

Unambiguous Identification of Fugitive Pollutants and Determination of Annual Emission Flux as Diurnal Monitoring Mode

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Abstract : Toxic air pollutants are investigated in a petrochemical industrial park in Taiwan by using a movable open path FTIR. The results show the qualitative and quantitative analysis of emission gases from plants, and also provide the emission rate of different compounds. More than twenty compounds under usual operation are found from this industrial park. The concentration variation with time can be correlated exactly with wind direction. It means that by changing the measuring points, the source of emission can be unambiguously identified.

An EPA proved PAL model is applied to estimate the emission rate of either a point or an area source. Local atmospheric stability is determined by releasing the SF₆ tracer. The origins of errors come mainly from the uncertainty of source's configuration and the variation of meteorological condition. Through the continuous measurement (half an hour base in this study) of OP-FTIR sensor, the maximum value of emission rate and the annual amount of emission can be derived.

The emission rate of the measured toxic gases are derived by the model technique and the results show that the emission amount are in the order of ten to hundred tons per year.

Keywords : Open-path FTIR, Industrial park, Toxic gases, Emission rate, PAL model.

1. Introduction

The demand on air monitoring technique, in recent years, causes increasing studies on the instrument performance and application of the equipment. Also, in

view of industrial hygiene and environmental health, the measurement of air quality in industrial parks can offer a related evidence of environmental impact to bio-sphere. The research of rural air quality in Taiwan by using FTIRs (Fourier-Transform Infrared spectrometry) in our

laboratory [1] is now switched for the measurement of air quality in the industrial park[2].

The characteristics of FTIR monitor have been well documented in some papers and textbooks[1-5]. Viewing from measuring toxic gases in the industrial parks, the advantages of applying FTIRs include its non-selective multi-component's measurement, in-situ and real time data treatment and non-sampling long term monitoring. These characteristics make this method possible to search out most of the companies-related VOCs in the air as long as the existing concentration higher than the instrument detection limit (in the order of ppbv). Nevertheless, final qualitative and quantitative data give us only the atlas of air quality in the vicinity of plant but nothing to do with the releasing condition of process within the plant. One of the methods that can be used to estimate the total compounds' fugitive rate is the auxiliary of some dispersion models with the analysis data. According to the preliminary draft of operating the FTIRs by U.S. EPA[6], one of the recommendation methods to estimate the releasing rate is the PAL model[7] method. The demonstration and example of application also refer to the ref. 7. Margaret R. Leo et al.[8] in their paper of estimating VOCs emission rates from Superfund Sites gave a more detailed method of calculating the emission rate, and in another presentation [9], the authors further showed some of the real application results.

The using of the related model to estimate the emission rates in the field application involves the consideration of some topographic limitations that will not be found in the ideal case. Moreover, the dramatic variation of atmospheric instability can also influence the accuracy of estimation. In this paper, the measurement results of using OP-FTIRs are presented and a more pragmatic method for estimating the plant emission rate by using PAL model is also described.

2. Experimental

2.1 Apparatus

Hardware employed for this study is a ETG open-path FTIR system, consisting of a FTIR unit, a corner-cube based retroreflector and IBM compatible 486 PC. The Casagrain telescope attaches to the front of the FTIR sensor, and a standard mid-band MCT detector is supplied with a liquid Nitrogen cooler. A port for filling the detector with liquid Nitrogen is positioned on the top of the sensor enclosure. The retroreflector composes a panel of gold-coated precision corner cube mounted in a

protective housing and hold by the smaller tripod placed at the end of the measurement path facing the telescope.

A total of 64 interferograms were co-added for each spectrum. The single beam interferograms consisted of 32,768 data points over the range of 400 to 4500 cm^{-1} . This interferometer generates a maximum spectral resolution of 1 cm^{-1} . The software is the Galactic Corporation Lab Calc package, with enhancements provided by ETG. Reference spectra was provided by both laboratory calibrated 0.5 cm^{-1} resolution spectra[1] and commercial ETG through Infrared Analyses, Inc spectra. The difference of resolution between laboratory calibrated spectra and ambient 1 cm^{-1} spectra are equalized by smoothing the 0.5 cm^{-1} spectra. The accuracy of reference spectra are evaluated by comparing the integrated band strength with the other report data[10].

