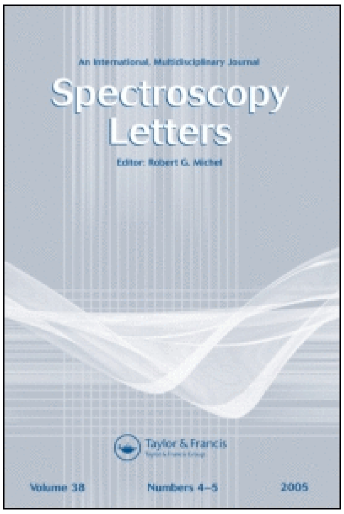

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Real-Time Monitoring of Transport of Chlorinated Hydrocarbons from Industrial Areas Using Open-Path FTIR Spectrometry with COL1SB

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Abstract: Open-path Fourier transform infrared (FTIR) spectrometry was used to continuously monitor 11 chlorinated hydrocarbon species in the region connecting two different industrial complexes for 24 hr. The single-beam spectra obtained from open-path FTIR were analyzed by newly developed software named COL1SB, which generates site-specific background spectra as well as path-averaged water vapor concentrations in addition to performing regression analyses. The path-averaged water vapor concentrations calculated by the COL1SB agreed very well with those measured by a thermo-hygrometer. In addition, site-specific background spectra were generated by accounting for chemical absorption of 50 chemical species. The accurate estimation of path-averaged water vapor concentrations, as well as the usage of site-specific background spectra, enables chlorinated hydrocarbons to be measured by open-path FTIR spectrometry at the ppb level. Among 11 chlorinated hydrocarbons considered here, trichlorofluoromethane, carbon tetrachloride, trichloroethylene, and tetrachloroethylene were identified as major chlorinated hydrocarbons having concentrations above 1 ppb. Wind affected the temporal variations of these chlorinated hydrocarbons, indicating the importance of local transport.

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However, the effect of wind differed from one species to another because of different source characteristics.

Keywords: chlorinated hydrocarbons, fence-line monitoring, hazardous air pollutants, open-path Fourier transform infrared spectroscopy

INTRODUCTION

Since the combustion of fossil fuels was recognized as a prime source of air pollution in the early years of industrialization, a great deal of effort has been made to evaluate the air pollutant emission from fossil fuel combustion. Only recently have hazardous air pollutants generated from industrial facilities gained public attention for their impact on human health. Compared to fossil fuel–derived air pollutants, the hazardous air pollutants group comprises a greater number of chemical species, and these pollutants often exist in lower concentrations, which poses a great challenge to air monitoring.

The ambient concentrations of hazardous air pollutants are typically evaluated by analyzing air samples by gas chromatography (GC). Although GCs are capable of accurately resolving numerous chemical species in air samples, air sampling and subsequent storage tend to introduce non-negligible errors into the measured concentrations. Furthermore, this conventional sampling method is often so severely limited in temporal resolution and duration that it may not be able to provide information necessary for evaluation of the impact on human health.

Open-path optical devices such as tunable diode laser absorption spectroscopy (TDLAS) and open-path Fourier transform infrared spectrometry (OP-FTIR) have emerged as new methods by substantially enhancing the temporal and spatial resolution for IR active hazardous air pollutants. For example, Lawson et al.[1] and Sauer et al.[2] used the TDLAS to measure HCHO in ambient air, and Brassington[3] used TDLAS to measure HCl in the plume of a coal-fired power station. Strang and Levine[4] used FTIR spectrometry to estimate the detection limits of the hazardous gases in the semiconductor industry. Xiao et al.[5] and Hall et al.[6] measured the HCl and ethylene chloride as byproducts of toxic waste incineration.

The current study extends the previous study[7] to do a real-time monitoring of chlorinated hydrocarbons to investigate their transport from industrial complexes to residential areas. OP-FTIR spectrometry is theoretically able to analyze several hundred chemical species in real-time to make it an ideal instrument for hazardous air pollutant monitoring. However, it suffers from high detection limits as many open-path instruments do. Recently, COL1SB (constrained L1-norm minimization with the synthetic background generation method) has been developed to improve the detection limits and precisions to make the OP-FTIR spectrometry applicable to ambient monitoring. Here, OP-FTIR with COL1SB was used to identify and quantify chlorinated hydrocarbons in the region of interests, and then the temporal behavior of the identified chlorinated hydrocarbons were investigated by analyzing associated meteorological conditions.

