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Application of Computerized Differentiation Technique to Remote-Sensing Fourier Transform Infrared Spectrometry for Analysis of Toxic Vapors

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A differential method was developed for overcoming the difficulty in collection of background spectra when a remote-sensing FTIR is used during field measurements of air contaminants. A background spectrum was generated by introducing a $\Delta\lambda$ interval for every sampled data point of the spectrum. Temporal variations in spectral intensity caused by instability of the interferometer and changing IR beam configurations were greatly reduced through the use of the differential spectrum. Multicomponent analysis was performed by means of using a least-squares fit program with the differential spectrum. Three sets of spectra were evaluated by use of both the differential technique and the traditional method, which employs a clean background spectrum. There was no significant difference found between these two methods when a clean background spectrum could be used. However, in the case of field air monitoring system evaluations (as opposed to laboratory-based instrument evaluations), clean background spectra are frequently not available. Although the differential technique results in an increase in the limit of detection, results demonstrated that this method has sufficient sensitivity to detect and quantify both individual and mixtures of toxic compounds in the workplace.

INTRODUCTION

The increasing interest in the application of remote-sensing Fourier transform infrared spectroscopy (RS-FTIR) for the measurement of toxic gases and vapors in the environment and the workplace has heightened the need for a data manipulation and analysis system. Such a system, which is based on the automated analysis of IR spectra, plays an important role in accurately acquiring and processing both quantitative and qualitative spectral information.

Normally, an IR transmittance spectrum is generated by means of ratioing a sample spectrum against a background spectrum. Ideally, the conditions under which sample and background spectra are collected should be identical except there are not analytes present in the background spectrum. Under these controlled circumstances, reproducibility and consistency of the measurement are the most important factors to guarantee accurate analyses. However, background spectra generated under actual field use conditions for the RS-FTIR may be irreproducible because of varying IR beam configurations and poorly controlled environments. Furthermore, both the sample and the background will often contain spectral features of large numbers of unknown interfering air contaminants. When spectra are collected in the workplace, these interfering contaminants may be present at significant concentrations. Consequently, the system may yield unreliable results, and the detection limit may be degraded.

The difficulty in acquiring reliable background spectra during field application of remote monitoring instrumentation may significantly limit the application of the RS-FTIR. Thus, the development of a method for acquiring valid background spectra has been particularly important in ensuring accurate analysis for low-ppm to ppb level contaminants in ambient air.

Methods have been developed to obtain valid background spectra which utilize either a synthetic background spectrum or library background spectra.[1,2] Other methods were tested to collect the background spectra either upwind of the sampling location or at very short path distances during RS-FTIR field measurements.[3] IR spectra obtained by using these methods may suffer baseline fluctuation and instability due to changes in background intensity, which is affected by relatively minor changes in the general sample composition and beam alignment. Least-squares fit (LSF) band-to-band analysis may be successfully applied to quantify single-compound spectra with a fluctuating baseline[4] but not for complex mixture spectra.[5] Better results can be achieved by the use of the LSF method of negligible baseline shifts between successive data points or the log of the difference between successive data points.[4] However, these methods will not solve the background contamination problem encountered in RS-FTIR field measurement. Use of a low-resolution spectrum as a background can result in a straight baseline spectrum. This approach is very useful in IR qualitative analysis but may introduce negative bias in quantitative analysis because the target compound cannot be totally eliminated, only reduced, in the low-resolution background spectrum.[6]

Another approach is the use of digital spectroscopic techniques that implement postacquisition data manipulation once an absorption spectrum is obtained. These methods were developed to identify, estimate, and remove unmodeled background constituents from an IR spectrum before quantification.[7-9] Small et al. succeeded in the application

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(1) Hanst, P. L. *Analyzing Air for ppb Concentrations of Trace Gases Using Spectral Subtraction*; Infrared Associates: Anaheim, CA, 1990.

(2) Xiao, H. K.; Levine, S. P.; Herget, W. F.; D'Arcy, J. B.; Spear, R.; Pritchett, T. *Am. Ind. Hyg. Assoc. J.* **1991**, *52*, 449–457.

(3) Kricks, R. J.; Minnich, T. R.; Pescatore, D. E.; Solonski, P. J.; Mickunas, D.; Simpson, O. A.; Pritchett, T. H. Perimeter Monitoring at Lipari Landfill Using Open-path FTIR Spectroscopy: An Overview of Lessons Learned. Presented at the Air & Waste Management Association 84th Annual Meeting, Vancouver, BC, Canada, June 1991.

