American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/aiha20

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To cite this article: Hongkui Xiao , Steven P. Levine , Julie Nowak , Mark Puskar & Robert C. Spear (1993) ANALYSIS OF ORGANIC VAPORS IN THE WORKPLACE BY REMOTE SENSING FOURIER TRANSFORM INFRARED SPECTROSCOPY, American Industrial Hygiene Association Journal, 54:9, 545-556, DOI: 10.1080/15298669391355026

To link to this article: https://doi.org/10.1080/15298669391355026

AM. IND. HYG. ASSOC. J. 54(9):545–556 (1993)

ANALYSIS OF ORGANIC VAPORS IN THE WORKPLACE BY REMOTE SENSING FOURIER TRANSFORM INFRARED SPECTROSCOPY

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A Remote Sensing-Fourier Transform Infrared (RS-FTIR) system was applied to identify and quantify air contaminants along the beam, ranging from single compounds to mixtures, in various workplaces. Gas chromatography (GC) was used to provide information of point concentration variation by means of analyzing charcoal tube samples placed along the beam path. The results indicated a correlation between the charcoal tube-GC and the RS-FTIR for the analysis of most compounds. Discrepancies were found for some compounds, such as acetone, due to inhomogeneous concentration distributions along the IR beam, and due to the overlap of the acetone signal with off-scale water peaks. The study also demonstrated that there was little effect on quantitative analysis from partial or complete IR beam blockages during measurement. Qualitative analysis of unexpected compounds using RS-FTIR was also evaluated. In addition, the ability of the RS-FTIR to detect a sudden release of chemicals was demonstrated in the study.

Emissions of organic vapors are, for both the environment and the workplace, concerns for safety and regulatory reasons. Many routine monitoring methods have the sensitivity necessary to monitor toxic gases and vapors at or below their threshold limit values (TLV®).(1) However, most methods require isolation of air samples or concentration of air contaminants before the contaminant can be identified and quantified. The whole measurement process involving sampling, shipment, and analysis in the lab could lead to sample loss through a variety of mechanisms, significant delays in obtaining results, and sometimes substantial costs.

An ideal air-monitoring method would provide accurate real-time qualitative and quantitative analyses of exposure conditions to enable evaluation of the effectiveness of control methods and assess the potential for human health effects. In addition, this ideal method would be capable of measuring both long-term Time Weighted Average (TWA) exposures, short-time exposures associated with Short-Term Exposure Limits (STELs), and Ceiling limits (C). These long- and short-term exposure standards are defined by the American Conference of Governmental Industrial Hygienists (ACGIH).(1) However, few monitoring methods exist to meet all these criteria.

In the past decade, many real-time or near-real-time instruments have been developed for personal monitoring, for conducting surveys in the workplace, as well as for continuous fixed-station monitoring in the workplace, on plant fencelines, and in the community. In some cases, real-time instruments are the best available method for monitoring an air contaminant. However, a continuing problem is that many real-time methods lack specificity and sufficiently low detection limits, and, in addition, most will fail to yield quantitative results when complex mixtures of similar compounds are encountered.

Since the early '80s, remote sensing techniques have been applied to environmental air monitoring.(2–11) Remote sensing is generally defined as the ability to detect an object or phenomenon without the detector being in direct contact with the object or phenomenon of interest. Among these techniques, Remote Sensing-Fourier Transform Infrared

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(RS-FTIR) spectroscopy is rapidly becoming a technique of choice for analyzing gases and vapors.(12) This is because FTIR has the potential for real-time monitoring and capabilities for both qualitative and quantitative analyses.(13–18)

Furthermore, unlike traditional air-monitoring methods, RS-FTIR is an open-path measurement tool. RS-FTIR provides information representative of the environment along the beam path and integrated over time. The result is a beam-path-average concentration, usually in ppm-meter, rather than a point concentration. The advantages of the remote-sensing approach are that sampling lines, pumps, manifolds, and cells are not needed, with resultant increases possible in recovery of labile and polar analytes. The sensitivity of the instrument theoretically can be increased in proportion to the pathlength of the beam when long path measurement is applied. However, in practice, sensitivity can only be increased with increasing pathlength if a homogenous environment is being sampled, and when the absorbance signal of the compound being measured is not obscured by the absorbance of atmospheric water vapor. Finally, since RS-FTIR collects data in seconds, it can continuously generate real-time data representing an averaging time from a few seconds to a few minutes, and/or to hours: C, STEL, and TWA, respectively.

The major disadvantages of RS-FTIR are: (1) interpretation of the beam-path-average concentration, and (2) beam blockage. Since current exposure standards, such as 8-hour TWA, STEL, and C, are based on personal or point monitoring, more caution is needed to use the beam-path information to assess workers' exposure. Moreover, selection of an appropriate instrument (IR beam) orientation in the workplace becomes an important issue. In this study, these disadvantages were investigated.

Because of the unique advantages of RS-FTIR over traditional air-monitoring methods, many studies have been conducted to apply this novel technique for environmental monitoring.(5,18–20) This study focused on the application of a RS-FTIR in three workplace settings for the analysis of organic vapor mixtures.

EXPERIMENTAL METHODS AND WORK SITE CONSIDERATIONS

RS-FTIR Instrument

The RS-FTIR built by Nicolet Instrument Corp. (Madison, Wis.) consisted of three modules: (1) an IR source and an interferometer, (2) a receiving telescope and a liquid nitrogen cooled Hg-Cd-Te (MCT) detector, and (3) a Dell 310 80386/387 20 MHz personal computer. In this study, a cylinder was used to purge dry nitrogen onto the window of the detector to eliminate condensation. The highest resolution achievable by the interferometer was 2 wavenumber (cm^{-1}). The sampling rate of the RS-FTIR is a function of scans per sample and spectral resolution. At 2 cm^{-1} resolution and 128 co-added scans per sample, the sampling rate was 1 sample/min. The sampling rate varied from 3 samples/min to 1 sample/10 min with different time resolutions of measurements and different total sampling times in this study.

