



# A Novel Bandpass Filter for the Analysis of Carbon Monoxide Using a Non-Dispersive Infrared Technique

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**Abstract:** In this study, two novel narrow bandpass filters (BPF) obtained from the high-resolution transmission molecular absorption (HITRAN) data for a carbon monoxide (CO) non-dispersive infrared (NDIR) analyzer were investigated and compared with a commercial BPF (4.64  $\mu$ m). The new BPF was made using a two-cavity filter method with different center wavelengths and bandwidths from the commercial BPF. The wavelengths of the two BPFs were 4.5  $\mu$ m and 4.65  $\mu$ m. The gas emission pattern of a coal-fired power plant was used as a case study. Various concentrations of target gases were used to theoretically estimate the interference, and to practically determine it. It was found that although the transmittances of the two new BPFs were lower than that of the commercial BPF, the signal-to-noise ratio caused by two novel BPFs was approximately 20. In terms of interference effect, carbon dioxide (CO<sub>2</sub>) was found as a strong interfering gas on the commercial BPF at 4.64  $\mu$ m and the new BPF at 4.65  $\mu$ m. In contrast, the new BPF at 4.5  $\mu$ m cut off the interference effect of all target gases. The measurement error of the NDIR analyzer applying the BPF at 4.5  $\mu$ m was similar to that of gas filter correlation (GFC) NDIR and was less than 1%. This indicates that the novel BPF at 4.5  $\mu$ m can be used instead of a GFC for a CO NDIR analyzer, thus overcoming the limitations of using a GFC.

Keywords: NDIR; bandpass filter; CO analysis; power plant

# 1. Introduction

Carbon monoxide (CO), which is produced mainly from the combustion process, is a toxic gas when its concentration is >35 ppm [1]. Besides being a greenhouse gas, CO has an important role in atmospheric chemistry [2–4]. CO has also been widely considered as a signature means of detecting fires [5,6]. Therefore, monitoring CO is an important issue. In the monitoring of CO, two main methods have been used: gas chromatographic technologies (e.g., gas chromatography-flame ionization detectors, gas chromatography-electron capture detectors, gas chromatography-mercuric oxide detectors and gas chromatography-mass spectrometry) and spectroscopic technologies (e.g., gas filter correlation (GFC)-NDIR, Fourier-transform infrared spectroscopy, tunable diode laser spectroscopy, and resonance fluorescence) [2]. Among these instruments, NDIR has been widely used for field monitoring of CO because its optics and detecting system are less complicated than that of other instruments [7]. Furthermore, NDIR technique is also suitable for in situ application because it is often less bulky than gas chromatographic technologies. In addition, the GFC-NDIR method is well-known as a standard method for monitoring CO [8].



The principle of the NDIR technique is based on the Beer-Lambert law [9],

$$I = I_0 \times \exp(-kCL) \tag{1}$$

where *I* is the intensity of light after penetrating the target gas,  $I_0$  is the initial intensity from the infrared (IR) source, *k* is the absorption coefficient for a specific gas and filter combination, *C* is the concentration of the target gas, *L* is the path length between the IR source and detector, and *kL* is defined as the sensitivity of the sensor [10].

Interference is one of the main issues with the NDIR technique. Figure 1 shows the absorption ratios of several compounds emitted from a coal-fired power plant.



**Figure 1.** Absorption ratios of several gases emitted from a coal-fired power plant observed from the high-resolution transmission molecular absorption (HITRAN) database [11]. (The absorption ratio at a spectral line was the fraction of that line's absorption intensity and the maximum adsorption intensity of that gas).

As shown in Figure 1, the spectra of NO, NO<sub>2</sub>, and SO<sub>2</sub> overlapped with  $H_2O$ . Hence, the analysis of these gases using NDIR would result in bias. Likewise, CO<sub>2</sub> caused an interference error for CO. To overcome this interference issue, new developments within the NDIR technique have evolved. A review on the development of the NDIR technology can be found elsewhere [12]. The general improvement of the CO NDIR analyzer is shown in Table 1.

Type of Non-Dispersive Infrared (NDIR)		Improvement Part	Advantages	
Analyzer [13] Greenhouse gases from ocean		Coupled with off-axis integrated cavity output spectroscopy to a Weiss-type equilibrator	Fast response due to faster gas equilibration process. Detection limit <40 ppt, high precision, stable	
Analyzer [14]	Gas emission from a stack	Cross-interference correction with multi-bandpass filter. Using fitted interference functions for nonlinear absorption compounds	High accuracy due to apply fitted interference functions	
Sensor [15]	$ \begin{array}{ll} \mbox{ Applied broad-spectral light-emitting} \\ \mbox{ Gas emission from} \\ \mbox{ combustion engine} \end{array} \  \  \  \  \  \  \  \  \  \  \  \  \$		LED is lower cost and smaller size than a laser system. Fast response due to high frequency of LED (250 Hz)	
Sensor [4]	Construction industry	Digital filter to remove noise. Applied sensor networks with Wi-Fi	Noise was removed by digital filter leaded to high accuracy. Stability in long-term operation due to integrated data from sensor networks	

 Table 1. Recent studies on CO non-dispersive infrared analysis.