2.2 Instrument Set-up

The open-path configurations used for data collection consisted of round-trip pathlengths of 160 to 800 meters. The decision of locations depends on the local prevailing wind direction and topography. The distribution of plants is another consideration factor for determination the measurement site. About two hours must be spent to transfer and set up the instrument from one place to another. Once the instrument is ready, auto-sampling mode is set and retrieves data at every half an hour period to obtain the time series plots of gases' concentration. Filling the liquid Nitrogen of MCT cooler should be done every six to eight hours. A 2000 watts gasoline engine power generator (from Suzuki Inc., Japan) is equipped to generate electric power for instrument operation if no other power supply is available. This power generator can last more than sixteen hours while the gasoline tank is full up.

2.3 Meteorological Data

During the measurement, the related meteorological data are from a movable meteorological station that is equiped in the roof of the van and another local meteorological station in the industrial park is also provided data for comparison purpose. The movable meteorological station on the van offer a more reliable data due to its closer to the FTIR sensor. Both of the meteorological stations are used to record data on a 5-minute time base. These data include ambient air temperature, relative humidity, barometric pressure, wind speed, wind direction, and solar radiation.

2.4 Tracer Release System

The SF₆ gas that is chosen for the instability decision owns its characteristics of inherent inert and non-toxic. One percent in nitrogen SF₆ is released and controlled by a mass flow controller with a constant rate of 5.6 l/min. The tracer releasing point is about 120 cm away from the ground and upwind of the FTIR measurement path.

3. Result and Discussion

3.1 Receptor Compounds Analysis

Petrochemical plants are the main manufacturers of polymer in Taiwan, and the plants are put together in the industrial parks. In order to control the air quality of the parks, a movable OP-FTIR was carried to a site at one of these industrial parks. Measurement activities at the industrial park were finished from march 9 to march 20 of 1995. The results put forward the measurement of air quality in four sites within the industrial park. Table 1 is the time and number of data measurements. Site A, B, C and D are the instrument set-up places as shown in Fig. 1.

Table 1. Measurement positions, time and file recorded information. Data were obtained in some petrochemical industrial parks of Taiwan from 03/9/95 to 03/20/95.

Sites	Date (Time)	File
A*	03/09/95 22:35-	CPC00001-
	03/11/95 10:21	CPC00087
B*	03/13/95 14:13-	TSRC0001-
	03/14/95 14:45	TSRC0053
C*	03/17/95 20:41-	DCC00001-
	03/18/95 19:20	DCC00047
D*	03/18/95 23:28-	USF00001-
	03/20/95 02:27	USF00067

* Relative positions are shown in Fig. 1.

These positions locate in the fenceline of plants. The arrangement distance between FTIR beam-path and plant is longer than 50 meters. To summarize all of the measurement tasks that had been done in this industrial park, the significant existing compounds in the ambient air that can be detected by FTIR sensor include Acrylonitrile, Hydrogen Cyanide, Vinyl Acetate, Cyclo-Hexane, Carbon Monoxide, Ethylene, Propylene, Ammonia, Methanol, Diethyl Ether, Acetic Acid, Methyl Acetate, n-Hexane, 1,3 Butadiene, Benzene, Methane, Ethylene Oxide, Styrene and F-12. The procedure of plant-related source decision will not be detailed in this

paper. The related paper can refer to reference 2.

Major pollutants in Fig. 1, Site A, are Cyclo-Hexane, Methanol and Vinyl Acetate. Major toxic compounds in Site B are Benzene, 1,3 Butadiene, Styrene, Cyclo-Hexane, n-Hexane and Ethylene Oxide. Acetic Acid and Vinyl Acetate are existing in Site C. Major pollutants in site D include Acrylonitrile, Acetic Acid, Methyl Acetate, Styrene, n-Hexane and Butadiene. The above-mentioned pollutants come from Acrylonitrile monomer and Methanol plants, EG and EO plants, SM monomer plant, Acetic Acid plant and a rubber plant.