Mirrors were used to direct the IR beam around the workplace. The mirrors are 1.0 ft^2, first-surface, aluminum-coated mirrors. There is no upper limit to the number of mirrors that can be used as long as sufficient signal emitted from the IR source is received by the detector to provide a signal/noise ratio high enough for the specified monitoring task. The instrument was designed for use with pathlength up to 40 m due to the IR beam divergence. Details about this instrument were fully described elsewhere.(21)

RS-FTIR Operations

The RS-FTIR system modules were loaded onto one small laboratory cart for transportation between the on-site laboratory and the workplace testing sites. All interferograms collected from the RS-FTIR were at 2 cm^{-1} resolution.

Background spectra were collected from a contaminant-free chamber where the IR beam pathlength, relative humidity, and temperature were constant. IR spectra were obtained by performing Fourier transforms of the interferograms. Standard reference spectra were obtained with a 10 m gas cell using gas standards of 50 ppm concentration (Scott Specialty Gas Co., Troy, Mich.).

Classic least square (CLS)(22) and iterative least square fit (ILSF)(23) programs were applied to perform quantitative and qualitative analyses of spectra, respectively. The CLS method matches a sample spectrum against reference spectra by utilizing all points within chosen analytical IR regions to give the best estimated concentration for each compound. Qualitative analysis is achieved by the ILSF program, which identifies compounds presented in the spectrum based on the confidence interval of each compound's concentration obtained from least square fit analysis.

Area Sampling and Analytical Methods

Work-area point sampling was accomplished by setting up the RS-FTIR in a manner where the beam intersected the employee's working area, while concurrently charcoal tubes were collected at a minimum of seven locations along or near the beam path. The sampling points encompassed all important work areas, in order to reflect closely workers' average exposures. The "point-average" concentration along the beam path was calculated from the values obtained from charcoal tubes for information of spatial concentration variation along the beam path during the same sampling period.

Charcoal tubes were placed approximately 3 m apart. The sampling rate for the charcoal tubes was 0.1 L/min. The sampling time varied from 15 min to 4 hours depending on the process monitored.

All charcoal tube (SKC, Cat. #226-09 Eighty Four, Penn.) samples were desorbed in carbon disulfide (CS_2) and were analyzed by gas chromatography (Hewlett Packard 5890 series II) with flame ionization detector. Separation of the compounds was performed using a 100 m (0.2 mm × 0.2

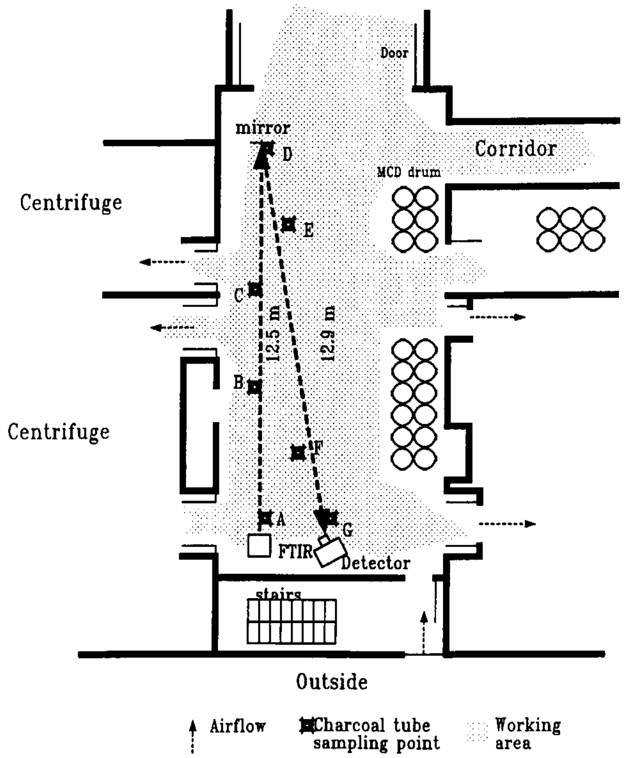

FIGURE 1. RS-FTIR beam configuration and charcoal tube placement at Site I

μm) DONA column. Initial oven temperature was set to 60 °C. This temperature was held for 25 min and was then ramped at 5 °C/min. to a final temperature of 200 °C, which was held for 12 min. The split/splitless injector and detector temperature were set to 205 °C. A split ratio of 8:1 was set with a 2 μL injection.

Unit Operations

The measurements of air contaminants by both the RS-FTIR and the charcoal tube-GC method were performed at three chemical production sites. At Site I, a pharmaceutical was separated from its solvent, methylene chloride (MCD), inside a centrifuge. Then, the MCD was transferred into the storage tanks and drums, and transferred to other facilities (Figure 1). The unit operation at Site II involved the separation of another pharmaceutical from its solvents using a filter press. Several solvents were used in storage tanks and reaction vessels located nearby (Figure 2). More chemicals were used in the process at Site III than those at Sites I and II. The third site was inside a production facility where a bulk pharmaceutical is manufactured (Figure 3). At Site III, the chemicals used included heptane, tetrahydrofuran, methyl bromide, and methylene chloride.

The samples collected using tubes were analyzed by GC for 14 organic compounds suspected to be present in the plant. The same set of compounds was also measured by RS-FTIR.

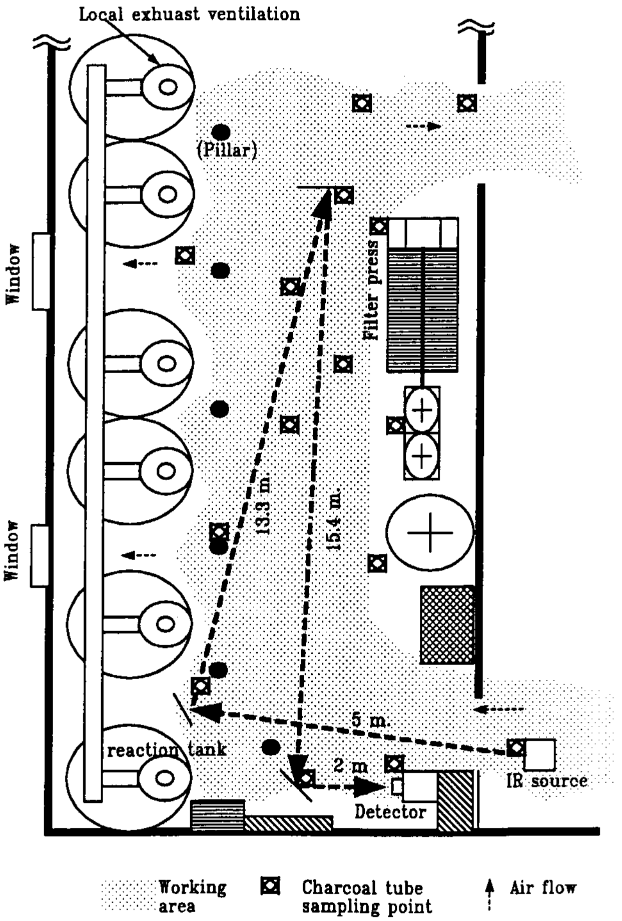

FIGURE 2. RS-FTIR beam configuration and charcoal tube placement at Site II

Analytical Considerations

Theory

The principle of measurement of chemical concentration by RS-FTIR is based on the Bouguer-Beer-Lambert law, which is defined as follows:

$$A(v) = a(v)LC \tag{1}$$

Here, $A(\nu)$ is absorbance of a specific chemical at a wavelength of ν, $a(\nu)$ is the absorptivity of the chemical at the same wavelength of ν. L is the beam pathlength, and C is concentration of this chemical. Since the RS-FTIR is an open-path measurement and gives both temporal and spatial integration measurements, the concentration (C) is a function of both time and path during the measurement. Therefore, a path average and time-weighted concentration is obtained through the measurement of the RS-FTIR. The TWA concentration (C) can be expressed as

$$C = \frac{1}{T}\int_{O}^{T}\left[\frac{1}{L}\int_{O}^{L} c(\ell,t)\,d\ell\right]dt \tag{2}$$

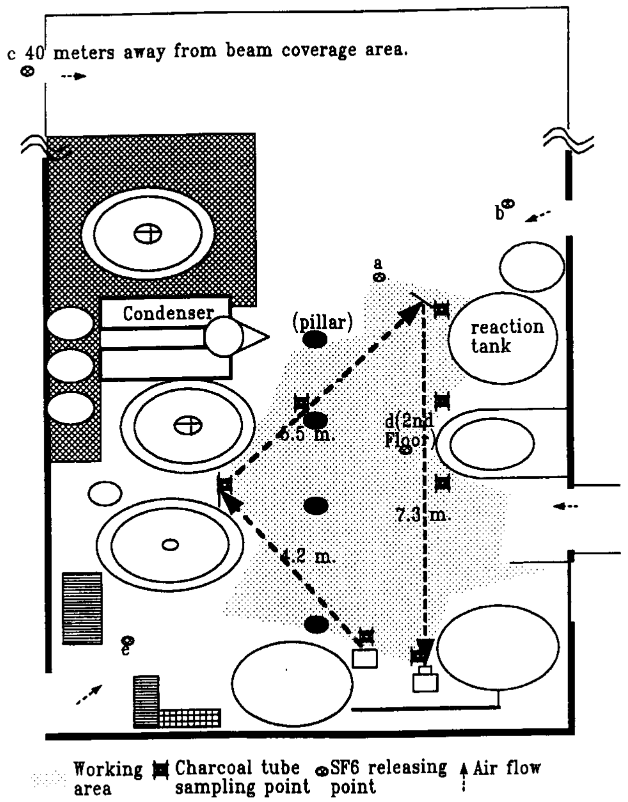

FIGURE 3. RS-FTIR beam configuration and charcoal tube placement at Site III

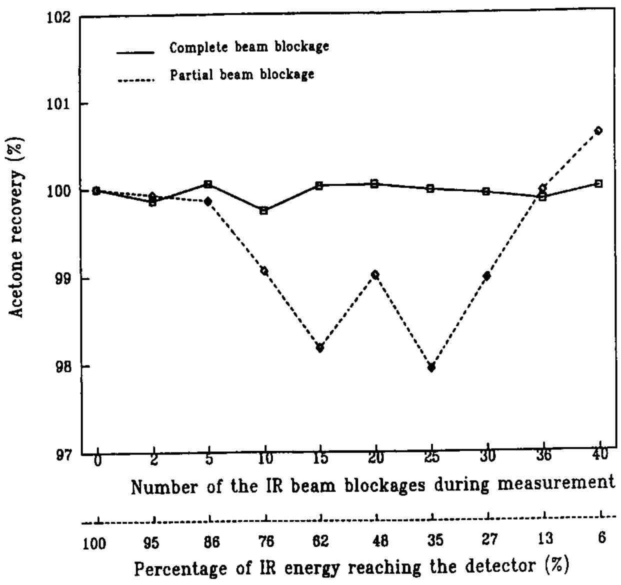

FIGURE 4. Effect of blocking the IR beam on quantitative analysis results

The measurement of the RS-FTIR results in a time-weighted and path-weighted average concentration. The unit of concentration is ppm at given time period (T) and pathlength (L). It offers only an average concentration along the beam path rather than a concentration at a specific point, unlike traditional air-monitoring methods. For example, if the concentration measured by RS-FTIR is 5 ppm at a given 20-m pathlength, it is not possible to recover information on the spatial distribution of contaminant along the path.

Beam Blockage

Even though careful consideration was given to workers' motion in the beam path for each sampling site, beam blockage during measurement occurred quite often due to traffic of worker or equipment. As a result, the beam blockage was partial or complete. When the beam was totally blocked during a scan, no modulated signal was received by the detector, and the instrument automatically reverted to the "standby" condition until the modulated signal was once again received by the detector. When partial beam blockage occurred, less IR energy was received by the detector, but the scan was included in the sample's co-added scans.

To test what effect blocking the beam would have on the quality of data produced, 125 ppm of acetone vapor in a 10-cm gas cell was introduced into the beam. The beam was then periodically blocked during the 128-scan measurement. Since the instrument resumed data acquisition after the object was removed from the beam, there was no effect on the IR absorption features of the species in the spectra. The quantitative results are shown in Figure 4. Recovery of the acetone concentration measured by the RS-FTIR was 100% without beam blockage, and ranged from 99.7% to 100.1% for measurements with different numbers of scans blocked. No measurement took place if the beam was completely blocked when the instrument was in the process of initiating a scan.