Type of Non-Dispersive Infrared (NDIR) Application Field		Improvement Part	Advantages	
Sensor [16]	Air monitoring in vehicles, building air conditioning systems	Uncooled small InSb-based detector with AlInSb barrier. Several single photodiodes with i-layer thickness connected in series	The barrier helped to remove thermal insulation. Hence, the size of the sensor was reduced. The i-layer helped to improve signal-to-noise <i>S/N</i> ratio, which leads to increase sensitivity. The detector could detect a wide band for multi-gas detection	
Sensor [17]	Environment monitoring	One IR source coupled with 4 pyroelectric detectors. Compensation parameter for temperature, humidity, and pressure	Multi-detectors for multi-gas detection. Effect factors were compensated resulted in high accuracy	
Sensor [12]	Fire warning	Applied photoacoustic detector	Help to improve selectivity and precision	

Table 1. Cont.

Although the interference effect is a pivotal issue for the NDIR analyzer, development of the CO NDIR analyzer has not advanced as much as the development of the sensor. The reason is that the GFC is the best available method to compensate for the interference in a CO NDIR analyzer, especially for an unknown emission source. However, the GFC method has limitations, such as gas leaks and a limited correction range [18]. Using a multi-bandpass filter is a good method, but leads to a cost increase, which is another issue. Therefore, this study was carried out to develop a non-interference bandpass filter (BPF) based on the high-resolution transmission molecular absorption (HITRAN) database for a CO NDIR analyzer of a continuous monitoring system. The scope of this study was the gas emission patterns of a coal-fired power plant.

# 2. Material and Methods

# 2.1. Apparatus

A GFC-NDIR analyzer (NMA-N500, Nara Controls Inc., Seoul, Korea) was used and modified for this study. Information about the analyzer is shown in Table 2.

Parameter	Value	Unit
Measurement range	0–200	ppm
Optical path length	8	m
Air flow rate	1	L/min
Gas chamber temperature	45	°C
Bandpass filter (BPF) for CO wavelength (half bandwidth)	4.64 (180)	μm (nm)
Reference BPF (half bandwidth)	3.95 (90)	μm (nm)

Figure 2 depicts the experimental set-up. Standard gases were purchased from Rigas Co., Ltd., Daejeon, Korea, which were produced based on the gravimetric method [19] (ISO 6142-1:2015). Humidity was produced using the bubble method at 25 °C (see Figure 2). The humidity was measured by a humidity sensor (645, Testo SE & Co. KGaA, Lenzkirch, Germany). Several gas mixtures were also used to investigate the response of the analyzer. A 25-L Tedlar bag (SKC Inc., Pittsburgh, PA, USA) was used to store the mixtures. They were re-checked by a multi-gas analyzer (60i, Thermo Fisher Scientific, Waltham, MA, USA). The experiment was repeated 3 times. The relative standard deviation of the repeated experiments was less than 1%. The transmittances of BPFs were measured using Fourier-transform infrared spectroscopy (FTIR) (MB3000, ABB Group, Mannheim, Germany).



Figure 2. Schematic diagram of experimental set-up. NDIR: non-dispersive infrared; MFC: mass flow controller.

# 2.2. Investigation of the Non-Interfering Wavelength for CO Gas Emitted from a Coal-Fired Power Plant

A case study on the gases emitted from a coal-fired power plant was conducted. Untreated gases emitted from a coal-fired power plant consist typically of 3 to 4% oxygen, 0–20 ppm of CO, 15 to 16% CO<sub>2</sub>, 5–7% H<sub>2</sub>O (vapor), approximately 73% N<sub>2</sub>, 0–1000 ppm of SO<sub>2</sub>, and 0–500 ppm of NO<sub>x</sub> [20,21]. Therefore, CO, CO<sub>2</sub>, NO<sub>x</sub> (NO + NO<sub>2</sub>), SO<sub>2</sub>, and H<sub>2</sub>O (vapor) were used as the target gases in this study. N<sub>2</sub>O is an interference gas for CO [13,15]. However, the emission of N<sub>2</sub>O from the combustion process was not a significant amount [15]. Therefore, the effect of N<sub>2</sub>O on CO measurement in this case was neglected.

The line-by-line absorption intensity from the HITRAN database [11] (hitran.org; Atomic and Molecular Physics Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA) was used as a reference. Since the main infrared (IR) absorption of CO is approximately 4.5 to 5.0  $\mu$ m (see Figure 1), the wavelengths of 2.5 to 10  $\mu$ m from the HITRAN database were considered. From the line-by-line absorption intensity, the maximum value of each gas was determined. Since different gases demonstrated different absorption levels, the absorption ratio was estimated for easy comparison. For a certain gas, the absorption ratio at a spectral line was the fraction of that line's absorption intensity and the maximum adsorption intensity of that gas. All absorption ratios which were >0.1% (i.e., 99.9% of absorbance) of all target compounds were scanned and matched to find the non-interfering range. Then, novel BPFs based on this range were made by the Seoul Precision Optics Co., Ltd., Shiheung, Korea.

Generally, the absorbance (A) of a gas can be obtained from the transmittance (T) through the following relationship.

$$T = I/I_0 = 10^{-A} \tag{2}$$

From Equations (1) (see Section 1) and (2), the relationship between gas absorbance and its concentration can be derived as

$$A = \log \left( I_0 / I \right) = \varepsilon C L \tag{3}$$

where  $\varepsilon = \log(e) \times k = 0.43 k$ .

