients of CO₂ are presented in Figure 1, while a generic setup implementing NDIR CO₂ concentration measurement is depicted in Figure 2.

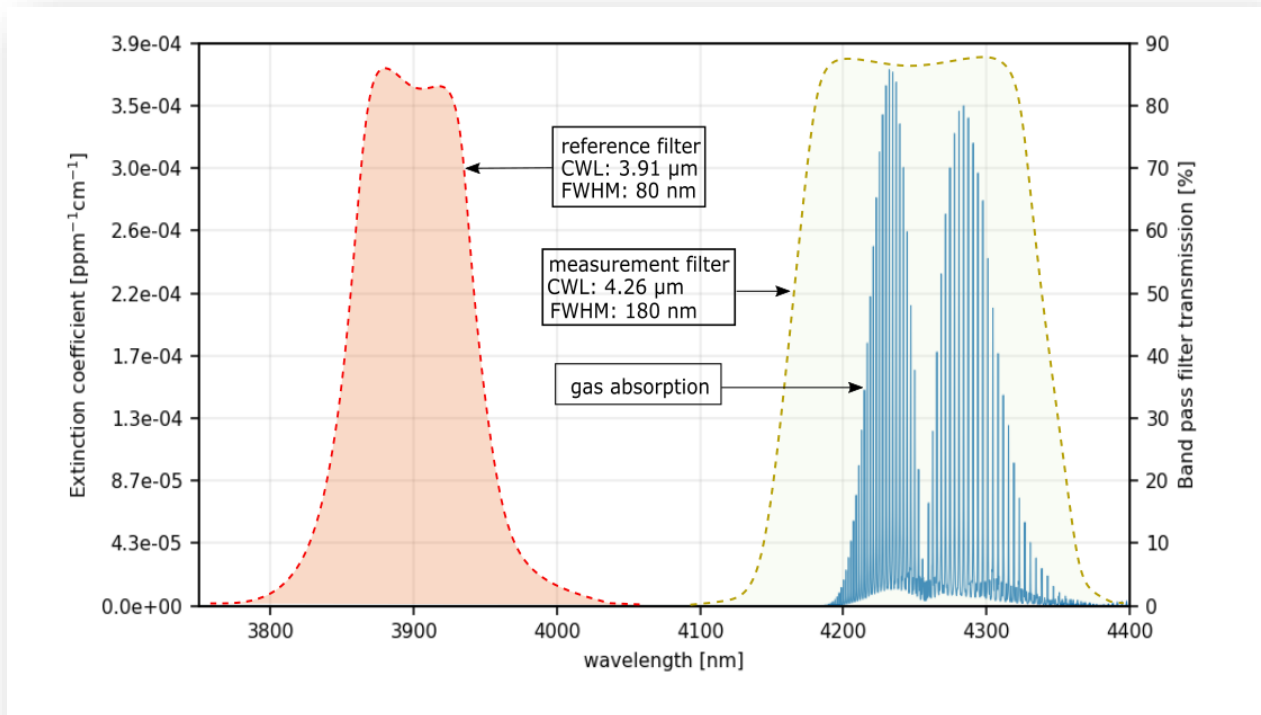


Figure 1: Extinction coefficient spectrum of CO₂ calculated using simulation tool Spectraplot based on [HITRAN](#) database and their application programming interface. Simulated at temperature = 300K, gas pressure = 1 atm.

For the CO₂ concentration measurements, an optical filter with a Center Wavelength (CWL) of 4.26 μm and a Full Width-Half Maximum (FWHM) of 180 nm may be employed to selectively filter the wavelengths to be transmitted to the measurement detector, while the optical filter for the reference detector exhibits a CWL of 3.91 μm and a FWHM of 80 nm, as illustrated in Figure 2.