The effect on quantitative accuracy was also investigated for the case of partial blockage of the IR beam. A 10-cm long gas cell filled with 125-ppm acetone was introduced into the beam. It was assumed that the IR energy reaching the detector was 100% when the instrument was fully aligned with the empty cell. Partial blockage of the beam was achieved by intentionally blocking the IR source. The varying percentage of IR energy reaching the detector was recorded from the intensity of the centerburst of the interferogram.

Figure 4 shows that beam blockage, similar to that of workers or equipment partially blocking the beam, resulting in varying the beam energy from 100% to 6%. The value of the acetone measurement varied from 100.6% to 97.9% of the true value over the range of beam energy reaching the detector. Although the variation of the recovery for partial blockage is larger than those for complete blockage, it is considered to be insignificant compared to the variation of field measurements. These results suggest that partial blockage of the beam will not effect the quantitative results.

Work Site Configurations

The IR beam was set to a height of five feet above floor level in order to intercept the breathing zone of workers whose work station or work path would lie along the beam path. The IR beam covered a selected area of the workplace, providing an estimation of the average concentration of contaminants where workers have jobs that are either fairly sedentary, or which are characterized by mobility primarily along the beam path.

The exact placement of the RS-FTIR system modules was determined primarily by the traffic patterns of workers and vehicles, to minimize interference with operations, and to reduce the frequency of beam blockage. Consideration was also given to the location of contaminant sources based on the processes, and to the airflow patterns observed with smoke tubes.

In order to determine the spatial variation of concentration in the beam, the placement of these charcoal tubes in the beam was of great importance. Once the beam configuration and charcoal tube location were decided, it usually took 20 to 30 min to set up the instrument before collection of data could begin. The longer the pathlength was and the more mirrors used, the more time was needed to setup and align the instrument.

Several important factors were considered in setting up the remote sensing instrument in the workplace: (1) the releasing source of target compound(s) was identified prior to measurement; (2) the beam configuration coverage was sufficient to estimate the exposure of the workers at each work station; and (3) the instrument did not interfere with normal working operations.

Work Site I. The measurement of methylene chloride took place in an air-conditioned corridor. The worksite health and safety program is designed to minimize methylene chloride exposures. However, under normal operation conditions, some methylene chloride will be emitted from storage drums in the hallway and from adjoined centrifuge rooms. The activity in the corridor was related to transportation of the storage drums.

The RS-FTIR beam was placed in a simple, straight-line configuration. Both the IR source and the detector were placed at one end of the hallway, and a mirror was used to reflect the IR beam emitted from the IR source back to the detector (Figure 1). Temperature and relative humidity in the hallway averaged 23.6 °C (74.5 °F) and 68% respectively. Seven charcoal tubes, as shown in Figure 1, were used to collect samples at fixed locations along the beam path.

Work Site II. The second testing site was located on the third floor of a filter press facility. Temperature and relative humidity in the building ranged from 23.9 to 28.9 °C (75 to 84 °F) and 50 to 84%, respectively. Building vibrations were felt when machines were running on the first floor. In this study, the effect of the vibration on results was not evaluated.

Monitored compounds were amyl acetate and ethyl acetate. These were released during the processes of charging reaction tanks and the operation of the filter press. Figure 2 shows one of the IR beam configurations used at Site II for measurement of amyl acetate. The available space for operation of the RS-FTIR was limited, due to workers' activities, such as checking the filter and reaction tanks, and charging chemicals into the tanks. The IR source was put at the outside door in the hallway, and the detector was inside the room. Three mirrors were used at different points in the working area to direct beam coverage. The factors of physical layout of equipment in the workplace, the working path of workers, and the instrument operation were primary determinants of the IR beam configuration.

Work Site III. The third testing site (Figure 3) was located on the first floor of a building. The testing environment of Site III was much more severe than the previous two sites with temperature and relative humidity at 22 °C–30 °C (72 °F–86 °F) and 72%–88%. In addition, water-wash hoses were operated on a frequent basis, resulting in wet floors and aerosolized water.

Operational activities at Site III were to monitor the temperature and the pressure of reaction tanks, and to transfer chemicals into or out of the tanks. The charging of chemicals took place on the second floor; however, some chemicals were transferred on the first floor under the bottoms of the tanks. The RS-FTIR modules were put at one end of the workplace and two mirrors were placed at the middle of the workplace to direct the beam coverage. The experiment was initially designed primarily to monitor methyl bromide. Other chemicals were also used during the process. In addition to the measurement of methyl bromide and other target compounds, SF6 was released at different locations in the building to check ventilation and plume patterns in this working environment.

Effect of water vapor. The major interference for methods using infrared spectroscopy, and for RS-FTIR methods in particular, comes from the absorption features of water vapor in the mid-IR region. The strong absorption of water vapor in IR spectra of ambient air can lead to errors in qualitative and quantitative analytical results due to the overlap of peaks of target air contaminants with the water-vapor peaks. The potential for error increases with increasing beam pathlength, especially if the concentrations of target compounds are very low.

In addition, very high humidity affects the operation of the detector. The dew point at the window surface of the MCT detector was easily reached in high-humidity environments, since the detector was cooled by liquid nitrogen, even though the detector window was insulated by a Dewar flask. This resulted in the condensation of water vapor on the detector window surface, with a resultant decrease in IR energy received due to beam blockage, scattering, and absorption. To eliminate this problem, a small tube was installed to purge dry nitrogen from a cylinder onto the detector window to prevent the condensation of moisture during the field measurements at Sites II and III.