Since k is the absorption coefficient for a specific gas and filter combination [9], the transmittance and bandwidth of the BPF should be considered. Within the spectral range of a certain BPF, there are many line-by-line spectra with different absorption intensities. Therefore, a total absorption intensity was calculated. The total absorption intensity of a gas with respect to a certain BPF was calculated to compare the effects of interferences [22]. The total absorption intensity was calculated based on Equation (4). The average transmittance was used because the transmittance displayed in the line-by-line spectra varied within the BPF spectral range. Therefore, using the average transmittance was better than using the maximum transmittance.

$$Total \ absorption \ intensity = \sum_{i=1}^{n} a_i \times N_{gas} \times T' \times L \tag{4}$$

where  $\sum_{i=1}^{n} a_i$  is the integration of all line-by-line absorption intensities from HITRAN database of each gas from line 1 to line *n* within each BPF spectral range (cm<sup>-1</sup>/molecule.cm<sup>-2</sup>),  $N_{gas}$  is the number of molecules of that gas (i.e., the number of molecules was converted from the concentration because the absorption intensity from HITRAN was calculated based on molecule) (molecule), *T*' is the average transmittance of the BPF (unitless) and *L* is the optical pathlength of the gas chamber (cm).

On the other hand, the signal-to-noise ratio (S/N), which is a more useful variable than only noise, is also an important factor in determining the quality of an instrument [23,24]. S/N should be higher than 3 in order to detect a signal [24]. The S/N depends on many factors. In terms of the BPF, the S/N caused by the BPF is proportional to the detectivity of the detector, which is presented through the following equation [23,25]

$$S/N = \frac{D^* \times P_{in}}{\sqrt{A_d \Delta f}} \tag{5}$$

where S/N is the signal-to-noise ratio,  $D^*$  is the detectivity of the detector,  $A_d$  is the active area of the detector,  $P_{in}$  is the IR intensity reaching the detector, and  $\Delta f$  is the bandwidth.

Since the same detector and IR source were always used for all experiments, the S/N fraction of the 2 BPFs could be derived as follows:

$$\frac{S/N_{BPF1}}{S/N_{BPF2}} = \sqrt{\frac{\Delta f_{BPF2}}{\Delta f_{BPF1}} \times \frac{T_1}{T_2}}$$
(6)

where  $\Delta f_{BPF1}$  and  $\Delta f_{BPF2}$  are the bandwidths of bandpass filter 1 (BPF<sub>1</sub>) and bandpass filter 2 (BPF<sub>2</sub>), respectively and  $T_1$  and  $T_2$  are the average transmittances of BPF<sub>1</sub> and BPF<sub>2</sub>, respectively. The average transmittance was employed instead of the radiant input because an identical IR source was used to supply the same IR radiant. In this equation, the bandwidth is the most important factor because the bandwidths of new BPFs were much lower than that of the commercial one while their transmittances were not much different.

For a direct current (DC) signal, *S*/*N* can be practically observed from a variety of signals as follows [24].

$$S/N = \frac{\overline{S}}{\delta_S} \tag{7}$$

where  $\overline{S}$  is the mean of signal and  $\sigma_S$  is the signal standard deviation.

Accordingly, the sensitivity, theoretical and experimental interference, and theoretical and experimental S/N of the 2 new BPFs and a commercial BPF were evaluated and compared.

# 2.3. Production of Novel BPFs

The new BPFs were made based on the results from Section 2.2. The novelty of these BPFs was their center wavelength and bandwidth. In general, BPFs at 4.64  $\mu$ m or 4.75  $\mu$ m have been widely used for CO analysis using the NDIR techniques, whereas the new BPFs had wavelengths of 4.5 and 4.65  $\mu$ m. In addition, the bandwidths of new BPFs were narrower than those of the commercial BPFs. The optical properties of the new BPFs will be introduced in more detail in Section 3.1. Two-cavity filter method was used to make the new BPFs with Germanium substrate and SiO coating material.

#### 2.4. Investigation of the Effect of Interfering Gas on the Novel BPFs

A commercial BPF at 4.64  $\mu$ m (180 nm) (NBPF 4.64; Seoul Precision Optics Co., Ltd., Shiheung, Korea) was selected to compare with the new BPFs. The description of the novel BPF will be introduced in more details in Section 3.1. Each BPF was applied to the NDIR analyzer to investigate its performance. Various concentrations of target gases were introduced into the analyzer to investigate the interference. The N<sub>2</sub> gas (99.999%, Dong A Co., Ltd., Gyeonggi, Korea) and CO standard gases at 10, 50, 100, and 298 ppm (Rigas Co., Ltd., Daejeon, Korea) were used to calibrate the analyzer. Based on the literature [20,21], the NO, NO<sub>2</sub>, and SO<sub>2</sub> levels were varied from 1 to 1000 ppm (Rigas Co., Ltd., Daejeon, Korea), and CO<sub>2</sub> levels were varied from 1 to 50% (Rigas Co., Ltd., Daejeon, Korea) to investigate the interference effect. In general, a cooler or a membrane is usually used to remove the H<sub>2</sub>O vapor before introducing the gas stream into the analyzer. Hence, it was presumed that the inlet air of the analyzer would be dry. However, these instruments could not completely remove all H<sub>2</sub>O vapor. Accordingly, we assumed that the inlet H<sub>2</sub>O vapor concentration of the analyzer was less than 25,800 ppm at 25 ± 2 °C. The H<sub>2</sub>O vapor levels, which were directly introduced into the analyzer, were varied from 1400 to 23,000 at 25 °C in this study.