MATERIALS AND METHODS

Analysis Software of OP-FTIR Derived Absorption Spectra

Description of COL1SB

The COL1SB method was developed to calculate the concentrations of hundreds of chemical species including Volatile Organic Compounds (VOCs) and inorganic compounds from absorption spectra derived by the OP-FTIR. Because a more detailed description is available elsewhere,[7,8] only the major features of COL1SB are briefly presented here.

The application of a regression analysis to absorption spectra often produces a physically unfeasible value such as a negative or excessively large number for a chemical species concentration because of complex coupling among chemical species being analyzed. COL1SB constrains a regression analysis to limit the value of solution from zero to a maximum allowed value. Also, COL1SB uses the L1-norm instead of the L2-norm to minimize the propagation of the local error occurred due to irregular field conditions or inappropriately resolved chemical interferences.

In addition, the COL1SB generates background spectra from the clean spectra by incorporating absorption by all the chemical species present. Here, the clean spectra represent single-beam spectra with no IR absorbing chemical species present and is derived from a zero-path spectrum. The chemical species concentrations are first calculated using the clean spectra as background spectra, and then the absorption effects by all other chemical species are added to the background spectra using the reference absorption spectra. These procedures are iterated until all the chemical species concentrations converge as shown in Fig. 1. Once all the chemical species concentrations have converged, the convergence test is also applied to the water vapor pressure. If the water vapor pressure is updated, then MALT[9] is used to recreate the reference water vapor, absorption spectra corresponding to the new water vapor pressure. The QASOFT[10] reference spectra are used to perform the quantitative analysis of all chemical species except water.

The ambient monitoring is susceptible to strong chemical interferences to make it difficult to select the appropriate spectral band for the analysis of most VOCs. The recommended spectral band is usually derived from laboratory experiments with only a few chemical species present and with well controlled experimental conditions to minimize chemical interference. Therefore, these recommended spectral bands need to be further optimized for given field

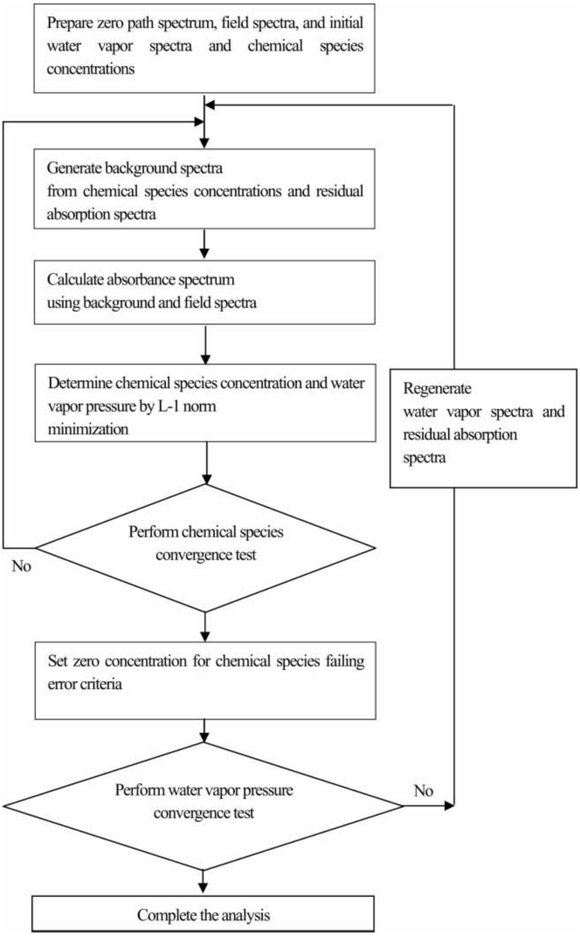


Figure 1. The schematic diagram of COL1SB.

conditions. COL1SB dynamically selects the appropriate spectral bands by imposing the following conditions.

$$A_{\mathrm{field}} > f_1 \times A_{\mathrm{water}} \tag{1}$$

$$A_{\mathrm{chemical}} > \frac{f_2 \times A_{\mathrm{field}}}{1 - f_2} \tag{2}$$

where A_{field} denotes the field absorbance, and A_{water} and A_{chemical} are the absorbance by water vapor and by the chemical species of interest, respectively. The first and second conditions exclude the absorption spectra in region where absorption by water vapor in high and by chemical species other than ones being analyzed, respectively. In the current study, f_1 and f_2 are model parameters set here to 1.05 and 0.09, respectively.