Determination of Minimum Detectable Concentration

Table I lists all the compounds quantitatively analyzed using the RS-FTIR during this study. All RS-FTIR quantitative analyses were accomplished by applying a least square fit program. A specific analytical region for each compound

TABLE I. Minimum Detectable Concentration of Compounds Analyzed by the RS-FTIR

Compound	*Analytical region (cm^{-1})*	*MDC*[A] *(ppm-m)*	*TWA*[B] *(ppm)*	*STEL*[C] *(ppm)*
Acetone	1170–1260	0.69	750	1000
Ammonia	780–1200	0.60	[D]	35
Amyl Acetate	1150–1320	0.12	125	[D]
Ethanol	980–1150	0.09	1000	[D]
Ethyl Acetate	1020–1300	0.06	400	[D]
Heptane	2800–3050	5.03	400	500
Isopropanol	2800–3050	0.10	400	500
Methanol	950–1100	3.69	200	250
Methyl Bromide	2900–3150	8.02	5	[D]
Methylene Chloride	720–800	0.57	50, A2[E]	[D]
Methyl Ethyl Ketone	1130–1230	1.01	200	300
Sulfur Hexafluoride	920–958	0.02	1000	[D]
Tetrahydrofuran	2780–3100	0.85	200	250
Toluene	2800–3150	2.56	100	150
Trichloroethylene	870–965	0.55	50	200
o-Xylene	720–770	0.55	100	150

[A] The unit of MDC is ppm-meters normalized to 1 meter pathlength

[B] Time-weighted average concentration

[C] Short term exposure limit

[D] No value assigned

[E] Suspected human carcinogen

was chosen for the quantitation of each compound. The minimum detectable concentration (MDC) is defined as the concentration of analyte that provides a detector response that exceeds the instrument noise level by three standard deviations above the mean of the instrument noise.(24) Since the response of the MCT detector varies with wavenumber, the noise level in different regions is different. The spectral noise levels were calculated for each analytical region chosen for each specific compound. The MDC for each compound is shown in Table I.

It should be noted that the unit of MDC is ppm-meter, normalized to a 1-m pathlength, rather than ppm.(25) Theoretically, the MDC is decreased with increasing the pathlength in a homogenous environment. If the absorption of water in the analytical regions chosen for quantitation does not increase linearly with increasing the pathlength, or if the instrument noise level increases, the decrease in the MDC will not be linear. From Table I, it can be seen that the RS-FTIR method can detect all the target compounds, except methyl bromide, at levels far below current PEL standards.

Each chemical vapor has its unique absorption at different frequencies (expressed in the units of wavenumber). It is relatively easy to analyze qualitatively and quantitatively a single compound spectrum based on the location and intensity of characteristic peaks. However, the reality of field measurements often is that the spectra are dominated by off-scale water absorption peaks. Complex mixtures are also often encountered during field measurements where only one or two compounds are expected. Furthermore, the concentrations of chemicals in the workplace of well-designed, well-maintained plants are usually in the low ppm range, or lower, due to the implementation of good safety and health practices.

These factors make it much more difficult to interpret IR spectra collected in the field than those collected in the laboratory. A professional experienced in spectroscopy, computer-aided interpretation methods, and industrial hygiene practice is needed to interpret such spectra.

The set of compounds analyzed by GC was determined based on a knowledge of the process at each site. Unlike the situation with the RS-FTIR method, the MDC of the charcoal tube-GC method was dependent on air-sampling volume. In this study, sampling times for both the charcoal tube-GC and the RS-FTIR were the same. The MDC of the charcoal tube-GC method was higher for most of the compounds than that of the RS-FTIR, due to small air-sampling volume.

RESULTS AND DISCUSSION

SF$_6$ test

Air-monitoring methods should have the ability to protect workers from unexpected releases of airborne contaminants. Therefore, at Site III, SF$_6$ was released to evaluate the ability of RS-FTIR to detect a sudden release and subsequent ventilation of the building. SF$_6$ was chosen for this test because it is not used or produced in this or nearby facilities, it is nontoxic, it has a unique peak in the IR fingerprint region, and it can be detected at low concentrations.

During a short time (10 sec) at different locations in the site (shown as locations "a"–"e" in Figure 3), 100% buoyant SF$_6$ was released from a compressed gas cylinder . There was no measurement of the amount of SF$_6$ released. The RS-FTIR operation was set to collect individual samples for each release every 20 sec and during the 10 min of each test. The IR beam coverage only occupied a small area of the building.

The concentration/time profile of SF$_6$ measured by the RS-FTIR system is shown in Figure 5. A characteristic concentration/time profile was observed in all tests. Each decay curve was an average of three replicate runs. Results indicated that if SF$_6$ was released near or within the beam coverage area, such as point "a" or "e", SF$_6$ was immediately detected and reached its maximum concentration, around 0.3 ppm, within the first 20 sec time period. As expected, the further away the SF$_6$ release point from the IR beam, the longer time it took for the RS-FTIR to detect SF$_6$, and respond to a maximal concentration. Although point "c" was about 40 m away from the beam coverage area, SF$_6$ was still detected by the RS-FTIR. A decay curve of SF$_6$ concentration at point "c" was observed. However, it is not clearly visible in Figure 4 due to Y-axis scale. The maximum concentration observed was 14 ppb, at 128 sec.

The results illustrate that SF6 released from these locations in the building were quickly carried into the beam coverage area. Although this was not a quantitatively modelled test, these results also indicate that, under the circumstances tested, the beam information can be very useful to detect a sudden release of an air contaminant.

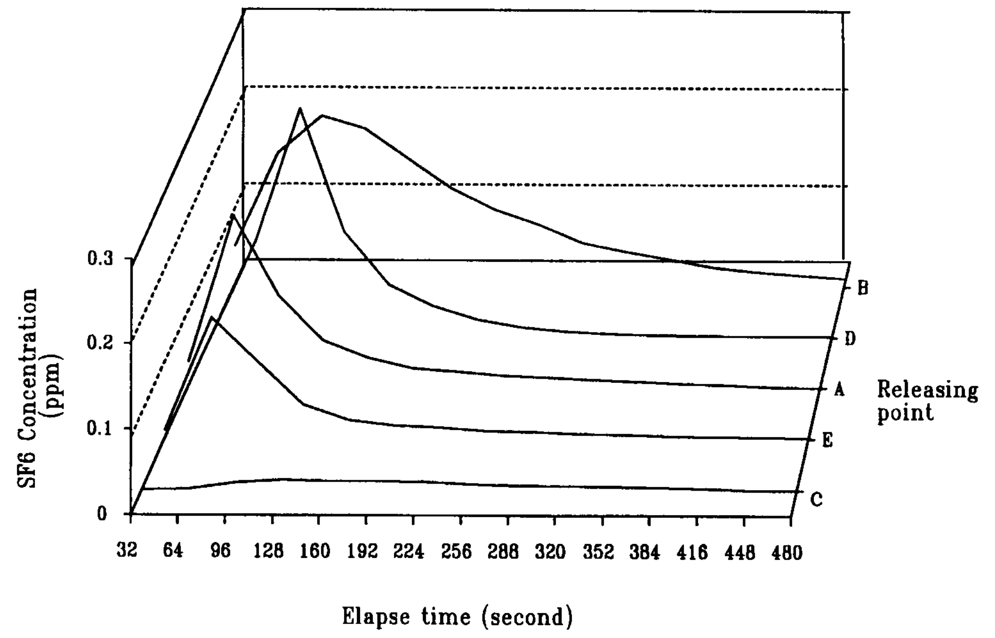

FIGURE 5. Concentration decay curves for sudden releases of SF6 at different locations in Site III

Work Site I

The first step in analyzing an IR spectrum is to determine what compounds are present. False quantitative results are usually obtained when the qualitative information is inadequate, especially when the spectra of mixtures are analyzed. The inventory of all the target and nontarget compounds was provided by Abbott Laboratories and was the basis for a defined reference library of spectra.