Several gas mixtures were also used to investigate the performance of the analyzer with the original structure (i.e., GFC-NDIR), the novel BPF, and the BPF at 4.64 µm. Based on the Korean emission regulations for a new coal-fired power plant, the  $SO_2$  and  $NO_x$  concentrations should be  $\leq$ 50 ppm [26]. Moreover, CO and CO<sub>2</sub> concentrations were selected based on the literature [20,21] because there were no emission regulations for these gases. Consequently, gas mixtures consisting of CO (10, 100, and 200 ppm), NO (50 ppm), CO<sub>2</sub> (15%), NO<sub>2</sub> (50 ppm), SO<sub>2</sub> (50 ppm), and H<sub>2</sub>O (~14,360 ppm) were generated and introduced into the analyzer to determine the measurement errors. The measurement errors were obtained from the relative percent difference between the standard gas and the analytical results. NO, CO, NO<sub>2</sub>, and SO<sub>2</sub> were diluted from 2000 ppm of the standard gases (Rigas Co., Ltd., Daejeon, Korea). CO<sub>2</sub> was diluted from 50% of the standard gas (Rigas Co., Ltd., Daejeon, Korea). H<sub>2</sub>O was diluted from 80% of relative humidity. N<sub>2</sub> was used as the balancing gas. A 25-L Tedlar bag was used to prepare gas mixtures. N2 was introduced into the Tedlar bag with the flow rate controlled by a mass flow controller (M3030VA, Line Tech Ltd., Co., Daejeon, Korea). Standard gas samples were introduced into the Teblar bag with a 500 mL glass syringe (500MAR-LL-GT, SGE Analytical Science Pty. Ltd., Ringwood, Australia). Each gas was introduced into the NDIR analyzer for 15 min. Results from the first 5 min were ignored due to equilibrium concentration in the analyzer. The values from the last 10 min were collected. Each experiment was repeated 3 times. The signal was recorded every second. The relative absorbance of each gas was practically calculated based on the log of the detector signal from the reference channel to the detector signal from the CO channel.

# 3. Results and Discussion

## 3.1. Non-Interfering Wavelengths for CO Gas Emitted From a Coal-Fired Power Plant

From the HITRAN, the non-interfering wavelengths for CO in the presence of CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, and H<sub>2</sub>O were found to be in the range of 4.76–4.78 (bandwidth = 20 nm), 4.55–4.75 (bandwidth = 200 nm), and 4.46–4.54  $\mu$ m (bandwidth = 80 nm). Due to technical limitations, a new BPF at 4.5  $\mu$ m (i.e., BPF\_1) with a half bandwidth of 50 nm and a new BPF at 4.65  $\mu$ m (i.e., BPF\_2) with a half bandwidth of 60 nm were manufactured. In general, a BPF filter consists a sort of thin-film layers. The bandwidth of the BPF depends on the number of layers. The more thin-film layers there are, the narrower the bandwidth of the BPF is. However, the transmittance of the BPF is also influenced by the BPF thickness and the tolerance of the coating process [27]. Therefore, it is a challenge to reduce the bandwidth as much as the values above while maintaining a high transmittance. The transmittance should be high enough to retain a good *S*/*N* ratio for the analyzer. The commercial BPF at 4.64  $\mu$ m with a half bandwidth of 180 nm was labelled as BPF\_3.



**Figure 3.** Spectra of target band pass filters (BPF\_1, BPF\_2, and BPF\_3) observed from the Fourier-transform infrared spectroscopy.

As shown in Figure 3, the full bandwidth at transmittance  $\geq 0.1\%$  of the two new BPFs was much narrower than that of BPF\_3. The full bandwidths of the BPF\_1, BPF\_2, and BPF\_3 were 141, 262, and 567 nm, respectively. Table 3 shows a summary of the specifications for each BPF. The maximum transmittances of the BPF\_1 and BPF\_2 did not differ greatly from that of BPF\_3. The average transmittances of BPF\_1, BPF\_2, and BPF\_3 were 26.8%, 24.6%, and 27%, respectively. With the optical path length of 8 m, the values for sensitivity *kL* of BPF\_1, BPF\_2, and BPF\_3 were  $5.45 \times 10^{-16}$ ,  $1.82 \times 10^{-15}$ , and  $2.19 \times 10^{-15}$  (1/molecule·cm<sup>-2</sup>) respectively. This indicates that the sensitivity of BPF\_3 was four times higher than that of BPF\_1 and 1.2 times higher than that of BPF\_2. However, the theoretical fraction of  $S/N_{BPF_3}$  to  $S/N_{BPF_2}$  was only 0.74. The theoretical  $S/N_{BPF_3}$  was not much different from the new BPFs because its average transmittances were similar to that of others. From Equation (7), the practical S/N of BPF\_1, BPF\_2, and BPF\_3 was approximately 2.5 times higher than that caused by BPF\_1 and BPF\_2 due to their relatively lower values for maximum transmittance. However, these S/N values were much higher than 3. Therefore, these new BPFs can be applicable [24].