Finally, the calculated chemical species concentration is checked against the following error criteria.

$$\text{Criterion I}: \quad R > 0.6 \tag{3}$$

$$\text{Criterion II}: \quad C > 3\sigma \tag{4}$$

where R denotes the correlation coefficient between calculated and measured absorption spectra, and σ is a standard deviation of measured spectra. A more detailed description of each criterion can be found elsewhere.[8] If the calculated chemical species concentration and accompanying absorption spectra failed to satisfy the above criteria, then its concentration was set to zero by assuming it existed below the detection limit.

Calculation of Path-Averaged Water Vapor Pressure

Water vapor may be the most predominant species affecting the quantification of most chemical species by OP-FTIR. Therefore, the performance of OP-FTIR often relies on the accurate handling of water vapor lines. Numerous efforts have been formulated to calculate the site-specific water vapor spectra and account for water vapor inhibition. One of the most frequently used methods is to calculate the site-specific water vapor pressure at each selected spectral band of the chemical species of interest. Because it is usual to analyze several different chemical groups, the calculated water vapor pressures may be different from one spectral band to another. Despite of the apparent inconsistency, this method, denoted here as BWC (bandwidth-wise water vapor concentration method), has been widely used by commercial analysis software mainly because it yields the best fit of water vapor spectra at the given spectral band. The other method, denoted here as OWC (overall water vapor concentration method), is to treat water vapor as just another chemical species to determine at the specific spectral band, which was chosen as the region of $3074 \sim 3090\,\text{cm}^{-1}$ in the current study.

The artificial field spectra for urban areas from Hong and Cho's work[7] were employed here to critically test the performance of BWC and OWC. The artificial field spectra were generated by 19 chemical species and a water vapor pressure of 7.5 Torr. The spectrum of 5 Torr of water vapor was chosen as a reference water spectrum for the regression analysis. In addition, the regression analysis was repeated with the spectrum of 10 Torr of water vapor as the reference spectrum.

The estimated water vapor pressures using BWC are listed in Table 1 for the selected bands as illustration. Also shown is the average relative error for the chemical species calculated in the listed bands. The calculated water vapor pressures ranged from 6.39 Torr to 7.34 Torr with 5 Torr reference water vapor spectrum, whereas they ranged 7.62 Torr to 8.43 Torr with 10 Torr

Table 1. The calculated water vapor pressures and average relative errors using the water reference spectrum with 5 and 10 Torr

		Water vapor pressure for reference water spectrum			
		5 Torr		10 Torr	
Selected bands	Analyzed chemical species	Average relative error (%)	Calculated water vapor pressure (torr)	Average relative error (%)	Calculated water vapor pressure (Torr)
744~780	Acetylene	57.25	6.388	26.67	8.430
880~916	1-butene, 1-pentene	87.80	6.840	57.36	8.146
1,040~1,067	Ozone	3.63	6.514	2.26	8.348
2,848~2,949	Propane, *n*-butane	74.71	6.905	57.08	8.018
2,640~2,712	Formaldehyde	0.53	7.375	0.71	7.623

reference water vapor spectrum. The nonlinearity associated with water vapor spectra was probably responsible for the inaccurately estimated water concentrations, which contributed to the inaccuracies associated with chemical species concentrations. OWC method also exhibited a similar behavior; the water vapor concentration was calculated to be 6.48 Torr with 5 Torr reference water vapor spectrum and 8.27 Torr with 10 Torr reference water vapor spectrum.

Figure 2 shows that the averaged relative errors increases greatly, as the water vapor pressure of reference spectrum is further away from the field water vapor pressure of 7.5 Torr. OWC is more accurate than BWC only when the water vapor pressure of reference spectrum is exactly same

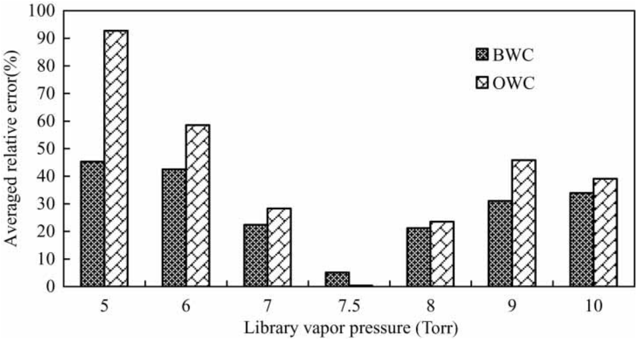


Figure 2. The total average relative errors with respect to water vapor pressures of reference spectra for the case of field water vapor pressure of 7.5 Torr.

as the field water vapor pressure. However, the accuracy of OWC deteriorates faster than BWC as the water vapor pressure of reference spectrum deviates from the field water vapor pressures.