A qualitative analysis computer program, ILSF, was used to analyze the spectra collected from the field. The compounds identified by this program were carefully checked by looking at the detailed structure of spectral features, and were compared with results obtained by GC.

The reference compounds for GC analysis of Site I samples included methanol, ethanol, acetone, isopropanol, methylene chloride, ethyl acetate, methyl chloroform, trichloroethylene, and amyl acetate. The GC detected only the presence of MCD during the two days of measurements. The results of the RS-FTIR showed that methanol was present, in addition to MCD.

Seven charcoal tubes placed along the beam path were used to obtain point average concentrations. These are labeled "A"-"G" in Figure 1. GC and IR data are shown in Table II. On the first day, the sampling time for both the tubes and the IR beam was 90 min. On the second day, three 15-min samples were taken at each sampling point. These are designated T1, T2, and T3 in Table II.

TABLE II. Point Concentration of Methylene Chloride (ppm) by Charcoal Tube-GC vs Results of RS-FTIR at Site I

Methylene Chloride Concentration (ppm)															
											RS-FTIR Path Average				
	Sampling	*Sampling Point Concentration by Charcoal Tube-GC*												*Pathlength*	*Difference*
Day	*time (min)*	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*Avg*[B]	*SD*[B]	*Avg*[C]	*SD*[C]	*N*[D]	*(meter)*	*%*[A]
Day One	90	2.5	3.3	4.2	3.3	NA[E]	4.2	2.1	3.0	0.74	4.02	0.37	59	20	28
Day Two (T1)	15	6.2	7.2	5.8	7.2	5.6	3.4	4.9	5.8	1.24	5.60	0.86	14	28	3.5
Day Two (T2)	15	3.1	3.2	3.1	3.7	2.5	1.6	2.7	2.8	0.62	4.83	0.19	14	24	52
Day Two (T3)	15	5.2	4.8	4.6	5.6	6.9	<2.6	3.4	4.4	2.03	4.34	0.17	12	21	1.4
Day Two[F]	45	4.8	5.1	4.5	5.5	5.0	2.5	3.7	4.4	1.67	4.92	0.24	40	25	11

[A] Relative difference of concentration between the point average and path average

[B] Point average concentration and standard deviation for each run

[C] Path-average concentration at given actual measurement pathlength and standard deviation

[D] Number of analyses performed by RS-FTIR during the time period

[E] Not Available

[F] Average concentration of Day Two at times T1, T2, and T3

TABLE III. Averaged Point Concentration From Charcoal Tube-GC vs Path-Averaged Concentration From RS-FTIR at Site II

				Concentration in the filter press in ppm (standard deviation)				
	No. of Samples[A]	*Sampling Time (min)*	*Pathlength (meter)*	*Acetone*	*Methylene Chloride*	*Amyl Acetate*	*Ethyl Acetate*	*Methanol*
Day One								
GC[B]	8	230		0.58 (0.09)	<0.20	0.51 (0.18)	[D]	[D]
RS-FTIR[C]	39	230	17	0.02 (0.05)	0.12 (0.20)	0.54 (0.28)	0.05 (0.02)	1.95 (0.03)
Day Two								
GC	10	240		2.69 (1.36)	0.36 (0.12)	0.11 (0.03)	[D]	[D]
RS-FTIR	42	240	40	0.79 (1.35)	0.35 (0.30)	0.44 (0.10)	nd[E]	0.21 (0.04)
Day Three T1								
GC	15	30		<2.3	<0.97	<0.5	<0.93	[D]
RS-FTIR	39	30	36	nd[E]	0.03 (0.10)	0.08 (0.02)	0.39 (0.03)	0.89 (0.03)
Day Three T2								
GC	15	160		1.07 (0.25)	0.66 (0.08)	<0.33	0.59 (0.29)	[D]
RS-FTIR	28	160	36	0.27 (0.39)	0.94 (0.21)	0.36 (0.18)	0.62 (0.25)	0.23 (0.01)

[A] For GC: number of charcoal tubes placed along the beam path in each run. For RS-FTIR: number of interferograms taken in each run

[B] Point average concentration along the beam path and standard deviation in parentheses

[C] Path average concentration and standard deviation in parentheses

[D] Compounds not included into quantitative set of GC

[E] Not detected

The difference between point path average and beam path average concentration ranges from 1.4% to 52% during the two days of measurements. It is interesting to note that relative standard deviation (RSD) of point measurements is always higher than that of beam path measurement in this site. However, this may be due to the fact that the point measurement may have been monitoring uniquely different concentrations at specific points along the beam. The RSDs for both point measurements and beam measurements range from 21.2% to 46.6% and 3.9% to 15.4%, respectively. These results suggested that variation of the concentration of methylene chloride throughout the area was relatively small, compared to that of the point concentrations at different sampling locations over the sampling period. This spatial variation along the IR beam path is a major contribution to the discrepancies of measurement between the charcoal tube-GC and RS-FTIR.

Work Site II

At Site II, measurements were made during a three-day period. Results are shown in Table III. On the first day, air samples were collected where a filter press was in use. The principal target compound was amyl acetate, which was used as a solvent. Average point concentrations of amyl acetate from eight point samples along the beam path was 0.51 ppm, while the path-average concentration by RS-FTIR was 0.54 ppm. Acetone was detected by GC, but not in most IR measurements. Traces of methylene chloride and ethyl acetate were also detected by RS-FTIR, but not by GC.