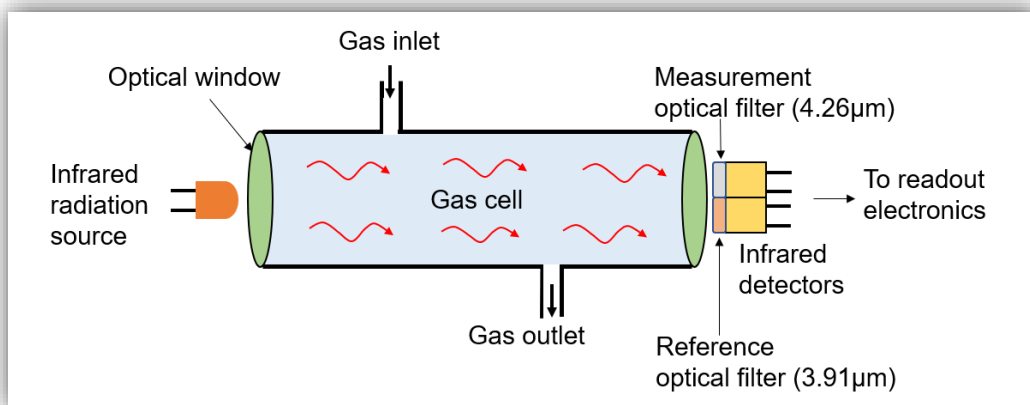


Figure 2: Schematic showing the working principle of NDIR CO₂ concentration measurement setup

Recalling the Beer Lambert law from Equation 1, the radiant power transmitted to the detector through a gaseous medium with a defined concentration and a defined optical path length can be expressed mathematically as

$$I = \int \Phi_{\Omega}(\lambda) T(\lambda) \exp[-\varepsilon(\lambda) c l] d\lambda \quad \text{Equation 2}$$

$$= I_0 \exp(-\varepsilon l c),$$

where

$\Phi_{\Omega}(\lambda)$ [W] is the spectral radiant power of the infrared radiation source emitted in the direction of the solid angle element Ω , whereas Ω is chosen considering the area of the detector,

$T(\lambda)$ [%] is the wavelength dependent transmission spectrum of the optical bandpass filter and

$\varepsilon(\lambda)$ [$\text{cm}^{-1} \text{ppm}^{-1}$] or [$\text{mol}^{-1} \text{cm}^2$] is the wavelength dependent molar extinction coefficient.

The change in transmitted radiant power as a function of concentration $\frac{dI}{dc}$ [W ppm^{-1}] can then be phrased as

$$\frac{dI}{dc} = \frac{d [I_0 \exp(-\varepsilon l c)]}{dc} = -\varepsilon l I_0 [\exp(-\varepsilon l c)]. \quad \text{Equation 3}$$

Equation 3 clearly reveals that the change in the transmitted radiant power is an exponential function depending on the concentration. Hence, the change in transmitted radiant power per concentration change I' [W ppm^{-1}] may be calculated for given concentrations as;

$$I' = \frac{\Delta I}{\Delta c} = \frac{I_1 - I_2}{c_2 - c_1}, \quad \text{Equation 4}$$

where

I_1 [W] and I_2 [W] are the transmitted radiant powers calculated using Equation 2 at the concentrations c_1 [ppm] and c_2 [ppm], respectively.

This allows to estimate the performance of a defined NDIR system with known detector parameters over the concentration range of interest.

Performance of NDIR gas measurement systems

The performance of such an NDIR gas measurement system is characterized by the detection limit DL [ppm] or in other words, the minimum concentration change that can be detected by the system. The detection limit is largely dependent on the performance characteristic of the employed infrared detectors. It is calculated as the ratio of noise equivalent power of the detector (NEP) [W] to the change in transmitted radiant power for 1 ppm of gas concentration according to Equation 5.

$$DL = \frac{NEP}{I'}. \quad \text{Equation 5}$$

NEP of an infrared detector is defined as the signal power that gives a signal-to-noise ratio of 1 and is calculated using the Equation 6.

$$NEP = \frac{\sqrt{A}\sqrt{\Delta f}}{D^*}, \quad \text{Equation 6}$$

where

A [cm²] is the active area of the infrared detector,

Δf [Hz] is the bandwidth and

D^* [cm Hz^{1/2} W⁻¹] is the specific detectivity of the infrared detector.

For any NDIR system, an infrared detector with a higher D^* is important to achieve low detection limits and a high measurement resolution of gas concentration.

Furthermore, for some challenging applications, a high measurement rate is also necessary. An infrared detector's frequency response is the main contributing factor to the measurement rate of the NDIR system. The dependency of the measurement rate of the system on the detector's bandwidth is given by the Nyquist criteria as

$$f_s \geq 2f, \quad \text{Equation 7}$$

where

f_s [Hz] is the required bandwidth of the detector and

f [Hz] is the desired measurement rate.