Because the true absorbance of most lines in the water spectrum is so high, and the spectrum is measured with a resolution that is numerically greater than the FWHH (full-width at half height) of these lines, the absorbance varies nonlinearly with partial pressure. The nonlinearity associated with water vapor spectrum is particularly important because of its strong influence on the IR spectra of analytes absorbing in the same region. As shown above, the average relative error could be as large as 25%, even in the case that the initial water vapor pressure differs from that of field conditions only by 0.5 Torr. Therefore, it is very important to accurately derive the path-averaged water vapor pressures unless nonlinear regression analysis methods are used.

In the current study, the water vapor pressure measured by conventional meteorological devices is used to derive the initial reference water vapor spectrum. And then, all the chemical species concentrations including water vapor are calculated by the linear regression analysis method implemented in COLS1B. The calculated water vapor pressure is used to regenerate the reference water vapor spectrum. This procedure is continued until the water vapor pressure converges.

Figure 3 demonstrates that OWC with the above proposed iteration method yields very accurate water vapor pressure in a few iterations for the case of the 7.5 water vapor pressure. This iterative procedure can be easily implemented onto BWC by using the averaged water vapor pressures of all the spectral bands considered, which results in a similarly good convergence.

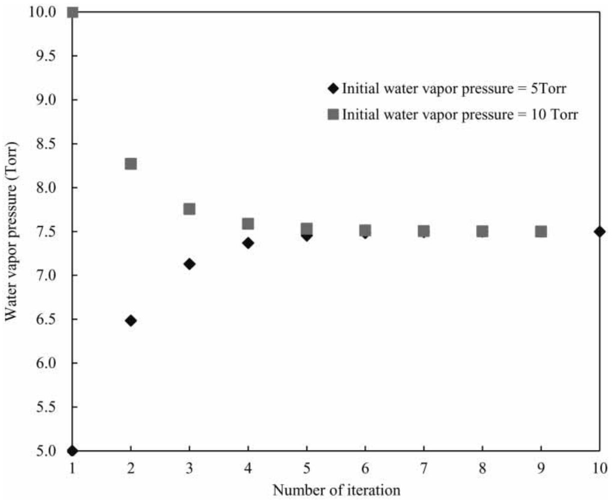


Figure 3. The water vapor concentration versus the number of iterations with the OWC method.

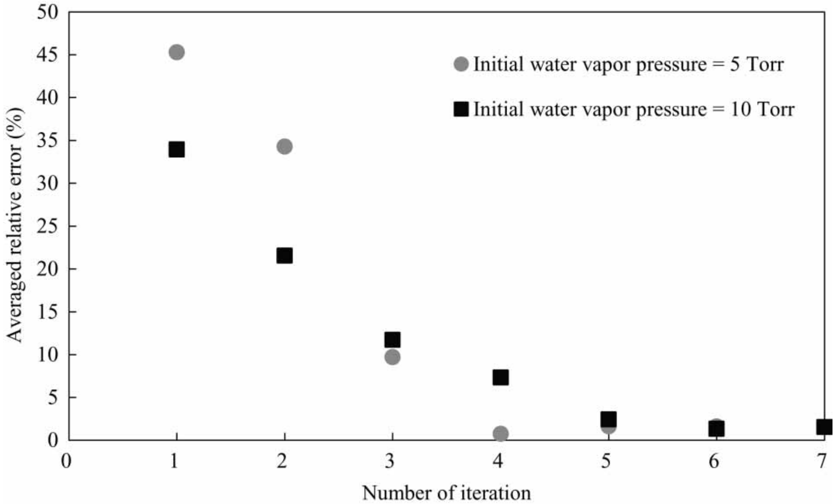


Figure 4. The average relative errors versus the number of iterations with the OWC method.

As shown in Fig. 4, the average relative error also decreases rapidly as iteration proceeds. Because COL1SB is built on the iterative methods as described by Fig. 1, the current iteration procedure for water vapor concentrations can be easily incorporated without much additional effort. Furthermore, this iterative generation of the reference water vapor spectrum can be easily extended to other chemical species to handle a strongly nonlinear behavior.

Monitoring Conditions

The current study aims at demonstrating the applicability of the OP-FTIR in monitoring hazardous air pollutants, especially chlorinated hydrocarbons. Many of hazardous air pollutants are released to the air by vaporization of solvents commonly used in industrial applications. Therefore, it is of interest to do a monitoring study during the summer in the industrial region. The humidity is usually quite high in summer in many countries to make water vapor inhibition more severe, with a concomitant increase in detection limits. In the current study, the monitoring was performed from the night of July 12 for 24 hr to represent typical summer atmospheric conditions.