Table 3. Specification of BPFs using in this research.

BPF	Center Wavelength (µm)	Half Band Width (nm)	Full Bandwidth * (nm)	Maximum Transmittance (%)	Average Transmittance (%)
BPF_1	4.5	50	141	70.1	26.8
BPF_2	4.65	60	262	75.4	24.6
BPF_3	4.64	180	567	83.8	27

Note: \* Full bandwidth from 0.1% of transmittance.

Although BPF\_1 and BPF\_2 were made with very narrow half bandwidths, their real full bandwidth was still over the range estimated from HITRAN. Hence, the theoretical and practical interference should be investigated. The theoretical interference is discussed in this section. The practical interference will be discussed in Section 3.2. Based on the absorption intensity from HITRAN, the optical path length of the analyzer, the average transmittance of BPFs, and the various concentrations of target gases, the total absorption intensity of each gas was evaluated. These values are depicted in Figure 4.



**Figure 4.** Total absorption intensity of CO, NO, NO<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O. The concentration of CO was from 1 to 298 ppm; that of NO, NO<sub>2</sub>, and SO<sub>2</sub> was from 1 to 1000 ppm; that of CO<sub>2</sub> was from 10,000 to 500,000 ppm; and that of H<sub>2</sub>O was from 1431 ppm to 22,972 ppm at 25 °C, 1 atm.

As shown in Figure 4, NO, NO<sub>2</sub>, and SO<sub>2</sub> did not reveal significant effects on any BPFs. H<sub>2</sub>O had a slight effect on BPF\_2 at low concentrations of CO. CO<sub>2</sub> showed a strong effect on CO measurement. This cross-interference between CO and CO<sub>2</sub> is well-known [13–15]. The CO<sub>2</sub> gas demonstrated a strong effect on BPF\_3 because the linear regression of CO<sub>2</sub> was the closest to that of CO (i.e., the slope between two curves was  $2.3 \times 10^{-4}$ ). In contrast, CO<sub>2</sub> showed less effect on BPF\_1 and BPF\_2. At 50% CO<sub>2</sub>, the slope between two curves at BPF\_1 was about 0.074 and that at BPF\_2 was approximately 0.017. This indicates that BPF\_1 reduced more interference effect than the other two BPFs.

The interference ratios caused by mixing gases were also estimated. The concentration of target gases in the mixture was described in Section 2.3. The interference ratios are depicted in Figure 5.



**Figure 5.** Interference ratios of target gases with respect to different mixtures. (**a**) 10 ppm of CO; 50 ppm of NO, NO<sub>2</sub>, and SO<sub>2</sub>; 15% of CO<sub>2</sub>; and 14,360 ppm of H<sub>2</sub>O. (**b**) 100 ppm of CO; 50 ppm of NO, NO<sub>2</sub>, and SO<sub>2</sub>; 15% of CO<sub>2</sub>; and 14,360 ppm of H<sub>2</sub>O. (**c**) 200 ppm of CO; 50 ppm of NO, NO<sub>2</sub>, and SO<sub>2</sub>; 15% of CO<sub>2</sub>; and 14,360 ppm of H<sub>2</sub>O. (**c**) 200 ppm of CO; 50 ppm of NO, NO<sub>2</sub>, and SO<sub>2</sub>; 15% of CO<sub>2</sub>; and 14,360 ppm of H<sub>2</sub>O.

As shown in Figure 5, at 10 ppm of CO, CO<sub>2</sub> revealed significant interference on all BPFs. However, the lowest effect appeared on BPF\_1. On the other hand, H<sub>2</sub>O showed significant effects on BPF\_2. The higher the CO concentration, the lower the effect of CO<sub>2</sub>. At 100 ppm of CO, CO<sub>2</sub> denoted the lowest effect on BPF\_1, followed by BPF\_2 and BPF\_3. At 200 ppm of CO, CO<sub>2</sub> showed less effect on both of BPF\_1 and BPF\_2. In all cases, CO<sub>2</sub> demonstrated significant effects on BPF\_3. In terms of H<sub>2</sub>O, significant effects on all BPFs could not be found at high CO concentrations. Although the full bandwidth was large, BPF\_1 compensated more for the interference effect of CO<sub>2</sub> and H<sub>2</sub>O than the other two BPFs.

# 3.2. Effect of Target Gases on the Novel BPFs

Various concentrations of a single target gas were used to determine the real interference effect on new BPFs, as well as the commercial BPF. The CO calibration curves are presented in Figure 6. Relative absorbances were calculated from the log of ratio values between detector signals from the reference channel (i.e., reference BPF at 3.95  $\mu$ m) and detector signals of the CO measurement channel (i.e., BPF of CO gas). It was found that all BPFs showed good performance in terms of calibration ( $r^2 > 0.99$ ).



Figure 6. CO calibration curves associated with BPF\_1, BPF\_2, and BPF\_3.

The SO<sub>2</sub>, NO<sub>2</sub>, and NO gas concentrations were varied at the following values: 1, 10, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 ppm. The CO<sub>2</sub> concentrations were varied as 1%, 2%, 3%, 4%, 6%, 10%, 12%, 23% and 50%. The H<sub>2</sub>O (vapor) was varied as 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80% of relative humidity at 25 °C (i.e., from 1400 to 23,000 ppm). The interference of target gases on each BPF is depicted in Figures 7–9.