During the second day, the RS-FTIR was placed in the corridor between two filter press rooms. Four-hour TWA concentrations were measured by both the GC and RS-FTIR methods. MCD was found at 0.36 and 0.35 ppm by GC and RS-FTIR, respectively. However, larger differences were found between the point-average concentration and path-average concentration for acetone and amyl acetate. The large discrepancies might be attributed to inhomogeneous concentrations of acetone and amyl acetate released from the filter press room adjacent to the hallway. High concentrations were expected to be present near the room door area and low concentration away from the door. Because the releasing source of the MCD was located on the first floor and in other buildings, the distribution of the concentration of the MCD was expected to be more uniform in the hallway on the testing floor than that of amyl acetate and acetone.

On the third day, the measurements were taken in a filter press room where chemicals were being charged into reaction tanks (Figure 2). Two sets of samples (T1, T2) were taken during the different process periods. During the first time period (30 min) the press was prepared for operation. The process background levels for these compounds were lower than the MDC of the charcoal tube-GC method. The concentration of these compounds elevated during the second time period when the press was charged. The concentrations of the MCD and the ethyl acetate obtained from the GC method were 0.66 and 0.59 ppm, compared to 0.94 and 0.62 ppm from the RS-FTIR method. The level of amyl acetate was 0.36 ppm, but below the MDC of the GC method (< 0.33 ppm).

A total of five compounds were found in the air at Site II. Although methanol was not expected to be present and was not included in the GC quantitative set, it was detected and confirmed by RS-FTIR. Acetone readings from beam measurement were consistently lower than those from point measurement, while the variations for both methods were the same. This fact suggested that there was a bias associated with the RS-FTIR method for measurement of acetone. By examining the IR spectra, we found the window chosen for quantifying acetone is dominated by water peaks present at concentrations greater than the linear ranges, which may lead to low readings for acetone quantitation.

TABLE IV. Averaged Point Concentration from Charcoal Tube-GC vs Path-Averaged Concentration from RS-FTIR at Site III

	Time-Weighted Average Concentration (ppm)^A					
	Day One		Day Two		Day Three	
Compound	*Charcoal Tube-GC*	*RS-FTIR*	*Charcoal Tube-GC*	*RS-FTIR*	*Charcoal Tube-GC*	*RS-FTIR*
Methanol	<3.50	0.53	<2.00	0.34	<7.53	0.72
Ethanol	<2.30	1.33	<1.40	1.24	<5.25	2.82
Isopropanol	<1.20	1.12	<0.70	0.75	<2.69	1.70
Methylene Chloride	<0.30	0.14	<0.27	0.14	8.70	9.01
Methyl Ethyl Ketone	<0.60	<0.23	<0.35	<0.23	<1.38	<0.23
Tetrahydrofuran	2.77	2.53	0.23	1.65	1.68	3.41
Heptane	<0.10	0.23	0.10	0.02	0.24	0.16
Trichloroethylene	0.20	0.11	<0.10	0.25	<0.41	1.50
Toluene	<0.15	<0.50	<0.10	<0.50	<0.38	<0.50
o-Xylene	<0.10	<0.13	<0.10	<0.13	<0.28	<0.13
Ammonia		0.25		0.07		1.96
No. of Samples	7	50	14	78	42	104
Pathlength (meter)		17		17		17
Sampling Time (min)	149	149	460	460	377	377

^{A}For GC: point average TWA concentration; for RS-FTIR: path average TWA concentration

Work Site III

At Site III, both GC and RS-FTIR were set up to measure methyl bromide (MB) before, during, and after the MB charging process. Although MB was the primary target compound of concern, both methods failed to detect it during this experiment. However, the TWA concentrations of eleven other compounds were determined by both the charcoal tube-GC and RS-FTIR methods. It should be noted that the GC result for each day was an average of between 2 and 6 samples at each point collected during different sampling periods.

The MDC of the GC method for all the target compounds is higher than that of RS-FTIR during these measurements due to the small air-sampling volume. Four compounds were detected by the GC method, while eight compounds were reported to be present by the RS-FTIR. The results are shown in Table IV.

The advantage of TWA concentrations as shown in Table IV was to give an average measure for assessment of workers' exposure over sampling periods ranging from 2.5 to 7.5 hours. However, this measure did not reflect fluctuation of the concentration during the sampling period. For example, on Day Three, the TWAs of the MCD measured by the GC and the RS-FTIR were 8.70 and 9.01 ppm, respectively, and were the average of six time-period samples. The MCD concentrations varied from 0.93 to 28.13 ppm during these six different processing periods. Tetrahydrofuran was detected by both the GC and the RS-FTIR on each of the three days. Methyl ethyl ketone, toluene, and *o*-xylene were not found by either the GC or the RS-FTIR methods.

Table V shows that average concentrations at seven sampling points were obtained from the GC and RS-FTIR during six time periods on Day Three. A more detailed comparison between the two methods can be made with these results. The concentration of the MCD, for example, was < 0.5 ppm by GC and 0.32 ppm by RS-FTIR during the first 74-min sample. During the following five samples, the average point concentrations of the MCD were 1.8, 26.53, 7.48, 0.93, and 28.13 ppm by GC during the different processing times. During the same sampling times, RS-FTIR gave 1.16, 26.68, 10.65, 1.09, and 28.68 ppm, respectively. The coefficient of correlation of these two methods was 0.9948. The more detailed concentration profile as a function of time can be done easily by the RS-FTIR. However, the GC-tube method cannot perform comparable short-term exposure measurements due to the linear decrease in MDC with time.

Large variations of the MCD concentration during the entire sampling period were due to the different processes during which the MCD was pumped into reaction tanks. This led to short-term releases of MCD into the air. On the other hand, the variation of tetrahydrofuran concentrations on Day Three was expected to be small, since the processes did not involve charging of tetrahydrofuran (Table V). The results obtained with the RS-FTIR were invariably higher than those obtained using the GC method. There is no explanation for this discrepancy at this time.

The ability to detect unknown compounds in the field by RS-FTIR was once again demonstrated during the Site III measurements. Methanol and ammonia were not expected to be present, but were found by RS-FTIR. They were not included in the calibration set of the GC and, indeed, the sampling and analysis methods were not suitable for the collection of NH3. Therefore, no data is available from the GC for comparison. Methanol might come from nearby facilities where use was found. Ammonia was found to be present by the RS-FTIR during most of the Site III study period.