Monitoring Site

The current study aims at monitoring transport of air pollutants from the SHIWHA and BANWOL industrial complexes to the neighboring residential

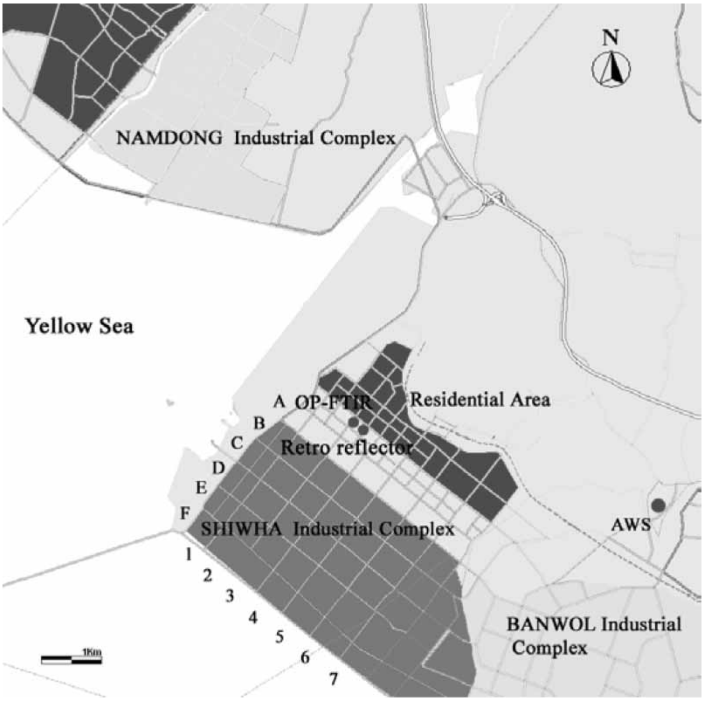


Figure 5. The monitoring site location.

area. Therefore, the monitoring site was located in between these two areas as shown in Fig. 5. In addition to the SHIWHA and BANWOL industrial complexes, the NAMDONG industrial complex area is located at the northeast of the monitoring site, which may influence the chosen monitoring site depending on wind direction.

The SHIWHA industrial complex houses more than 2300 companies, among which 650 companies have permits for air pollutant emissions. These include a sewage treatment plant, industrial waste incinerators, chemical plants, paper manufacturing facilities, and oil and solvent regeneration plants. Most of these facilities are located on the 1 and 5 block in the SHIWHA industrial complex shown in Fig. 5. The residential area, mostly consisting of apartment complexes, is located 175 m from SHIWHA industrial complex. A 30-m-high small hill was artificially built in this 175-m gap. The OP-FTIR spectrometry was positioned at the top of the artificial hill to monitor the transport of air pollutant from the SHIWHA industrial complex to the residential area.

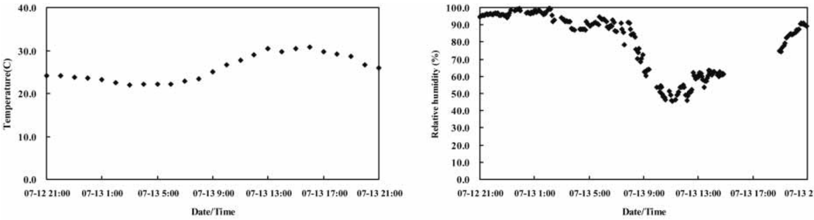
The monostatic AIRSENTRY OP-FTIR with MCT detector was employed here, and the distance between the light source and retro-reflector was set to 350 m. The number of scans was set to 64 to improve the signal-to-noise ratio, so that approximately 5 min was required to get one field spectrum. The spectral resolution was 1 cm^{-1} and cosine apodization was applied.

Meteorology

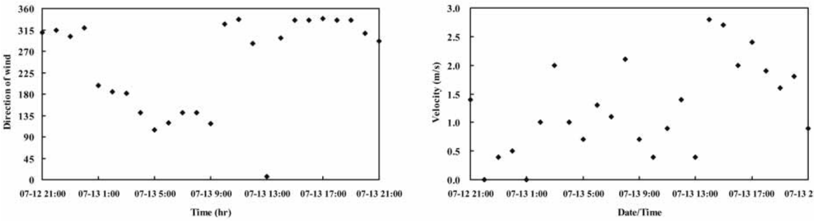
The ambient chemical species concentrations are strongly influenced by associated meteorological conditions such as wind speed and direction and solar radiation. An automatic weather station (AWS) is located 5 km east of the present monitoring site to provide wind velocities and directions. The humidity and temperature were measured by a portable thermo-hygrometer at the OP-FTIR monitoring site instead of using the measurements of the nearby meteorological station to improve the accuracy.