(4) Haaland, D. M.; Easterling, R. G.; Vopicka, D. A. *Appl. Spectrosc.* **1985**, *39*, 73–84.

(5) Xiao, H. K.; Levine, S. P.; Nowak, L.; Puskar, M.; Spear, R. *Am. Ind. Hyg. Assoc. J.*, in press.

(6) Puskar, M. A.; Levine, S. P.; Lowry, S. R. *Anal. Chem.* **1986**, *58*, 1981–1989.

(7) Maddams, W. F. *Appl. Spectrosc.* **1980**, *34*, 245–267.

(8) Osten, D. W.; Kowalski, B. R. *Anal. Chem.* **1985**, *57*, 908–917.

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of digital filters directly to passive RS-FTIR interferograms in order to extract information associated with a target analyte.[10,11] However, this method was limited to analysis of one or two species without overlapping peaks.

Wavelength modulation techniques have been widely used in molecular spectroscopy for background correction and for analysis of weak absorption and overlapping peaks since the multiplet structure is more easily recognized in derivative spectra than in the correspnding conventional spectra.[12-15] A wavelength modulation technique was developed to obtain the background correction and used to correct for more complex spectral interference.[16,17] The theory, application, and limitations of derivative spectroscopy have been discussed in several papers.[18-21] Another proposed system for obtaining wavelength derivative spectra involves a computer that performs a differentiation with respect to time while the wavelength is swept linearly in time.[22]

Postacquisition manipulation techniques might be useful to correct or remove background interferents in multicomponent analysis. However, they can be used only after the IR spectra are obtained from the process of ratioing the sample spectrum against the background spectrum.

In general, electronic differentiation offers simplicity and low cost, but suffers from the inability to obtain derivatives at fixed wavelength intervals. It is susceptible to signal-to-noise degradation caused by purely temporal changes in spectral intensity not accompanied by genuine changes in wavelength dependence. Wavelength modulation generally provides a superior signal-to-noise ratio (SNR) in absorption spectrometry or in any spectral measurement in which a time-dependent background signal is involved.[23] It proved to be an effective method for background correction. However, adding a modulation system to the RS-FTIR will lead to increased cost and complexity.

In this study, a method was developed to obtain a background spectrum from each sample spectrum in order to minimize the effects of background fluctuation on the quantitative results. A differential IR spectrum was obtained by means of ratioing between the sample and a background spectrum obtained from the sample spectrum. Unlike grating IR or wavelength scanning systems, the RS-FTIR is free of short-term temporal changes in spectral intensity since the entire IR region is collected as the same time in one scan. The intensity in differential spectra is truly wavelength dependent.

EXPERIMENTAL METHODS

Instrument. The open path RS-FTIR (Nicolet Instrument Corp., Madison, WI) consisted of three modules: (1) and 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. The IR light emitted from the source went through the interferometer before passing through space to reach the remote detector. Plane mirrors were used to direct the IR beam to cover the monitoring area and reflect the beam to the detector. The highest resolution achievable by the interferometer was two wavenumbers (cm^{-1}). The sampling rate of the RS-FTIR was a function of scans per sample and spectral resolution. At 2-cm^{-1} resolution and 128 coadded scans per sample, the sampling rate was 1 sample/min. Details about this instrument were fully described elsewhere.[2]

Method. The first step in this method was to obtain a single-beam spectrum by performing a Fourier transform on each interferogram. Then, a program written in C (Microsoft C 5.0) was used to generate a wavelength-shifted spectrum by introducing a $\Delta\lambda$ interval at each data point of a single-beam spectrum. The single beam $[I(\nu)]$ and its wavelength-shifted spectra $[I(\nu + \Delta\lambda)]$ were regarded as the sample (I) and the background (I_0) spectra, respectively. The conventional method for obtaining an absorbance spectrum $[A(\nu)]$ was then used to ratio the sample (I) and background (I_0) spectra, which is defined as

$$A(\nu) = -\log[I(\nu)/I_0(\nu)]$$

Consequently, a differential spectrum was obtained when the sample spectrum $[I(\nu)]$ was ratioed against its own spectrum with a $\Delta\lambda$ difference in the wavelength $[I(\nu + \Delta\lambda)]$. This can be expressed as follows:

$$D(\nu) = -\log[I(\nu)/I(\nu + \Delta\lambda)]$$

Here $D(\nu)$ is the value of the differential spectrum at wavelength ν.