The qualitative analysis of RS-FTIR data was performed using a combination of ILSF and manual inspection of the IR spectra. Most compounds identified as present by ILSF analysis were confirmed by the process information provided by Abbott Laboratories. However, a false positive result was encountered during Site II and III field testing. Methyl ethyl ketone (MEK) was reported by ILSF analysis of the IR spectra collected from these two field locations. The beam-path average concentration reported by RS-FTIR was from 2.3 to 6.7 ppm. These values were far higher than the point-path average values obtained using the GC. The GC results ranged from < 0.35 to < 1.38 ppm.

TABLE V. Concentrations of Air Contaminants at Site III During Different Sampling Period Times on Day Three

	Concentration (ppm)[A]							
	Set 1		Set 2		Set 3		Set 4	
Compounds	Charcoal Tube-GC	RS-FTIR	Charcoal Tube-GC	RS-FTIR	Charcoal Tube-GC	RS-FTIR	Charcoal Tube-GC	RS-FTIR
Methanol	<5.8	0.565	<6.0	0.596	<9.9	0.972	<10.3	0.864
Ethanol	<4.0	2.525	<4.1	3.18	<7.0	2.02	<7.2	4.5
Isopropanol	<2.1	0.612	<2.2	1.105	<3.5	1.06	<3.7	7.2
Methylene Chloride	<0.5	0.319	1.8	1.16	26.53	26.68	7.48	10.65
Methyl Ethyl Ketone	<1.1	<0.23	<1.1	<0.23	<1.9	<0.23	<1.9	<0.23
Tetrahydrofuran	0.8	2.322	1.6	2.83	1.2	3.68	1.96	4.68
Heptane	<0.2	0.023	<0.2	0	<0.3	0.205	<0.3	0.125
Trichloroethylene	<0.3	2.332	<0.3	0.387	<0.6	6.92	<0.6	0.175
Toluene	<0.3	<0.5	<0.3	<0.5	<0.5	<0.5	<0.5	<0.5
o-Xylene	<0.2	<0.13	<0.2	<0.13	<0.4	<0.13	<0.4	<0.13
Ammonia		0.996		1.75		1.13		8.54
No. of Samples[B]	7	9	7	14	7	40	7	38
Sampling Time (min)	74		91		48		45	

[A] For Charcoal Tube-GC: point average concentration; for RS-FTIR: path average concentration

[B] Sampling rate for RS-FTIR varied during different operation periods

Further study of the spectra showed that spectral features of water and isopropanol interfered with the analysis of MEK in the IR region 1100–1200 cm^{-1}. The false positive result of MEK was eliminated when the analytical region was changed from the fingerprint region (1250–700 cm^{-1}) to the C-H stretch region (3150–2800 cm^{-1}) of the spectrum.

CONCLUSION

As expected from the operational principle of the FTIR and previous laboratory work,(26) there is agreement between the beam path and the average over the point measurements along the path, except where there were spectral interferences in the FTIR analyses or MDC problems in the GC analyses. Where good quantitation was possible by both methods, the differences observed were consistent with what might be expected in the presence of spatial inhomogeneities in the concentration of the vapors over the sampling periods. The air contaminant source characteristics and ventilation patterns in the workplace were key factors when IR beam (path) and charcoal tube (point) measurements are compared. The measurement of the RS-FTIR reflects a temporal variation during sampling period while the measurement of the charcoal tube indicates a spatial variation along the sampling path. Again, since the sampling geometries are different, we can expect such discrepancies between the results from RS-FTIR and GC methods in some of the workplace data.

In this study, the RS-FTIR demonstrated the ability to measure both short-term (15 min and ceiling) and long-term (8 hours) exposure, as well as detect sudden releases in the workplace. Although there is a concern about IR beam interruptions due to moving workers or equipment in the workplace, little effect was found on the quantitative result of both partial and complete blockages of the IR beam.

Good knowledge of the field test location and nearby plants is helpful to define a reference IR spectral library on which quantitative and qualitative analyses are based. Furthermore, the combination of the qualitative results obtained when using automated software and operator's experience is the key in identification of the unexpected contaminant. This instrument, when used by experienced operators, has great potential for evaluation of workplace exposure, especially for field risk assessment.

This is the first workplace demonstration of the use of the RS-FTIR system for air monitoring. In comparison with the charcoal tube-GC method, the RS-FTIR showed the advantages of its diversities of sampling method, such as real time, short and long term, and ability to perform qualitative and quantitative analyses of multicomponent mixtures. More studies are needed to evaluate correlation between the beam-concentration and a TWA for each worker at his or her work station.

Clearly, the SF_6 experiment was only a preliminary test and something might be made of the differences across sample sets in Table V. Methylene chloride, for example, shows considerable variability where methanol is quite steady. This may suggest using the RS-FTIR to look for any departure from routine operation, such as sudden or fugitive releases.

ACKNOWLEDGMENTS

The authors would like to thank Abbott Laboratories for its generous support and collaboration in this project. Their support stems from a long-time focus to seek better ways to provide a safe and healthy work environment. In particular, we thank Dr. L. Hecker, Director of Corporate Industrial Hygiene and Toxicology, and J. Kravcisin McClain of the Chemical and Agricultural Products Division. The efforts of William Herget, Nicolet Analytical Instrument, are greatly

TABLE V. Extended

Concentration (ppm)^A			
Set 5		Set 6	
Charcoal Tube-GC	RS-FTIR	Charcoal Tube-GC	RS-FTIR
<6.73	<0.656	<9.2	0.87
<4.8	2.75	<6.4	1.97
<2.3	0.47	<3.3	1.73
0.93	1.09	28.13	28.68
<1.2	<0.23	<1.6	<0.23
0.84	2.86	4.47	5.43
<0.2	0.01	<0.3	0.87
<0.4	0.16	<0.4	0.15
<0.3	<0.5	<0.5	<0.5
<0.2	<0.13	<0.4	<0.13
	1.03		0.37
7	7	7	10
69		50	

appreciated for valuable guidance and technical support. We also acknowledge the long-term support of National Institute for Occupational Safety and Health grant R01-OH02666, and the guidance of NIOSH grant personnel.

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