3.2 Procedures to Estimate Emission Rate

According to the suggestion of FTIR preliminary draft in reference 6, both the ratio and the dispersion model technique can be used to determine target compound emission rates from the receptor. Ratio technique in most of the application (under the permission condition) is superior to the model prediction technique [11]. However, some limitations restrict or lower the feasibility of tracer ratio method. In view of the area source emission (the case of study in this paper), ratio technique needs also auxiliary model to estimate the emission rate. Under the assumption of homogeneous source distribution, the emission rate of area source can be estimated by a series of procedures. Suggested procedures given by reference 6 and 8 are as follows:

Step 1. Make ground-level measurements upwind and downwind of the source to identify source attribution.
 Step2. Use an appropriate area source dispersion model to predict point concentrations along the measurement path based on relative emission rates and on actual meteorology and source configuration.
 Step3. Use an appropriate numerical technique to integrate the function defined by the point concentration values predicted along the crosswind measurement path.
 Step4. Scale the modeling results using the measured path-integrated source attribution to estimate the area emission rate.

The method that is used to estimate the area source emission rate in our laboratory is basically in accordance with the procedures described above. Some modifications, however, are needed before actual application. The modification procedure is described as follows:

Step 1. Arrange the FTIR sensor upwind and downwind along the prevailing wind direction according to the location and configuration of the plants. Under the circumstance of one prevailing wind direction (the case of Fig. 1), the attribution of source can be identified.

Step2. Use the Turner's equation (based on Gaussian dispersion theory) and the known downwind SF₆

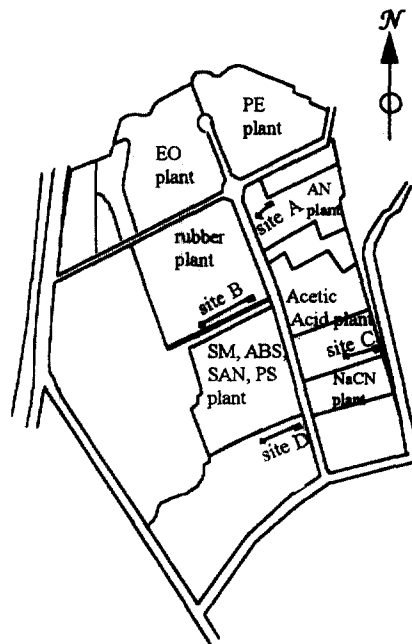


Fig. 1 The atlas of some industrial park in Taiwan. The related positions of site A-D are also shown in the figure.