Finally, multicomponent analysis was performed on the differential spectra by using a least-squares fit program.[4] It is assumed the differential value obeys Beer's law. Thus, the multicomponent situation for the measured differential value can be summarized as

$$\begin{array}{c} D_1 = k_{11}c_1 + k_{12}c_2 + k_{13}c_3 + \dots + k_{1n}c_n \\ \underline{D_2 = k_{21}c_1 + k_{22}c_2 + k_{23}c_3 + \dots + k_{2n}c_n} \\ D_1 = k_{m1}c_1 + k_{m2}c_2 + k_{m3}c_3 + \dots + k_{mn}c_n \end{array}$$

In matrix terms the expressions can be rewritten as

$$\mathbf{D} = \mathbf{KC}$$

This matrix notation represents the **K** matrix approach to multicomponent analysis. In the calibration step, the least-squares solution for **K** is

$$\mathbf{K} = \mathbf{DC}^{\mathrm{T}}(\mathbf{CC}^{\mathrm{T}})^{-1}$$

Where **D** and C are the differential value and concentration matrices for the standards. C^T represents the transpose of C.

The calculation of unknown component concentration is then

$$\hat{\mathbf{C}} = (\mathbf{K}^{\mathrm{T}}\mathbf{K})^{-1}\mathbf{K}^{\mathrm{T}}\mathbf{D}$$

Where $\hat{\mathbf{C}}$ is the calculated concentration matrix and **D** is the differential value matrix of the "unknown" sample.

All quantitative analyses in this study were performed by using a weighted LSF program with a method that assumes that the baseline is linear over each peak.[4]

IR Spectra. All interferograms were collected and analyzed at 2-cm^{-1} resolution with 128 coadded scans. Two types of spectra were produced from each interferogram. Absorbance spectra were obtained from ratioing the sample against the background spectra in the traditional method. Differential spectra were generated by means of using the differentiation technique. The results from these two types of methods were compared and used to evaluate the differentiation technique. Three data sets used for the comparison were collected (1) within a closed gas cell or with an open path system (2) in a controlled ventilation chamber and (3) in the field.

Calibration standards were single-compound spectra collected by using a 10-m gas cell. The concentrations of standards ranged from 4.5 to 5.5 ppm/m and were certified by gas chromatography.

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(9) Karstang, T. V.; Kvalheim, O. M. *Anal. Chem.* **1991**, *63*, 67–772.

(10) Small, G. W.; Kroutil, R. T.; Ditillo, J. T.; Loerop, W. R. *Anal. Chem.* **1988**, *60*, 264–269.

(11) Small, G. W.; Harms, A. C.; Kroutil, R. T.; Ditillo, J. T.; Loerop, W. R. *Anal. Chem.* **1990**, *62*, 1768–1777.

(12) Cardona, M. *Modulation Spectroscopy*, Solid State Physics Series Supplement 11; Academic Press: New York, 1969.

(13) Da Costa, V. M.; Coleman, L. B. *Rev. Sci. Instrum.* **1990**, *61m*, 2113–2120.

(14) Funfschilling, J.; Williams, D. F. *Appl. Spectrosc.* **1976**, *30*, 443–446.

(15) Maddams, W. F. *Appl. Spectrosc.* **1980**, *34*, 345–267.

(16) Skogerboe, R. K.; Lamothe, P. J.; Bastiaans, G. J.; Freeland, S. J.; Coleman, G. N. *Appl. Spectrosc.* **1976**, *30*, 495–500.

(17) Epstein, M. S.; Rains, T. C.; O'Haver, T. C. *Appl. Spectrosc.* **1976**, *30*, 324–329.

(18) Cameron, D. G.; Moffatt, D. J. *Appl. Spectrosc.* **1987**, *41*, 539–544.

(19) Hager, R. N., Jr.; Anderson, R. C. *J. Opt. Soc. Am.* **1970**, *60*, 1444–1449.

(20) O'Haver, T. C.; Green, G. L. *Anal. Chem.* **1976**, *48*, 312–318.

(21) Griffiths, T. R.; King, K.; Hubbard, H. V. A. *Anal. Chim. Acta* **1982**, *143*, 163–176.

(22) Olson, E. C.; Alway, C. D. *Anal. Chem.* **1960**, *32*, 370–373.

(23) Harnly, J. M.; O'Haver, T. C. *Anal. Chem.* **1977**, *49*, 2187–2193.