As shown in Fig. 6, the temperature ranged from 21°C to 31°C, representing typical summer conditions in the region. It was raining 2 days prior to the monitoring. It was partly cloudy with cloud cover ranging from 4.3 to 4.8. The relative humidity was quite high exceeding 90% except in the daytime, which again constitutes a typical summer condition. This high relative humidity promotes a strong water interference to make OP-FTIR analysis difficult.

As also shown in Fig. 6, the principal wind direction was northwest initially and then switched to south at midnight of July 12. The wind slowly changed its direction to eastward for the next 10 hr, and finally a north wind prevailed during the rest of the day. Considering the geographical locations of the industrial complexes presented in Fig. 5, the chosen monitoring site might be influenced by emissions from NAMDONG industrial complex



(a) Temperature (b) Relative humidity



(c) Direction of wind (d) Wind speed

Figure 6. The measured meteorological parameters from 21:00 on 12 July to 21:00 on 13 July.

under a northwestern wind and by emissions from SHIWHA and BANWOL industrial complex under southern or southwestern winds. There was only a light wind for the first 12 hr, recording mostly below 1.5 m/s. As the wind direction changed to north in the late morning, the wind velocity increased steadily exceeding 3 m/s during the afternoon.

RESULTS

A number of organic and inorganic species may be emitted and exist at an appreciable level in industrial regions. The OP-FTIR spectrometer is able to analyze several hundred organic and inorganic chemical species strongly absorbing IR radiation. Among these several hundred chemical species, 50 chemical species were suspected to exist over detection limits and selected for analyses as shown in Table 2. The averaged concentrations for methane, ozone, ammonia, alkanes, and alkenes were measured to be 1700 ppb, 17 ppb, 45 ppb, 5.5 ppb, and 1.3 ppb, respectively. The current work focuses on chlorinated hydrocarbons emitted from neighboring industrial complexes. However, many other chemical species than chlorinated hydrocarbons was included in analyses as noted to adequately resolve chemical interferences. Here, the temporal behavior of chlorinated hydrocarbons was mainly

Table 2. The chemical species included in the current OP-FTIR spectrum analysis by COL1SB

Group	Chemical species
Inorganics[4]	Carbon monoxide, ammonia, ozone, water
Alkanes[8]	Methane, ethane, propane, *n*-butane, *i*-butane, *n*-pentane, *n*-hexane, *n*-heptane
Alkenes[7]	Acetylene, ethylene, propylene, 1-butene, 1-pentene, isoprene, isobutylene
Aromatics[4]	Toluene, *m*-xylene, ethylbenzene, styrene
Aldehydes[4]	Formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde
Alcohols[4]	Methanol, ethanol, isopropanol, isobutanol
Chlorinated and fluorinated hydrocarbons[12]	Hydrogen chloride, hydrogen fluoride, chloromethane, chlorodifluoromethane, trichlorofluoromethane, dichlorodifluoromethane, chloroform, carbon tetrachloride, 1,1-dichloroethylene, 1,2-dichloroethane, tetrachloroethylene, trichloroethylene
Miscellaneous VOCs[7]	Acetone, dimethylsulfide, hydrogen sulfide, diethylamine, methylamine, triethylamine, PAN

discussed along with chemical species concentrations having strong chemical interferences such as water vapor, carbon monoxide, and methane.

Water Vapor Pressure

The current developed COL1SB was designed to accurately calculate a path-averaged water vapor concentration from field absorption spectra. The humidity and temperature were measured at the monitoring site by the thermo-hygrometer. The corresponding water pressure was then calculated to verify the OP-FTIR derived water vapor pressure. The data reported from the thermo-hygrometer every minute were averaged to yield 5-min data to keep the consistency with OP-FTIR measurements. It may be noted here that the point measurement done by the thermo-hygrometer may not be directly comparable to the OP-FTIR measurement. However, the water vapor is one of the most abundant chemical species and exists rather uniformly within a certain radius to allow the present comparison between point and line measurements.