As shown in Figure 7, BPF\_1 was not significantly affected by NO, NO<sub>2</sub>, or SO<sub>2</sub>. This pattern was similar to that of the theoretical estimation. On the other hand,  $H_2O$  and  $CO_2$  revealed effects at low ppm concentrations (i.e., 10 ppm) of CO in the theoretical estimation, but the experimental results did not show these effects of these gases.

As shown in Figure 8, NO, NO<sub>2</sub>, and H<sub>2</sub>O did not demonstrate interference effects on BPF\_2. In contrast, a slightly negative effect caused by SO<sub>2</sub> was found. Particularly, CO<sub>2</sub> revealed strong effects on BPF\_2. The effect of CO<sub>2</sub> was stronger on BPF\_2 than on BPF\_1 because BPF\_2 had a larger bandwidth than BPF\_1, and the total CO absorption intensity in this band was higher than that of BPF\_1. BPF\_3 was also strongly affected by CO<sub>2</sub> (Figure 9). At 50% of CO<sub>2</sub>, the error concentration of CO was about 50 ppm. The large bandwidth of BPF\_3 brought about the high absorption of CO<sub>2</sub>. However, the effect of CO<sub>2</sub> on BPF\_3 was weaker than that on BPF\_2 because the CO absorption intensity of BPF\_3 was the highest (i.e., largest full bandwidth) based on HITRAN data. This pattern was a little different from the theoretical evaluation, which showed a stronger effect of CO<sub>2</sub> on BPF\_3 than BPF\_2. This difference might be a result of their different transmittance values. The maximum and average transmittance of BPF\_3 were higher than those of BPF\_2. Moreover, due to the multi-pathway gas chamber of the analyzer, this gap increased many times after the IR beam had reached to the detector. When the same IR source and detector were used, IR intensity which reached to the detector

with BPF\_3 would be higher than that with BPF\_2. Based on Beer–Lambert law, the detector with BPF\_2 would be more sensitive to CO and  $CO_2$  gases than that with BPF\_3. This resulted in the increase of the effect of the  $CO_2$ . In addition, the errors in the HITRAN data and the observed bandwidth of BPF by the Fourier-transform infrared spectroscopy (FITR) might also cause this bias.

An example of the analyzer signal with respect to the interference of CO<sub>2</sub> is presented in Figure 10. Linear regression of these analyzer signals was also estimated to compare their patterns. As shown in the figure, the analyzer signals with respect to BPF\_2 and BPF\_3 denoted an increase pattern (i.e., positive slope,  $r^2 = 0.7224$  and 0.2938 respectively). In addition, the response of the analyzer with respect to BPF\_2 for CO<sub>2</sub> was very clear compared to that of BPF\_3 (i.e., slope =  $2 \times 10^{-4} > 4 \times 10^{-6}$ ). In terms of using BPF\_1, the signal was not influenced by CO<sub>2</sub> (i.e., the slope was almost zero and  $r^2 <<1$ ).



**Figure 7.** Interference effect of NO, NO<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O on CO with respect to BPF\_1. The error bar in the figure is the standard deviation of the repeated experiment.



**Figure 8.** Interference effect of NO, NO<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O on CO with respect to BPF\_2. The error bar in the figure is the standard deviation of the repeated experiment.



**Figure 9.** Interference effect of NO, NO<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O on CO with respect to BPF\_3. The error bar in the figure is the standard deviation of the repeated experiment.



**Figure 10.** Non-dispersive infrared (NDIR) analyzer signal associated with different BPFs and CO<sub>2</sub> concentrations.

To investigate the performance of the analyzer employing these BPFs, different gas mixtures based on the emission patterns of a coal-fired power plant were introduced into the NDIR analyzer. Table 4 shows the measurement errors with respect to the mixing gases.

CO Std. (ppm)	GFC-NDIR		BPF_1		BPF_2		BPF_3	
	Mean of Analytical Values (ppm)	Mea. Error (%)						
10	10.04	0.40	10.08	0.83	283.74	2737	18.87	88.7
100	100.22	0.22	100.22	0.22	362.93	263	105.94	5.94
200	200.17	0.08	199.84	0.08	505.79	153	205.08	2.54

**Table 4.** Comparison between standard gas concentrations and analytical results for CO gas associated with different BPFs.

Note: Measurement error (Mea. error) is obtained from the relative percent difference between the CO concentration of standard and analytical results. CO std. is concentration of CO standard gas.

As shown in Table 4, the measurement errors associated with BPF\_2 were very high due to the strong effect of CO<sub>2</sub>. In the case of the BPF\_3, the error was very high (88.7%) at 10 ppm of CO, but it was lower at 100 and 200 ppm of CO. However, the error was still higher than 2%. Therefore, BPF\_3 could not be employed itself for the NDIR analyzer. The commercial BPF\_3 coupled with GFC helped to remove the interference of CO<sub>2</sub>. The measurement errors of the GFC-NDIR were all less than 1%. This pattern was similar to that of BPF\_1. Although there was an error at 10 ppm of CO when BPF\_1 was applied for the NDIR analyzer, the measurement error was still less than 1%. This result was comparable to the results of other studies. Sun et al. (2013) developed a multi-NDIR analyzer using multiple BPFs coupled with a cross-interference algorithm to compensate for the interference. It was reported that the measurement error of CO was less than 1% with an analytical range of 0–850 ppm [14]. In another research, a combination of array filters and detectors was applied to the multi-gas NDIR sensor, in which the measurement error of CO was less than 1.5% with an analytical range of 0–1000 ppm [6].