The first data set was acquired with a 10-m closed gas cell attached to a FTIR. The spectra of single compounds and mixtures were taken when vapors were introduced into the gas cell. Background spectra for obtaining absorbance spectra were collected using nitrogen gas in the gas cell before introducing the sample. The concentrations of single compounds were certified using gas chromatography (GC) with a precision of 2% of the concentration by Scott Speciality Gases (Troy, MI).

The mixture samples were introduced into the gas cell by using the U.S. EPA (Environmental Response Team, Edison, NJ) dynamic vapor dilution system. The concentrations of components in the mixture were determined by EPA using a GC method. In addition, a seven-component mixture spectrum was synthesized electronically. Two of the components of the mixture were H_2O and CO_2.

The second data set was collected in a well-controlled ventilation chamber where the RS-FTIR was placed in a straight line setting. The chamber was 7.9 (*L*) × 6.7 (*W*) × 2.7 (*H*) m for a total volume of 143 m^3. Two 0.6-m-deep plenums completely covered the opposing side walls to distribute the supply and exhaust air. The IR beam path length was 7 m. Different chemical vapors were generated in the chamber. Contaminant-free background spectra were collected before and after chemicals were released and ventilated. These backgrounds were regarded as "optimal" background spectra since the conditions under which sample and background spectra were collected were identical. Absorbance spectra obtained from ratioing the backgrounds were almost free of water interference since there was little change in relative humidity in the chamber during the measurement. Thus, the concentration of each chemical calculated from these spectra was regarded as a reference value.

The third data set was obtained when the RS-FTIR was used for field measurements in a workplace where different chemicals were used and manufactured.[5] Temperature and relative humidity ranged from 78 to 88 °F and 70 to 90%, respectively. The IR source and the detector were placed at one end of the workplace and the mirrors were used to direct the IR beam to cover the working area and reflect the beam back to the detector. The total IR beam path length was 30 m. A tracer gas, sulfur hexafluoride, was released on site. A spectrum collected prior to each release of the SF_6 was used as background to obtained the absorbance spectra.

RESULTS AND DISCUSSION

Background Correction. To examine the reproducibility of spectra, a series of spectra were collected at different times and using different beam configurations. First, a single-beam spectrum was used as background for sample spectra subsequently collected. Ideally, a ratioed spectrum should be a straight line domainted by random noise. When the time interval between collection of the sample and background spectra was 3 min, the baseline of the ratioed spectrum exhibited signs of fluctuation. Higher levels of baseline fluctuation were encountered when an interval of 30 min was used. This indicated that the reproducibility of measurements decreased and instrumental imperfections became gradually noticeable when the time interval became longer. Ultimately, nonspecific absorption will dominate the spectra and has a great effect on the detection limit and the quantitative analysis of minor components in the sample. In addition, there were slight changes in the amount of H_2O and CO_2 during the measurements as the intensity of peaks around 1200–1300 cm^{-1} and at 720 cm^{-1} gradually increased with time as shown in Figure 1. The curved baselines of spectra B and C in Figure 1 were attributed to the irreproducibility of measurement that caused slight changes in the intensity of single-beam sample spectra around 1100–800 cm^{-1}.

In the RS-FTIR field measurement, the process usually used to acquire a contaminant-free background spectrum is to take that spectrum at one location and then change to a different IR beam configuration to acquire the sample spectrum. The difference in the IR beam configurations between background and sample measurement may strongly influence the linearity, noise, and nonanalyte spectral features evident in the baseline. As shown in Figure 2, the background spectrum was collected when the system was put in a straight line configuration without a reflecting mirror. The sample spectra were then collected under different configuration conditions with the use of one, two, and three reflecting mirrors (configurations I–III, respectively). These curved baselines may result from beam misalignment, instability of the interferometer, and electronic drift, which causes the detector to have a slightly different response, as well as temporal changes in the environmental conditions. As a result, this fluctuation may lead to higher minimum detection limits and inaccurate quantitative results. To overcome this problem, the ideal solution is that the background spectrum much be collected using the same beam configuration and very close in time to the collection of the sample spectrum.

