Step-scan T cell-based differential Fourier transform infrared photoacoustic spectroscopy (DFTIR-PAS) for detection of ambient air contaminants

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Abstract A step-scan differential Fourier transform infrared photoacoustic spectroscopy (DFTIR-PAS) using a commercial FTIR spectrometer was developed theoretically and experimentally for air contaminant monitoring. The configuration comprises two identical, small-size and low-resonance-frequency T cells satisfying the conflicting requirements of low chopping frequency and limited space in the sample compartment. Carbon dioxide (CO_2) IR absorption spectra were used to demonstrate the capability of the DFTIR-PAS method to detect ambient pollutants. A linear amplitude response to CO₂ concentrations from 100 to 10,000 ppmv was observed, leading to a theoretical detection limit of 2 ppmv. The differential mode was able to suppress the coherent noise, thereby imparting the DFTIR-PAS method with a better signal-to-noise ratio and lower theoretical detection limit than the single mode. The results indicate that it is possible to use step-scan DFTIR-PAS with T cells as a quantitative method for high sensitivity analysis of ambient contaminants.

1 Introduction

Trace gas detection has widespread applications such as in atmospheric monitoring [1], industrial processes control [2]

and human health. Spectroscopic techniques are one of the main detection methods for atmospheric measurements of trace gases [3]. There has been a continuing and increasing interest in photoacoustic spectroscopy (PAS) as a gas detection method due to the advantages of high sensitivity, simplicity and robustness of implementation [4]. PAS is ideally a zero-background technique, since the signal is generated only by gas optical absorption. However, spurious signals can originate from nonselective absorptions in resonator windows and absorbing background gases. In order to suppress the noise level and improve SNR performance, various designs of PA setups have been proposed [5]. A differential setup characterized by two identical Helmholtz resonators and a beam splitter was introduced [6] to reduce window noise. Also, a differential Helmholtz cell with a symmetric design of two identical resonators and a high reflectivity blade chopper was reported for suppressing window noise and improving light energy efficiency [7]. Another differential setup equipped with a cantilever photoacoustic cell and broadband IR radiation source was proposed to enhance photoacoustic sensitivity [8]. Furthermore, a differential excitation mode photoacoustic spectroscopic scheme has been implemented using blackbody sources [9].

In this paper, a step-scan differential FTIR-PAS (DFTIR-PAS) method based on a commercial FTIR spectrometer is presented for air contamination monitoring. Two identical T cells [10] have been found to be the most appropriate resonators considering the conflicting requirements for low chopping frequency and the limited sample compartment space. The DFTIR-PAS configuration can simultaneously eliminate spurious signals by background gas and window absorptions, as well as external background noise. Considering the broadband FTIR spectral source, this design provides a realistic approach for high-performance multiple

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gas detection with the small-volume sample compartments of modern FTIR spectrometers, thereby creating the possibility of constructing a portable FTIR-PA spectrometer for field applications.

2 Instrumentation and experiments

The DFTIR-PAS configuration based on a commercial FTIR spectrometer (Bruker, Vertex 70) is depicted in Fig. 1. The spectrometer features a mid-infrared (MIR) source (intensity 30 mW). The incident light is directed into the sample and reference resonator chamber, sequentially, with 50 % square-wave duty cycle, the optical square waveform being shaped by a chopper and alternatively transmitted and reflected using a homemade one-side-coated (mirror) blade. This approach effectively maximizes light energy utilization efficiency as it avoids beam splitting. The sample resonator contains a mixture of a targeted gas and other background gases (e.g., ambient air), while the reference resonator is filled up with only the background gases. The photoacoustic signals from the two resonators are combined by a mixer and detected by a lock-in amplifier. The output of the lock-in amplifier is recorded and stored in the FTIR spectrometer memory. The configuration is flexible for switching between the single and the differential lockin detection modes, providing an easy approach to investigate each cell separately and compare directly with the differential mode.