As shown in Fig. 7, the water vapor pressures derived by the OP-FTIR compared very well with those by the thermo-hygrometer both for magnitudes and trends. These two measurements were almost identical until the early morning of July 13 and then the OP-FTIR measured water vapor pressure changed a little more slowly for the next 6 hr mainly because of differences of spatial representation from the thermo-hygrometer measurements. After the water vapor pressures were stabilized on the afternoon of July 13, the

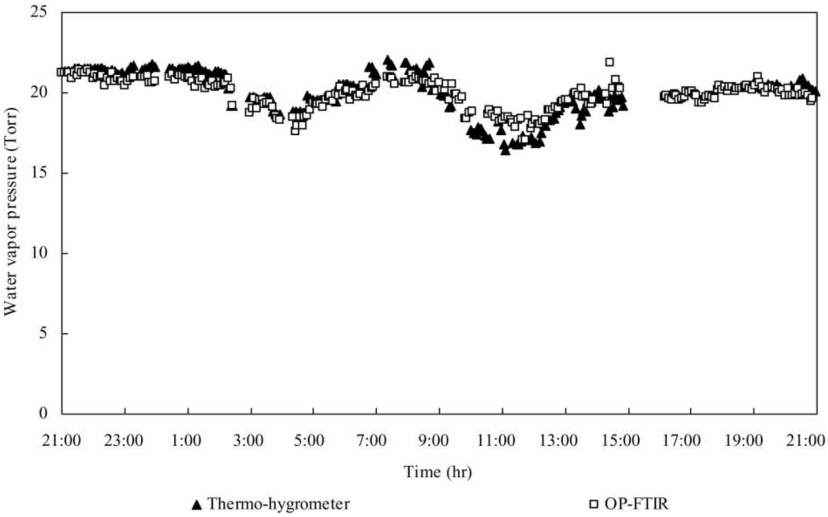


Figure 7. The comparison of the water vapor pressures measured by the portable thermo-hygrometer with those measured by OP-FTIR.

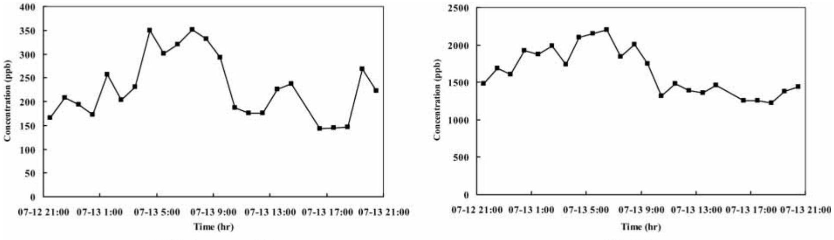
two measurements again became identical. The accurate estimation of path-averaged water vapor pressure demonstrated here is required to adequately handle the effect of water interference on other chemical species absorption spectra.

Carbon Monoxide and Methane Concentrations

The carbon monoxide and methane are the most abundant carbon-containing species actively absorbing IR radiation other than the carbon dioxide. The carbon monoxide is mainly produced by incomplete combustion, whereas the methane mainly results from natural processes. Although the carbon monoxide is a primary air pollutant, the observed temporal behavior in Fig. 8 does not exhibit the typical primary pollutant diurnal variation, high in the nighttime and low in the daytime. Rather, the carbon monoxide sustained the highest concentration during daytime mainly because of associated wind fields favoring transport of air pollutants.

The carbon monoxide concentration appeared quite low on the night of July 12 when a northwestern wind prevailed. As the wind direction changed to south or southeast after the midnight of July 12, the carbon monoxide concentrations increased to more than 300 ppb, as it was influenced by the adjacent SHIWHA industrial complex. The wind changed its direction to north on the late morning of July 13 to diminish the air pollutant transport from the SHIWHA industrial complex and to subsequently decrease the carbon monoxide concentration. It may be noted here that the carbon monoxide exhibited multiple peaks, which might not be thoroughly explained only by examining meteorology. However, this is very typical behavior of primary pollutant concentration in regions directly affected by several different sources.