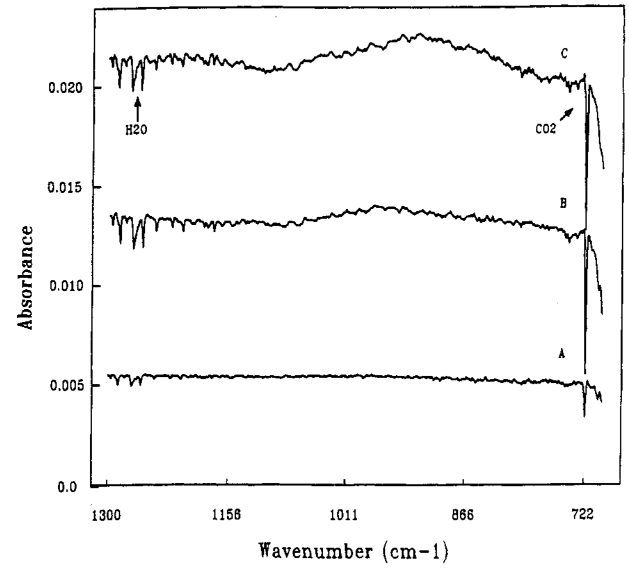

Figure 1. Reproducibility of the remote measurement with the IR beam configuration held constant. (A) Time interval between sample and background measurement was 3 min; (B) time interval was 30 min; (C) time interval was 2 h.

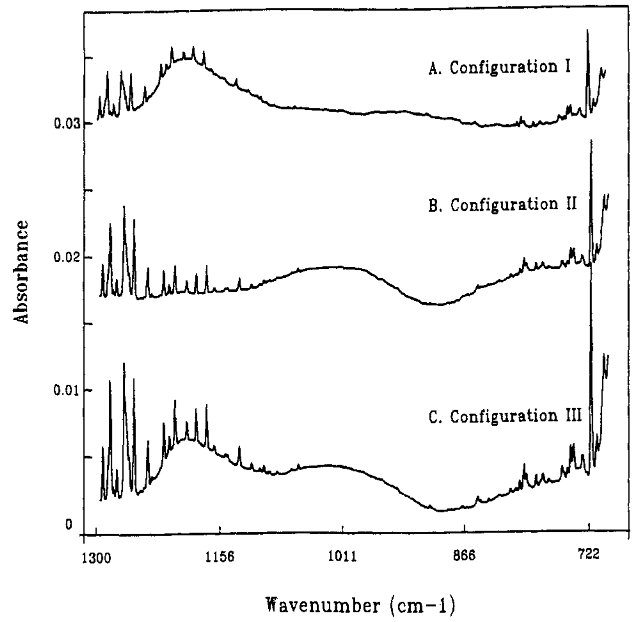

Figure 2. Reproducibility of the remote measurement with different IR beam configurations. (A) Configuration I utilized one mirror to increase the beam coverage area; (B) configuration II utilized two mirrors; (C) configuration III utilized three mirrors. (See refs 2 and 5 for details.)

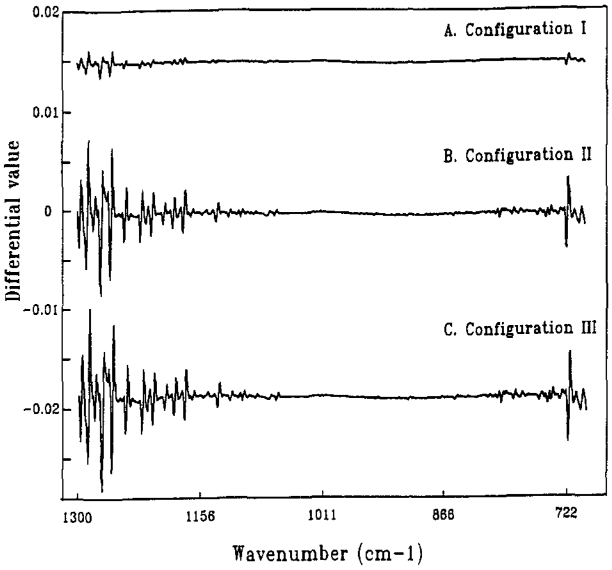

Figure 3. Background correction utilizing the differential technique applied to the data shown in Figure 2.

This problem became significant when the RS-FTIR system was applied to monitoring toxic gases and vapors in a workplace where the sampling time required from 15 min to 8 h to obtain time-weighted average concentrations.[5] The time interval between collection of the sample and background spectra was so long that ratioed spectra were dominated by artifacts and nonlinear baselines. These artifacts might overlap with the peaks of minor components in the spectra and thereby turn the analyte peaks into shoulder peaks on the curved baseline. In addition, unexpected background interferents were introduced. Hence, quantitative errors resulted from analysis of such spectra.