Figure 2 depicts the geometry of the T cell and the gas dilution and mixing arrangements. The basic T cell consists of three parts: an absorption cylinder which is responsible for incident light absorption; a resonance cylinder which mainly determines the resonance frequency; and a buffer cylinder which is the connector of the two foregoing cylinders [10]. A Primo[®] EM 158* electronic condenser microphone (sensitivity 25 mV/Pa at 1 kHz) is located on the top (cap) of the resonance cylinder. We chose CO_2 (supplied by Linde[®] Gas/AGA) as the preferred test gas for analysis, and several concentrations were prepared using a homemade mixer. The designated concentrations were premixed in the mixture bag and were kept for a few hours before being introduced into the photoacoustic cells. All measurements were conducted under STP conditions.

3 Theory

The spectrometer is fundamentally based on the principle of a Michelson interferometer which produces an interferogram, a digital plot of light intensity, $I(\delta)$, versus mirror position (also known as optical path difference, OPD, and symbolized by δ). A spectrum, $B(\sigma)$ vs. wave number, σ , is



Fig. 1 Schematic of the step-scan DFTIR-PAS system

obtained when a digital Fourier transform (FT) is applied to the interferogram data. The transformation is expressed mathematically as Eq. 1.

$$B(\sigma) = \int_{-\infty}^{\infty} I(\delta) \cos\left(2\pi\delta\sigma\right) \mathrm{d}\delta. \tag{1}$$

In a step-scan interferometer, the moving mirror is moved in discrete steps and halted at each retardation position at which the interferogram is sampled. Assuming there are N such positions/points in one interferogram, $I(\delta_j)$ is the detector signal recorded at position δ_j ($j \in [0, N - 1]$). To perform the Fourier transformation, each point is multiplied by the corresponding point of an analyzing cosine wave of unit amplitude and the resultant values are added. Considering that the interferograms are digitized at equal intervals (the retardation between adjacent sampling points is h, and $\delta_j = jh$), the spectrum signal for any wave number σ_m can be given as Eq. 2 which is the discrete version of Eq. 1 for an interferogram symmetric about the point of zero OPD.

$$B(\sigma_m) = I(0) + 2 \sum_{j=1}^{N-1} I(jh) \cos(2\pi \sigma_m jh) j : 1, 2, 3 \dots$$

$$\leq N - 1, m : 1, 2, 3 \dots M$$
(2)

The summation in Eq. 2 is performed for all wave numbers of interest in the spectrum. The wave number range is determined by the types of optical sources and the current filters. *M* stands for the number of wave number ordinates considered in one spectrum ($m \in [1, M]$).

The phase difference between the outputs of the two cells, φ , is ideally equal to π as a result of the opposite phase light modulation described in the previous section. $H_1(jh, x)$ is the



Fig. 2 Gas dilution arrangements

heat source generated in the sample resonator by absorption of the modulated light I(jh) (light intensity at the moving mirror position *jh*). $H_1(jh)$ is a function of the absorption coefficient α which, in turn, is a function of wave number ν and is uniquely associated with detection gas *k*. The length of the absorption cylinder of the T cell is *L* (optical absorption path length), so the total absorbed light intensity ($H_1(jh)$) is

$$H_{1}(jh) = \int_{0}^{L} H_{1}(x, jh) dx = \int_{0}^{L} \alpha_{k}(v) I(jh) e^{-\alpha_{k}(v)x} dx$$

= $I(jh) \left(1 - e^{-\alpha_{k}(v)L}\right).$ (3)

The photoacoustic signal $(S_1(jh))$ generated in the sample cell is given by

$$S_{1}(jh) = H_{1}(jh) \frac{C}{L} R_{\text{mic}}(\omega_{1}) = I(jh) \left(1 - e^{-\alpha_{k}(\nu)L}\right) \frac{C}{L} R_{\text{mic}}(\omega_{1})$$
(4)

where $R_{\rm mic}$ is the microphone sensitivity; ω_1 is the modulation angular frequency and is equal to the fundamental resonance angular frequency of the T cell. *C* is the cell constant which describes how the absorbed heat is converted to an electrical signal output [8]

$$C = (\gamma - 1)G\frac{L}{V}\frac{Q_1}{\omega_1}P_1(r_{\rm mic})$$
(5)

Here, $\gamma = C_p/C_v$ is the ratio of the specific heats, *V* is the cell volume, and *G* is a geometrical factor which depends on the beam profile. Q_1 is the quality factor at resonance ω_1 , and P_1 is the pressure amplitude at the microphone position r_{mic} . The parameter *C* is approximately calculated to be 2063 Pa/cm⁻¹/W [10]. The absorption coefficient of the desired gas (*k*) is defined as [11] $\alpha_k(v) = N_{tot}c(k)E_k(v)$; N_{tot} is the total number density of molecules; c(k) and $E_k(v)$ are the concentration and the absorption spectrum of the *k*-th component, respectively.