In other words, the considered infrared detector needs to be able to sample the received optical signal at a rate at least twice the desired measurement rate. Therefore, for an exemplary measurement rate of 100 Hz, an infrared detector should be chosen with a bandwidth of at least 200 Hz. Conventional infrared detectors such as pyroelectric detectors and thermopiles have strong limitations at frequencies > 10 Hz. trinamiX PbSe detectors offer a fast response (>10 kHz) in addition to their high detectivity.

Exemplary applications

Capnography is a good example for NDIR spectroscopy, where the CO_2 concentration in the exhaled breath of a person is monitored over expired volume or time. By evaluating the five characteristics of a capnogram, i.e., frequency, rhythm, height, baseline and shape, deductions about the health of the patient can be drawn. For this purpose, both a fast measurement rate and a high sensitivity of the infrared detector are must-have requirements.

For a hypothetical but realistic capnography sensor consisting of an isotropic infrared radiation source with an opening angle of 15° , an optical power output of $250 \mu\text{W}$ and an optical path length of 8 mm, a detection limit can be calculated using the equations above. The detector is considered to be on the main optical axis of the radiation source.

Figure 3 clearly reveals the exponential decrease of the change in transmitted radiant power as a function of concentration calculated by means of Equation 4 for the concentration range up to 200000 ppm (~ 150 mmHg), which is typical for mainstream breath monitoring systems.

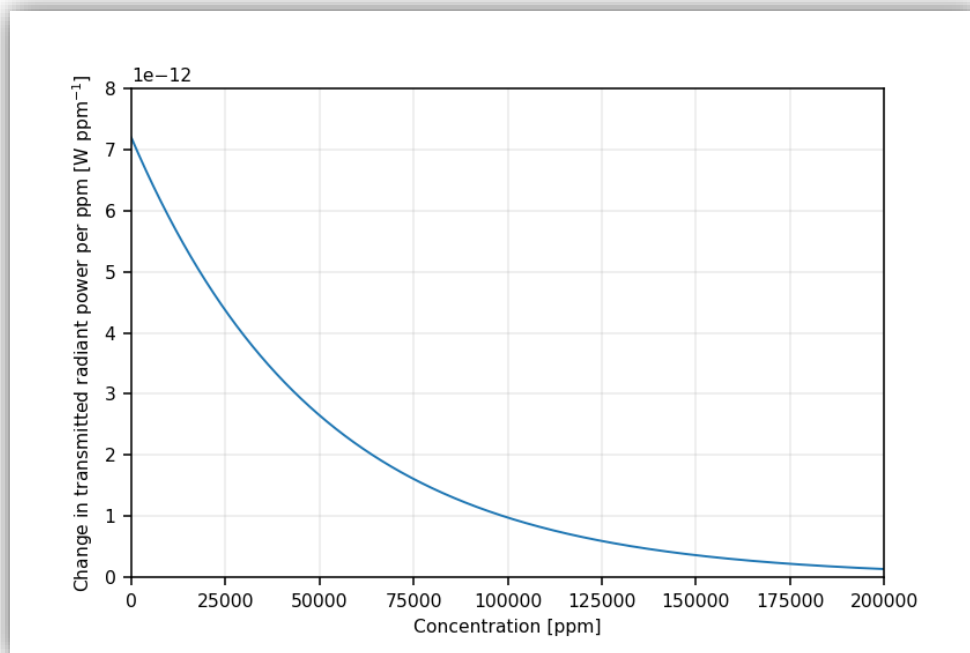


Figure 3: Change in transmitted radiant power per ppm change in concentration as a function of CO_2 concentration.

Figure 4 compares the theoretical detection limits of a state-of-the-art pyroelectric detector ($D^* = 2.5 \times 10^8 \text{ Hz}^{1/2}/\text{W}$) and the trinamiX lead selenide (PbSe) detector ($D^* = 1.8 \times 10^{10} \text{ Hz}^{1/2}/\text{W}$) as a function of concentration, calculated for an active detector area of 0.64 mm^2 and a measurement rate of 40 Hz, assuming a commonly used respiration rate range between 0 and 150 breaths per minute and at least 16 concentration measurements per breath.