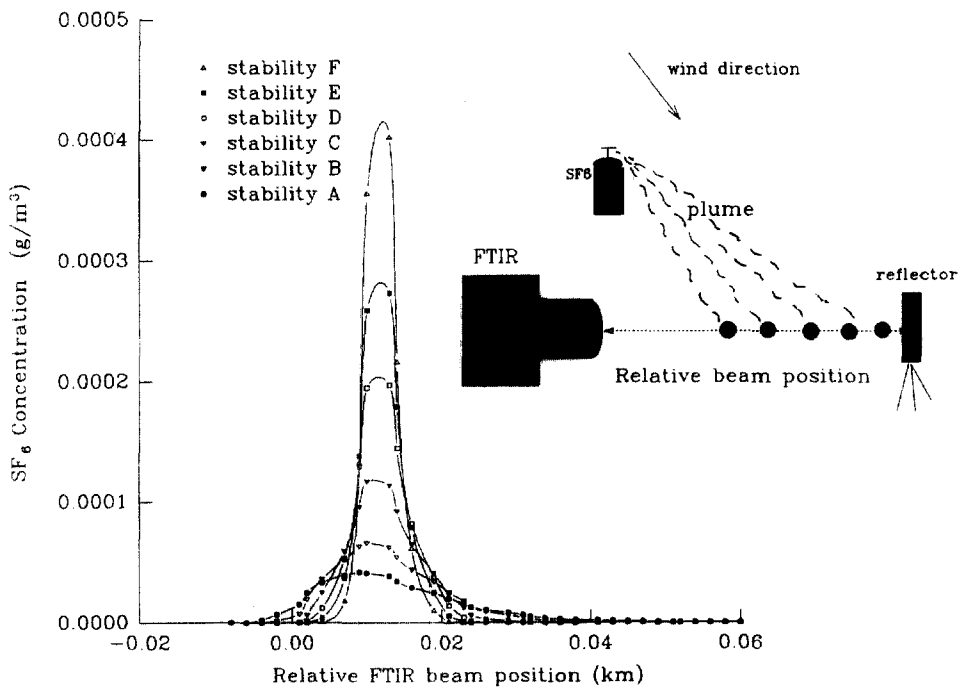


Fig. 2 The prediction SF6 concentration along the FTIR beam path

concentration along with the known concentration and emission rate of SF₆ itself, the P-G atmospheric stability can be determined in the vicinity of plant. The relationship between standard deviation σ_z and stability is determined by Pasquill-Gifford curve. If the downwind distance is shorter than 100 meters, the values of σ_z should be derived from ISC model (see ref. 6). The FTIR beam in the downwind is supposed to capture the plume entirely in the crosswind direction. Generally speaking, the day time stability varies from A to D and the night time stability varies from D to F [6,12]. If the experimental results show that the measurement values are not exactly equal to the values of stability A-F, then, the closest stability value should be selected. The target value of the measurement can be derived by multiplying the result derived from the selected value with the percentage of the difference.

Step3. Use PAL (ref.7) area source dispersion model to predict area source concentrations which are along the measurement path. The concentration are derived based on relative emission rates, source configuration and σ_y , σ_z values that are determined from known stability in step2. If FTIR beam is not exactly vertical to the wind direction, the downwind points concentration should be derived by calculating every points concentration along FTIR beam path with a spacing of less than 2 meters. Downwind points concentrations are calculated by using different σ_y and σ_z values in the PAL model.

Step4. Calculate the prediction path-integrated values (concentration \times path length) by multiplying the downwind points concentration with spacing values (2 meters, in our case).

Step5. Scale the modeling results by using the measured path-integrated source attribution to estimate the area emission rate.

3.3 Measurement results and emission rate estimate

Stability determination

The release of SF₆ tracer must, theoretically, coincide with the FTIR data collection. However, in view of the fact that FTIR is a continuous monitor with half an hour period data collection rate, it's difficult to demand a continuous SF₆ releasing. Nevertheless, For the purpose of precision, the times of release of SF₆ should be as many as possible.

During the measurement (Table. 1), eight SF₆ releasing tasks were done at different places and time. Table. 2 summarizes the relative time and places of SF₆ releasing activity. The concentration of SF₆ is one percent. Use a MFC (mass flow controller) to keep a constant release

rate of 5.6 l/min. FTIR beam path is longer than 150m. Quantitative reference SF₆ spectrum used here is a laboratory calibrated spectrum with its integrated band strength of 4439 atm⁻¹cm⁻² within 920cm⁻¹ and 960cm⁻¹. This band strength value is compared with the commercial SF₆ spectrum provided by Infrared Analysis Inc.. The band strength value has a band strength of 4413atm⁻¹cm⁻². The difference of these two values is smaller than 1%.

Table 2. SF₆ releasing positions, time and file name.

Sites	Date (Time)	File name
A*	03/11/95 10:07	CPC00086
C*	03/13/95 07:46	TSRC0015
	03/14/95 09:05	TSRC0042
D*	03/18/95 00:24	DCC00028
	03/18/95 07:36	DCC00049
E*	03/19/96 00:50	USF00005
	03/19/95 10:20	USF00023
	03/20/95 02:08	USF00066

* Relative positions are shown in Fig. 1.

Fig. 2 is one of the results that is measured in site B. Fig. 2 shows a model prediction SF₆ concentration (ordinate axes/g m⁻³) along with the FTIR beam path (abscissa axes/km) with a spacing of 2 meters. Each curve of Fig. 2 represents a stability condition. The area under the curve is equal to half the path-integrated values of FTIR measurement. Closest two curves in Fig. 2 will have a different percentage area value of smaller than 20% ((stability1-stability2)/stability1). On the other hand, error stability decision will result in a 20% error of each stability of emission rate estimate. The result of stability determination is summarized in Table 3.