Figure 8 also shows that the methane concentration did not contain distinctive multiple peaks, but it varied smoothly with time because of its stronger dependency on area sources. Taking out the phenomena associated with multiple peaks, the methane had a similar temporal variation to the



(a) Carbon monoxide

(b) Methane

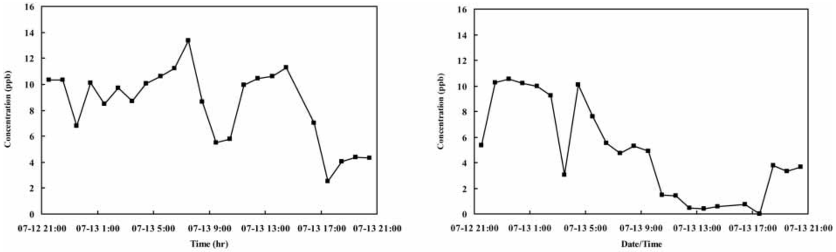
Figure 8. The hourly average carbon monoxide and methane concentrations measured by OP-FTIR.

carbon monoxide, high from the night of July 12 to the late morning of July 13. This indicates that the transport from the SHIWHA industrial complex also played an important role in determining the methane concentration.

Chlorinated Hydrocarbons

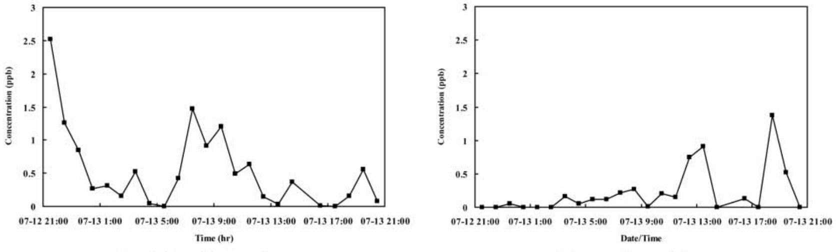
Recently, hazardous air pollutants have become a public concern for their harmful effect on human health. Chlorinated hydrocarbons are major hazardous air pollutants and are frequently found in industrial regions, resulting from vaporization of solvents. Because the absorptivity of several bands in the IR spectra of chlorinated hydrocarbons is high, OP-FTIR spectrometry is suitable for their measurement. All the 11 chlorinated chemical species whose absorption spectra are available in QASOFT[10] were included in the current analysis. There are hydrogen chloride, chloromethane, chlorodifluoromethane, trichlorofluoromethane, dichlorodifluoromethane, chloroform, carbon tetrachloride, 1,1-dichloroethylene, 1,2-dichloroethane, tetrachloroethylene, and trichloroethylene.

Among the 11 chlorinated chemical species analyzed, only 4 species, carbon tetrachloride, trichloroethylene, trichlorofluoromethane, and tetrachloroethylene, were detected and are presented in Fig. 9. Carbon tetrachloride was found to be the most abundant chlorinated species and exhibited a diurnal



(a) Carbon tetrachloride

(b) Trichloroethylene



(c) Trichlorofluoromethane

(d) Tetrachloroethylene

Figure 9. The hourly average chlorinated hydrocarbon concentrations measured by OP-FTIR.

variation similar to carbon monoxide and methane. The trichloroethylene also behaved similarly to the carbon tetrachloride until the wind direction switched to north at the late morning of July 13. The trichloroethylene remained in very low concentration under the northern wind, which had persisted for the rest of the day. The trichlorofluoromethane was detected in lower concentrations than carbon tetrachloride and trichloroethylene and showed a quite different temporal behavior probably because of different source characteristics. Finally, the tetrachloroethylene was barely detected and appeared to have a concentration of almost 1 ppb.

CONCLUSIONS

Recently, OP-FTIR spectrometry has been widely used for source monitoring and fence-line monitoring corresponding to growing demand for online monitoring of hazardous air pollutants and VOCs. The high concentration of chemical species in industrial regions reduces the problems associated with high detection limits on one hand but promotes strong chemical interferences on the other hand. Moreover, humidity is quite often very high in the summer season, during which many hazardous air pollutants and VOCs reach their yearly maximum values.

The current work demonstrated that the COL1SB adequately handles chemical interferences to qualitatively and quantitatively determine chlorinated hydrocarbons. Especially, a new method was developed to derive a path-averaged water vapor pressure from the absorption spectrum instead of using humidity measurement by a hygrometer. In addition, the online monitoring enabled by the OP-FTIR spectrometer might be used to investigate the transport of chlorinated hydrocarbons for the given meteorological conditions.

Theoretically, OP-FTIR spectrometry is able to measure several hundred organic and inorganic chemical species in real-time. However, the relatively high detection limit as well as the inadequate resolution of absorption spectra significantly deteriorates the capability of the OP-FTIR. However, as shown in the current work, the OP-FTIR coupled with the COL1SB may be used for qualitative analyses to identify chemical species existing in appreciable concentrations. And of course the chemical species existing above the detection limit can be quantitatively analyzed by OP-FTIR.

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