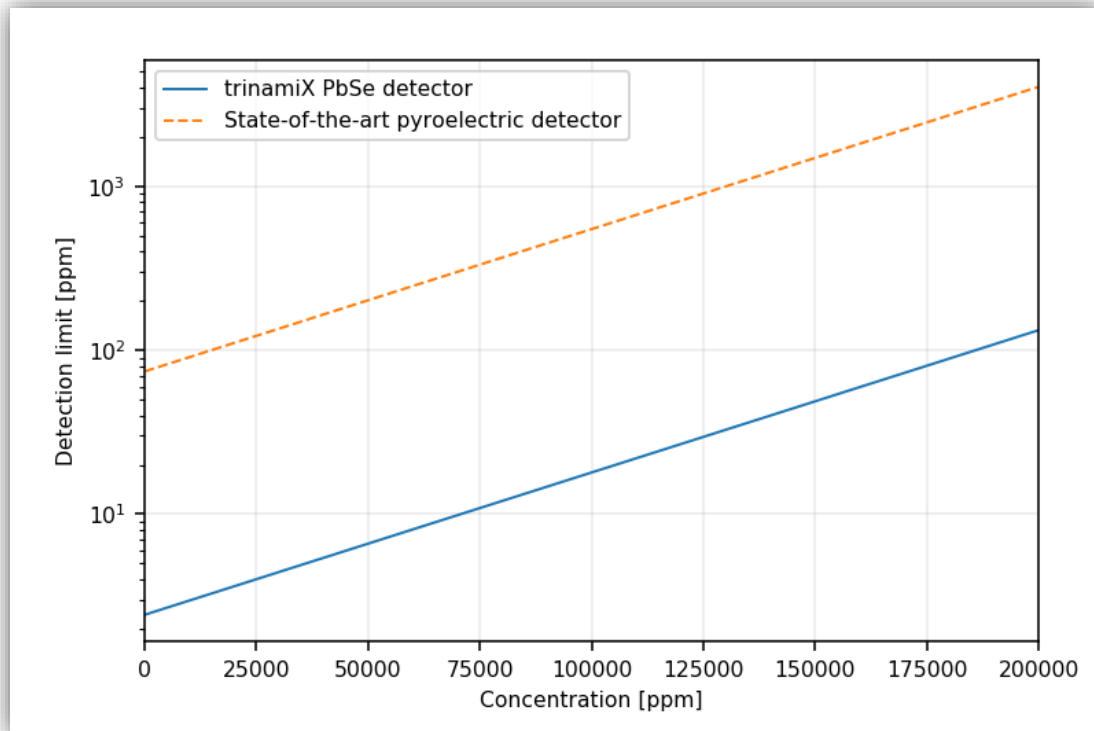


Figure 4: Detection limit as a function of CO₂ concentration for trinamiX PbSe and state-of-the-art pyroelectric detector calculated for the setup outlined above.

It is apparent from Figure 4 that while the pyroelectric detector achieves a maximum detection limit of 4000 ppm (~ 3 mmHg) at the end of the measurement range, the trinamiX PbSe detector reaches a detection limit of 135 ppm (~ 0.1 mmHg) because of its superior detectivity.

In real applications, such a low detection limit is not always necessary. Yet, the high detectivity of these detectors would allow the system to be designed with significantly shorter path lengths, smaller detector active areas, and less powerful infrared emitter, thus reducing volume of breath required, system cost and power consumption. Furthermore, a much better temporal resolution may be achieved due to their high bandwidth.

Simply put, the detection limit offered by a pyroelectric detector (4000 ppm) can be achieved by replacing it with a trinamiX PbSe detector, and at the same time, easing the system

requirements significantly and simultaneously improving the system parameters as detailed in the below example:

- Optical path length: 8 mm
- Smaller active area: $0.64 \text{ mm}^2 \rightarrow 0.25 \text{ mm}^2$
- Smaller optical power: $250 \text{ }\mu\text{W} \rightarrow 8 \text{ }\mu\text{W}$
- Faster response: 40 Hz \rightarrow 100 Hz