These results indicate that the new BPF\_1 can be applied to the CO NDIR analyzer instead of a GFC to compensate for the interference effect, especially for  $CO_2$ . BPF\_1 has the added advantage of having no leak problems. In addition, our test results showed that BPF\_1 had a good performance with up to 50%  $CO_2$  and up to 1000 ppm NO<sub>x</sub> and SO<sub>2</sub>. Therefore, it can be applied to monitor CO emission from a power plant as well as the combustion process. Although the new BPF could overcome some disadvantage of the GFC, the center wavelength of the new BPF was different to that of the reference BPF (i.e., 3.95 µm). Consequently, drift due to aging of IR source or detector and various of temperature would still occur [28]. Based on Planck's law, spectral intensity at a certain wavelength depends on temperature. When temperature varied, the IR intensity penetrated the reference BPF and target gas BPF would change, which resulted in changing the ratio between reference channel and measurement channel at the same target gas concentration and pressure. Hence, the base line of the analyzer would shift, which leads to increase the analyzer bias [26]. Accordingly, the effect of temperature as well as a new reference method on the analyzer should be investigated in the future.

# 4. Conclusions

A HITRAN database was used to investigate the non-interference wavelength for CO analysis using NDIR technology. The non-interference wavelength was determined with respect to the gas emission patterns of a coal-fired power plant. As a result, two new BPFs at 4.5  $\mu$ m (with a half bandwidth of 50 nm) and 4.65  $\mu$ m (with half bandwidth of 60 nm) were developed. The *S/N* ratios of the NDIR analyzer when the new BPFs were applied were approximately 20. In terms of interference compensation, the BPF at 4.5  $\mu$ m was found to remove the effect of CO<sub>2</sub> up to 50% and that of NO<sub>x</sub> and SO<sub>2</sub> up to 1000 ppm. The measurement errors of the NDIR coupled with BPF\_1 were similar to those of a GFC-NDIR analyzer, showing less than 1%. Therefore, BPF\_1 can be used instead of the GFC for a NDIR analyzer to monitor gas emission from any combustion process for which the main components include NO<sub>x</sub>, CO<sub>2</sub>, CO, SO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. In terms of BPF\_2, since its full bandwidth was still large, a narrower bandwidth of BPF\_2 should be produced, and its performance should be investigated with interference gases in the further work. Although the price of the filter was high, its price will

decrease in the end due to the increase of demand and the improvement of technology. The effect of temperature and new reference method should be investigated in future work. The investigation of BPFs for other compounds which typically require the use of a GFC for the NDIR analyzer would be a new direction in this NDIR field.

# 5. Patents

Korean patents 10-0897279 and 10-2018-0126957 resulted from the work reported in this manuscript.

**Author Contributions:** J.-C.K. and T.-V.D. conceptualized the work. Data curation was performed by J.-W.A. and I.-Y.C., The methodology was created by T.-V.D., T.-V.D. wrote the original draft, and review and editing was done by J.-C.K.

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# References

- 1. Pohanish, R.P. Sittig's Hanbook of Toxic and Hazardous Chemicals and Carcinogens, 6th ed.; Elsevier Inc.: Oxford, UK, 2012; ISBN 978-1-4377-7869-4.
- 2. Novelli, P.C. CO in the atmosphere: Measurement techniques and related issues. *Chemosphere* **1999**, *1*, 115–126. [CrossRef]
- 3. Tanimoto, H.; Sawa, Y.; Matsueda, H.; Yonemura, S.; Wada, A.; Mukai, H.; Wang, T.; Poon, S.; Wong, A.; Lee, G.; et al. Evaluation of standards and methods for continuous measurements of carbon monoxide at ground-based sites in Asia. *Pap. Meteorol. Geophys.* **2007**, *58*, 85–93. [CrossRef]
- 4. Yang, J.; Zhou, J.; Lv, Z.; Wei, W.; Song, H. A Real-Time Monitoring System of Industry Carbon Monoxide Based on Wireless Sensor Networks. *Sensors* **2015**, *15*, 29535–29546. [CrossRef]
- 5. Chen, T.; Su, G.; Yuan, H. In situ gas filter correlation: Photoacoustic CO detection method for fire warning. *Sens. Actuators B Chem.* **2005**. [CrossRef]
- 6. Fonollosa, J.; Solórzano, A.; Jiménez-Soto, J.M.; Oller-Moreno, S.; Marco, S. Gas Sensor Array for Reliable Fire Detection. *Procedia Eng.* **2016**, *168*, 444–447. [CrossRef]
- Worthington, B. 60 years of continuous improvement in NDIR gas analyzers. In Proceedings of the 50th Annual ISA Analysis Division Symposium—50 Years of Analytical Solutions, Houston, TX, USA, 10–14 April 2005; pp. 95–107.
- 8. ISO 12039:2001. Stationary Source Emissions—Determination of Carbon Monoxide, Carbon Dioxide and Oxygen—Performance Characteristics and Calibration of Automated Measuring Systems; ISO: Geneva, Switzerland, 2001.
- 9. Lee, R.; Kester, W. Complete Gas Sensor Circuit Using Nondispersive Infrared (NDIR). *Analog Dialogue* **2016**, 50, 1–9.
- Snakenborg, D.; Mogensen, K.B. Optimization of signal-to-noise ration in absorbance detection by integration of microoptical components. In Proceedings of the Seventh International Conference on Miniaturized Chemical and Biochemical Analysis Systems, Squaw Valley, CA, USA, 5–9 October 2003.
- 11. Harvard-Smithsonian Center for Astrophysics. *High-Resolution Transmission Molecular Absorption Database;* Harvard-Smithsonian Center for Astrophysics: Cambridge, MA, USA, 2018.
- 12. Dinh, T.-V.; Choi, I.-Y.; Son, Y.-S.; Kim, J.-C. A review on non-dispersive infrared gas sensors: Improvement of sensor detection limit and interference correction. *Sens. Actuators B Chem.* **2016**, *231*, 529–538. [CrossRef]
- Arévalo-Martínez, D.L.; Beyer, M.; Krumbholz, M.; Piller, I.; Kock, A.; Steinhoff, T.; Körtzinger, A.; Bange, H.W. A new method for continuous measurements of oceanic and atmospheric N<sub>2</sub>O, CO and CO<sub>2</sub>: Performance of off-axis integrated cavity output spectroscopy (OA-ICOS) coupled to non-dispersive infrared detection (NDIR). *Ocean Sci.* 2013, *9*, 1071–1087. [CrossRef]