In the FTIR step-scan mode, the incident light is correlated with OPD. Taking into account Eqs. 2, 6 gives the photoacoustic signal $(B_S(\sigma_m))$ when the cell is resonant at the fundamental frequency

$$B_{S}(\sigma_{m}) = \left(1 - e^{-\alpha_{k}(\nu)L}\right) \frac{C}{L} R_{\text{mic}}(\omega_{1}) \\ \times \left[I(0) + 2\sum_{j=1}^{N-1} I(jh) \cos\left(2\pi\sigma_{m}jh\right)\right] \\ j: 1, 2, 3 \dots N - 1, m: 1, 2, 3 \dots M$$
(6)

If the absorption coefficient is small ($\alpha_k(v)L \ll 1$), the photoacoustic signal depends linearly on the concentration and is given by

$$S_1(jh) = I(jh)CR_{\rm mic}(\omega_1)N_{\rm tot}c(k)E_k(\nu).$$
⁽⁷⁾

Therefore, the FTIR-PAS signal is described as

$$B_{S}(\sigma_{m}) = N_{\text{tot}}c(k)E_{k}(\nu)R_{\text{mic}}(\omega_{1})C \\ \times \left[I(0) + 2\sum_{j=1}^{N-1}I(jh)\cos\left(2\pi\sigma_{m}jh\right)\right] \\ j:1,2,3...N-1, m:1,2,3...M$$
(8)

Equations (7) and (8) are the results for only one absorbing gas present in the resonators. However, the signatures of many trace gases need to be detected in practical applications. Furthermore, these various trace gases exhibit unique narrowband absorption structures [12]. Thus, the photoacoustic signal in the sample resonator where a mixture of gases desired to be detected and other background gases (e.g., ambient air) are present, can be described as the superposition (sum) of various optical absorptions by those gases at STP

$$S_{1}(jh) = I(jh)CR_{\rm mic}(\omega_{1})N_{tot}\left[\sum_{k=1}^{T} c(k)E_{k}(\nu) + \sum_{k'=1}^{T'} c\left(k'\right)E_{k'}(\nu)\right]$$
(9)

where T is the total number of gases to be detected and T' is the total number of absorbing gaseous species mixed in with the residual (background) gas which can generate a spurious photoacoustic signal (e.g., water vapor in ambient air).

The reference resonator is usually filled with the background gas alone. The gas mixture can be regarded as an ideal gas as all operations are conducted at STP. Therefore, N_{tot} (the total number density of molecules) is identical in the two cells. Because the target gas concentration is extremely low, the other gas components inside the two resonators can be assumed to have the same concentrations. As a result, the photoacoustic signal ($S_2(jh)$)) can be described as:

$$S_{2}(jh) = I(jh)CR_{\rm mic}(\omega_{1})N_{\rm tot}\sum_{k'=1}^{T'} c(k')E_{k'}(\nu)e^{i\varphi}.$$
 (10)

Thus, instead of Eq. 8, the DFTIR-PAS signal from multiple gases desired to be detected is given by Eq. 11 which is independent of any background gas contributions to the signal, if the light directed into the two cells is modulated precisely opposite phase:

$$B_D(\sigma_m) = \left[I(0) + 2\sum_{j=1}^{N-1} I(jh) \cos(2\pi \sigma_m jh) \right]$$
$$R_{\rm mic}(\omega_1) CE_k(\nu) N_{\rm tot} \sum_{k=1}^T c(k)$$
$$j: 1, 2, 3 \cdots N - 1, \ m: 1, 2, 3 \cdots M$$
(11)

The foregoing analysis shows that the DFTIR-PAS modality may be an effective approach for monitoring gases the absorption spectra of which overlap those of other background gases, because the signals from the background gases are cancelled by the opposite phase signal from the reference resonator. This will be verified in future work.