Overall results of stability decision follow the criteria of step 2 and ref. 12, except for the results of site D. Most of the stability decisions are between C to E. The stability of site D is close to an *unstable* condition even in the night time. The reason is probably from the irregular variation of wind direction during measurement in site D.

Emission rate analysis

One of the demonstration results is shown in Fig.3. Fig.3 shows a series of VOCs quantitative results in site B. Site B is near a rubber plant that manufacture the raw material of rubber. The main materials which are used in this company include n-Hexane, Cyclo-Hexane, Benzene, Butadiene. Ethylene Oxide in Fig.3 infers from an EO plant in the north of site B. Before a further estimate of the emission rate of the compounds is made, here we do a

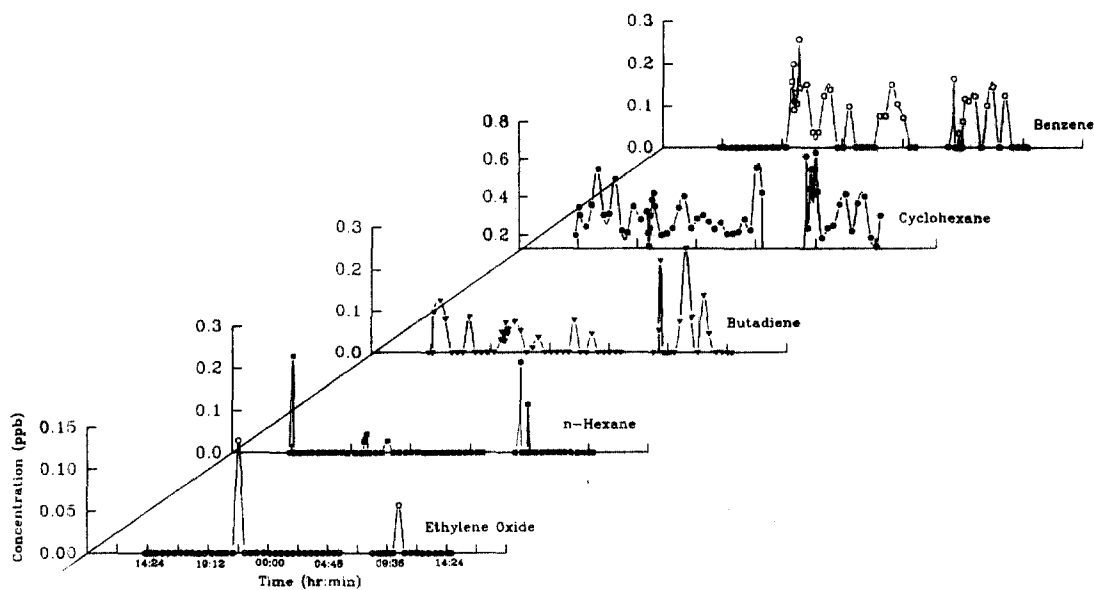


Fig. 3 The concentration vs. time for fugitive emission pollutants that are measured by OP-FTIR in site B. The compounds listed here include Butadiene, Benzene, Cyclohexane, n-Hexane and Ethylene Oxide.