- 14. Sun, Y.W.; Liu, C.; Chan, K.L.; Xie, P.H.; Liu, W.Q.; Zeng, Y.; Wang, S.M.; Huang, S.H.; Chen, J.; Wang, Y.P.; et al. Stack emission monitoring using non-dispersive infrared spectroscopy with an optimized nonlinear absorption cross interference correction algorithm. *Atmos. Meas. Tech.* **2013**, *6*, 1993–2005. [CrossRef]
- Thurmond, K.; Loparo, Z.; Partridge, W.; Vasu, S.S. A Light-Emitting Diode-(LED-) Based Absorption Sensor for Simultaneous Detection of Carbon Monoxide and Carbon Dioxide. *Appl. Spectrosc.* 2016, 70, 962–971. [CrossRef] [PubMed]
- 16. Camargo, E.G.; Tokuo, S.; Goto, H.; Kuze, N. Nondispersive Infrared Gas Sensor Using InSb-Based Photovoltaic-Type Infrared Sensor. *Sens. Mater.* **2014**, *26*, 253–262.
- 17. Tan, Q.; Tang, L.; Yang, M.; Xue, C.; Zhang, W.; Liu, J.; Xiong, J. Three-gas detection system with IR optical sensor based on NDIR technology. *Opt. Lasers Eng.* **2015**, *74*, 103–108. [CrossRef]
- Dinh, T.-V.; Ahn, J.-W.; Choi, I.-Y.; Song, K.-Y.; Chung, C.-H.; Kim, J.-C. Limitations of gas filter correlation: A case study on carbon monoxide non-dispersive infrared analyzer. *Sens. Actuators B Chem.* 2017, 243, 684–689. [CrossRef]
- 19. ISO 6142-1:2015. *Gas Analysis—Preparation of Calibration Gas Mixtures—Part 1: Gravimetric Method for Class I Mixtures;* ISO: Geneva, Switzerland, 2015.
- 20. McLarnon, C.R.; Steen, D. Combined SO<sub>2</sub>, NOx, PM, and Hg removal from coal fired boilers. In Proceedings of the Joint EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium, The MEGA Symposium, EPRI-DOE-EPA, Washington, DC, USA, 19–22 May 2003.
- 21. Granite, E.J.; King, W.P.; Stanko, D.C.; Pennline, H.W. Implications of mercury interactions with band-gap semiconductor oxides. *Main Group Chem.* **2008**, *7*, 227–237. [CrossRef]
- 22. Zhao, Y.; Pan, Y.; Rutherford, J.; Mitloehner, F.M. Estimation of the interference in Multi-Gas measurements using infrared photoacoustic analyzers. *Atmosphere* **2012**, *3*, 246–265. [CrossRef]
- 23. Jones, R.C. Performance of Detectors for Visible and Infrared Radiation. In *Advances in Electronics and Electron Physics*; Marton, L., Ed.; Academic Press: Cambridge, MA, USA, 1953; Volume 5, pp. 1–96, ISBN 0065-2539.
- 24. Douglas, A.; Skoog, F.; James Holler, S.R.C. *Principle of Instrumental Analysis*; Cengage: Boston, MA, USA, 2007; ISBN 978-8-57-811079-6.
- 25. Gonz'alez, F.J. Noise measurements on optical detectors. Rev. Mex. Fis. 2006, 52, 550-554.
- 26. Korea MOE. National Emission Standard for Coal-Fired Power Plant; Korea MOE: Sejong, Korea, 2017.
- 27. MacLeod, H.A. *Thin-Film Optical Filter*, 4th ed.; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2010; ISBN 978-1-42-007302-7.
- 28. Wong, J.Y.; Schell, M. Zero drift NDIR gas sensors. Sens. Rev. 2011, 31, 70–77. [CrossRef]



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