The sensitivity of the system is described by the smallest detectable concentration of a desired absorbing gas in the sample resonator. The concentration detection limit c_{min} set in the sample resonator is that of a photoacoustic signal equal to the noise amplitude (N_1) in the photoacoustic cell. So the detection limit, $c_{smin}(k)$, using a single cell is determined by Eq. 12. Here, for simplicity, only one absorbing gas in the sample resonator is considered for detection limit comparison of the single-ended and the differential FTIR-PAS modes.

$$I(jh)CR_{\rm mic}(\omega_1)N_{\rm tot}c_{s\min}(k)E_k(\nu_k) = N_1$$

= $N_{1T} + N_{1E} + N_{\rm window}(jh) + N_{\rm wall}(jh) + N_{\rm I}(jh)$ (12)

 N_{1T} and N_{1E} are the incoherent noise components caused by thermal fluctuations and microphone electrical noise in the sample resonator [13]; $N_{window}(jh)$ is the window heating noise; $N_{wall}(jh)$ is the noise generated by absorption and scattering of radiation on the resonator walls; and $N_{I}(jh)$ is the noise associated with incident light fluctuations. $N_{window}(jh)$, $N_{wall}(jh)$ and $N_{I}(jh)$ are the coherent noise components which are correlated with the incident light [5].

The noise level (N_2) in the reference resonator is given by

$$N_2 = N_{2T} + N_{2E} + \left[N_{\text{window}}(jh) + N_{\text{wall}}(jh) + N_{\text{I}}(jh) \right] e^{i\varphi}$$
(13)

where N_{2T} and N_{2E} are the incoherent noise components caused by thermal fluctuations and microphone electrical noise. The detection limit $c_{dmin}(k)$ of the differential system is determined by Eq. 14

$$I(jh)CR_{\rm mic}(\omega_1)N_{\rm tot}c_{d\min}(k)E_k(\nu_k) = N_1 + N_2$$

= $N' + [N_{\rm window}(jh) + N_{\rm wall}(jh) + N_I(jh)](1 + e^{i\varphi})$
(14)



Fig. 3 Amplitude and phase responses of the two cells vs. frequency

where N' is the incoherent background noise of the differential mode. In view of the fact that almost identical incoherent background noise levels were found in both the single and the differential setups from the experimental data, the coherent noise components could be totally cancelled out if the light waveforms directed into the two resonators were opposite phase, consistent with $\phi = \pi$ in Eq. 14.

4 Results

The simulated amplitude and phase responses of the two resonators and frequency-scan measurements obtained by chopping the excitation interference light from the MIR source in the spectrometer and detecting the signal with the lock-in amplifier are shown in Fig. 3. The simulation results were generated by Comsol 4.3 software [10]. The resonance frequencies of both cells were adjusted to be 342 Hz, which agrees with the experimental results [10, 14]. Both amplitude and phase responses showed excellent agreement between the two cells under single-mode operations, which laid the foundation for the subsequent high performance of the DFTIR-PAS system.

The spectroscopic selectivity of the step-scan DFTIR-PAS setup was tested, and the results are shown in Fig. 4. The spectra were normalized with the spectrum of the MIR source in the same wave number range. The results were measured with 6 cm⁻¹ resolution as better resolution would be impractically time-consuming. In the infrared absorption photoacoustic spectrum of 5000 ppmv CO₂, the rotational-vibrational levels, especially the strong absorption peak at around 2349 cm⁻¹, are clearly distinguishable with 6 cm⁻¹ resolution. The differential mode is capable of significant coherent noise attenuation, described by Eq. 14 and verified in the inset of Fig. 4. A straight line was fitted





Fig. 4 Infrared absorption DFTIR-PAS of 5000 ppmv concentration CO_2

to the spectrum in the case where no gas absorption exists (the range 4350–4450 cm⁻¹ was chosen) to calculate noise [15]. The standard deviation (2.045×10^{-5}) was calculated between the best-fitted curve and the experimental data and was taken to be the noise level. The DFTIR-PAS signal of CO₂ at the 2349 cm⁻¹ absorption peak was set at 0.0714 (an arbitrary value). Thus, the SNR of 5000 ppmv carbon dioxide was found to be 3491.4 (=7.140 $\times 10^{-2}/2.045 \times 10^{-5}$) for the differential mode, well above the value 1515.5 found for the single-ended mode. These spectrometer performance characteristics lead to a CO₂ detection limit of 2 ppmv for the differential mode and 4 ppmv for the single-ended modes.