Another essential application is **air pollution monitoring**. By employing trinamiX PbSe detectors, CO₂ concentration measurement systems may be integrated into a smartphone to monitor air pollution in real time. A detection limit of about 50 ppm in the CO₂ concentration range between 0 and 40000 ppm may be achieved by modifying the system parameters simultaneously to:

- Smaller optical path length: 8 mm \rightarrow 1 mm
- Smaller active area: $0.64 \text{ mm}^2 \rightarrow 0.25 \text{ mm}^2$
- Smaller optical power: $250 \text{ }\mu\text{W} \rightarrow 16 \text{ }\mu\text{W}$
- Slower response: 40 Hz \rightarrow 1 Hz

Summing it up, a higher detectivity and bandwidth mean a more robust, energy efficient and cost-effective CO₂ concentration measurement system, which may be miniaturized to such a level that it could be easily integrated even into smartphones, tablets, and wearable consumer and medical products.

Another challenge with gas sensing is the occlusion of the optical path. As an example, during capnometry, the water vapor from breath may condense on the optical components occluding the field-of-view of the detectors, thus causing error in the measurement. This error may be overcome with the design proposed in Figure 5, which makes use of a dichroic mirror, an optical component that spectrally separates the incident radiation in an optical axis into two wavelength ranges. This allows the detectors to be placed in the same optical axis enabling better reliability by avoiding differing occlusion factors for each detector. It also prevents loss in radiant power compared to conventional NDIR systems, where the detectors are positioned on different optical axes.

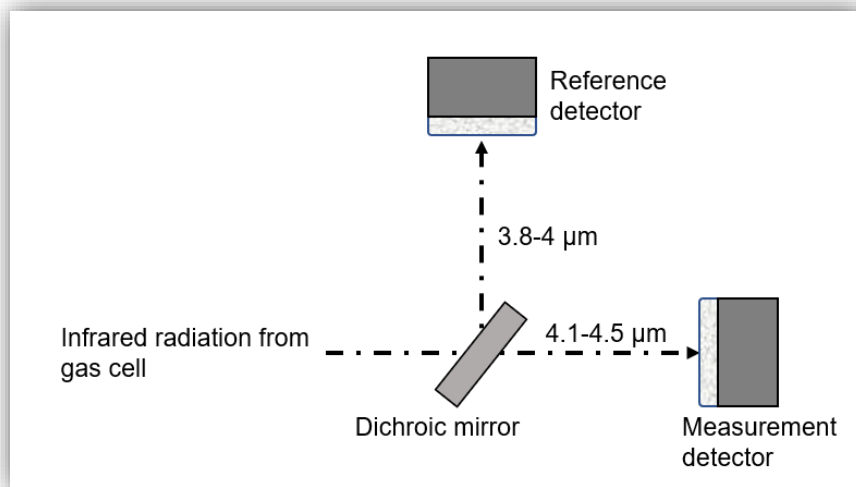


Figure 5: Schematic showing application of a dichroic mirror in the optical path. This customized solution improves the overall measurement accuracy and reliability of the CO₂ concentration measurement system.

trinamiX PbSe bare-chip detectors with their patented thin film encapsulation allow significant reduction in the footprint and cost of such designs, since they permit easy assembly of optical components on top of the detectors without any housing and mount. Hence, even complex optical setups can be realized in accordance with the emerging trend in miniaturization of optical sensor systems.

Complementing this, all trinamiX IR detectors can be supplied with signal processing electronics and a digital interface such as SPI or I²C to communicate with the host system.

Summary

trinamiX PbSe detectors incorporate key features including high resolution, high measurement rate and high selectivity required by challenging applications such as breath or pollution monitoring. trinamiX can also develop and supply customized components and modules such as integrated bandpass optical filters and interface electronics. This makes them the perfect solution for real-time, in situ detection applications in the mid infrared region up to 5 μm.

trinamiX complements this with technological expertise, unmatched experience and application-specific knowledge to support customers in successfully overcoming their CO₂ detection challenges.

About trinamiX:

trinamiX www.trinamixsensing.com is a wholly-owned subsidiary of BASF SE, the world's largest chemical company. Founded in 2015, the company has developed a wide-ranging portfolio of technologies and products around both Infrared detection as well as 3D imaging and distance measurement employing a team of more than 100 experts across a wide range of scientific disciplines.

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