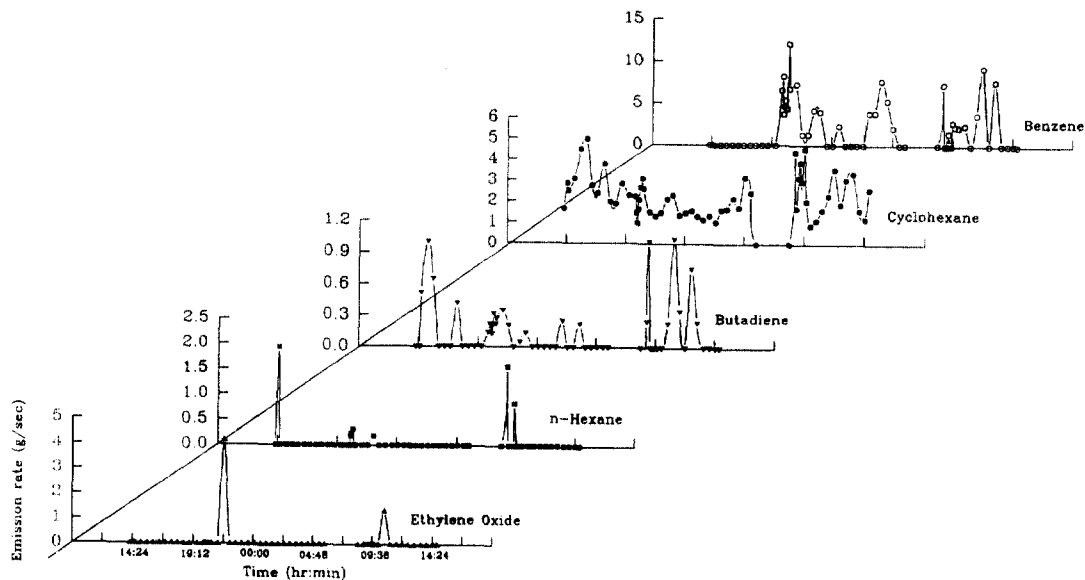


Fig. 4 The emission rate vs. time for fugitive emission pollutants. Butadiene, Benzene, Cyclohexane and n-Hexane release from the rubber plant emission. Ethylene Oxide are inferred to come from an EO plant.

Table. 3 SF₆ tracer predict stability value (A-F), and FTIR sensor measurement values in different site.

	Site A	Site B1	Site B2	SiteC1	SiteC2	Site D1	SiteD2	SiteD3
Stability A	0.0368	0.1442	0.1173	0.1217	0.0847	0.3252	0.4302	0.3987
Stability B	0.0466	0.1762	0.1439	0.1694	0.1177	0.4298	0.5792	0.5368
Stability C	0.0626	0.2232	0.1812	0.2504	0.1806	0.5664	0.8288	0.7682
Stability D	0.0888	0.2926	0.2348	0.3670	0.2934	0.7217	1.1167	1.0348
Stability E	0.1078	0.3359	0.2678	0.4398	0.3830	0.8089	1.2814	1.1870
Stability F	0.1402	0.4016	0.3172	0.5506	0.5262	0.9334	1.4467	1.3395
Measurement Values	0.0653	0.3178	0.2270	0.3240	0.3600	0.5386	0.6033	0.5297
Closest stability	C	D	D	D	E	C	B	B

hypothesis that day time stability in site B is D and night time stability in site B is E. This assumption is based on the results of Table. 3. but it is likely that the assumption may cause an over 40% error. It is necessary to emphasize again that the tracer stability decision must be as close to the FTIR data collection as possible. Fig.4 shows the results of emission rate estimate. Ordinate axis is the estimate emission rate (g/sec), and Abscissa axis is the measurement time series (hours:minutes). During the estimate, the exact scale of relative positions in map should be known. In our case, the distance between source area and sensor is calculated from a photo that was taken from aircraft. Wind direction and wind speed are supplied by a movable meteorological station near the FTIR sensor. From Fig.4, the results of emission rate estimate show that Cyclonexane has a year maximum emission of 150 tons per year. Benzene has an annual emission of 52 tons and butadiene has a maximum annual emission of 31 tons. n-Hexane and Ethylene Oxide have maximum emission rate of 1.8 g/sec and 4 g/sec, respectively. Care must be taken when deriving the amount of annual emission. In the case of the rubber plant, the measurement concentration of some compounds (e.g. Benzene, Butadiene, Cyclohexane etc.) under one wind direction is nearly constant. It means that the emission from the related source may be a continuous source, and this is why we can use the emission rate to calculate the annual emission amount. Contrast to these compounds, the emission of n-Hexane and Ethylene Oxide from rubber and EO plant is instantaneous. It is proper to report the data in the form of emission rate rather than in annual amount.

The emission rate of the other compounds that were detected in other places will not be detailed in this paper.

4. Conclusions

This paper demonstrates that a proper dispersion model is used to estimate the emission rate of fugitive toxic compounds in the petrochemical industrial park. The precision of estimate depends mainly on the decision of atmospheric stability and on the configuration of source attribution. Under the continuous measurement mode, this approach offers a more flexible and integrated consideration of fugitive gases monitoring. Further comparison of this technique with the other methods will be done to get the more precise results.

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