Figure 5 shows the concentration dependence of the amplitude and phase signals at the CO_2 absorption peak



Fig. 5 Step-scan DFTIR-PAS amplitude and phase responses at the absorption peak (2349 cm⁻¹) of CO_2

(2349 cm⁻¹) between 10,000 and 100 ppmv in the stepscan DFTIR-PAS experiments. The relationship between PA phase signal ϕ and CO₂ concentration can be expressed as [16]

$$\tan\left(\phi - \phi_0\right) = \omega_1 \tau \tag{15}$$

where τ is the relaxation time of the gas mixture at 1 atm, and ϕ_0 is the reference offset which is determined by the experimental setup (ϕ_0 was found to be 48.5° for the DFTIR-PAS system). The relaxation time at STP is approximately $\tau_{CO_2} = 7.5 \,\mu s$ for pure CO₂ [15]. τ can be calculated as $\tau = \tau_{CO_2}/c(CO_2)$ neglecting the relaxation time of N₂ because its vibrational relaxation time, approximately 4 ± 2 s at STP [17], is too long to contribute to the phase profile of Fig. 5b. Therefore, the theoretical PA phase signal increases as the CO₂ concentration in the mixture decreases, a trend borne out by the experimental phase data in Fig. 5b.

The foregoing results are comparable with the 4 ppm CO_2 detection limit in Ref. [15] which used a system operating at 470 mbar with an optical cantilever-based detector combined FTIR spectrometer. However, the displacement measurement of the cantilever needs another interferometer, which complicates the system design compared to the electret condenser microphones used here. A cantilever enhanced photoacoustic trace gas detection system using a mid-infrared LED with emission intensity 33 μ W at 4.25 μ m, and 11 ppm CO_2 detection limit has also been reported [18]. Its performance was significantly lower than the results reported here. Furthermore, the present results were obtained with a much less intense globar source of much wider spectral bandwidth, the intensity of which around 4.25 μ m was about 8 μ W as recorded by the optical power meter. Although the theoretical detection limit cannot be compared with some laser-based [19, 20] and optical parametric oscillator [21] detection methods with high power of several hundred mW, the step-scan T cell-based DFTIR-PAS system has inherent multicomponent gas detection capability advantages due to the very broad spectral range of the FTIR modality and its compatibility with small footprint spectrometers which gives rise to the potential for portable DFTIR-PAS use in the field. FTIR-PAS can detect several gas components during a single measurement as opposed to laser-related methods which can only measure one target gas. Owing to its inherent spectral baseline and noise suppression properties, the DFTIR-PAS modality may be an effective approach for resolving "hidden" gases, the absorption spectra of which are concealed due to overlapping with other background gases and are thus difficult or impossible to resolve under single-ended FTIR-PAS detection.

5 Conclusions

A step-scan DFTIR-PAS system based on a commercial FTIR spectrometer and homemade T-resonators was designed, assembled and tested. The DFTIR-PAS theory was developed and showed that the differential mode may cancel the coherent noise and the spurious photoacoustic signal generated by background gases. The nearly identical behavior of the two cells was found to be key to the high performance of the differential mode. The SNR of the differential mode was more than double that of the single mode, a consequence of the differential mode being able to effectively suppress coherent noise. The theoretical detection limit of the differential mode was calculated to be 2 ppmv. In mixtures of CO_2 with N_2 , the amplitude signal was found to scale linearly with the CO_2 concentration ranging from 10,000 to 100 ppmv. In combination with the agreement of the phase shift with theoretical results of the known gas relaxation time, it has been demonstrated that the step-scan T cell DFTIR-PAS system approach is a sensitive, broadband, quantitative spectroscopic technique for trace gas detection in air with enhanced reliability over single-ended alternatives due to efficient baseline noise suppression and maximum efficiency of the use of the incident light.

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