Use of the differential technique can effectively eliminate nonlinearities in the spectral baseline that are caused by the instability of the interferometer. Since the background spectrum was generated directly from each sample spectrum, temporal variations are ruled out in differential spectra. Furthermore, suppression is achieved of intensity variations observed even over a short time sequence when several open path spectra are acquired. When the differential technique was used to generate backgrounds for spectra obtained using beam configurations I-III, spectral baselines became straight (Figure 3, contrasted with Figure 2).

In the differential method, $\Delta I/\Delta\lambda$ plays an important role in suppressing the broad background due to IR blackbody radiation and variations in the curvative of the single-beam spectra. When the wavelength interval, $\Delta\lambda$, is fixed, the intensity of a given peak in the differential spectrum will depend on the change in the intensity (ΔI) with respect to the wavelength. High values of ΔI observed for sharp peaks lead to strong intensity of the peaks in the differential spectra. Figure 4 illustrates the fact that narrow peaks are enhanced greatly. In contrast, $\Delta\lambda$ is small relative to variations in the broad curved background; thus ΔI is very small and curved response is suppressed when this method is used. Therefore, the spectral intensity variation due to temporal and beam alignment variations, instability of the interferometer, and electronic drift, as well as broad curvature due to the blackbody radiation, can be greatly alleviated by use of the differential technique. The differential technique can also reveal low-intensity, sharp peaks within a spectrum. At the same time, the biggest and broadest peak (curvature background absorption) is minimized and becomes a flat line.

Minimum Detectable Concentration (Single Analyte in Closed Path Gas Cell). Minimum detectable concentration (MDC) has been defined many ways. In a study of the use of FTIR for air monitoring in the workplace, one of the definitions used was 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] The sensitivity of the RS-FTIR may be increased, and the MDC lowered, by increasing the IR beam path length, assuming that the path is filled with analyte. However, this can be true only when noise is kept constant, there is minimal interference from water vapor in the air, and controlled errors from beam divergence and optical alignment are assumed.

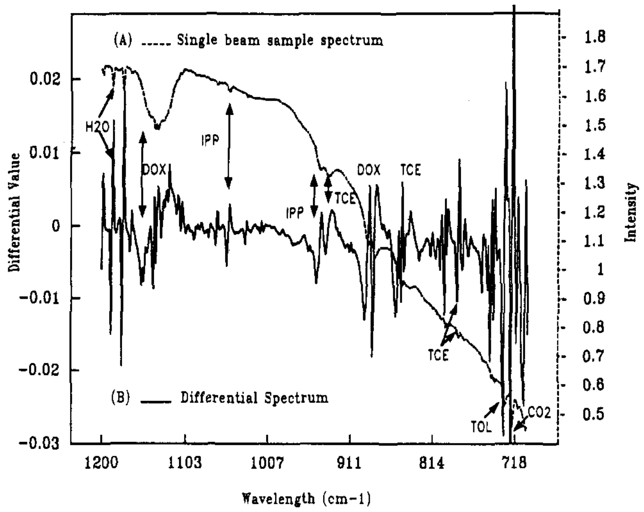

Figure 4. Mixture spectra collected in a ventilation chamber by using the RS-FTIR: DOX, 1,4-dioxane; IPP, 2-propanol; TCE, trichloroethylene; TOL, toluene. (A) Single-beam sample spectrum. (B) Differential spectrum with $\Delta\lambda = 2$ cm^{-1}.

Figure 4 illustrates the fact that the intensity of a narrow peak increases when compared to broad bands. Thus, sharp features of low intensity might be observed even if they lay within a broad, intense peak. As shown in Figure 4, the trichloroethylene peak at 853 cm^{-1} was very weak and occurred on a steeply sloping baseline of the single-beam spectrum (A), but that peak is highly enhanced in the differential spectrum (B). However, the process of differentiation usually degrades the SNR.[20] Thus, random measurement errors may be aggravated in the differential mode.

In this study, 26 compounds were used for determination of the MDC on their absorbance and differential spectra. An optimal background spectrum collected in a well-controlled environment was used to obtain each absorbance spectrum. Differential spectra were generated with $\Delta\lambda$ ranging from 2 to 14 cm^{-1}. The noise levels in the region used for quantitation were calculated on the basis of at least 50 data points. The height of the peaks used for each compound was picked on the basis of normal quantitative analysis and was determined as the signal level.

As Table I shows, the MDC in the differential spectra was higher than those in the absorbance spectra. This is due to an increase in noise level in the differentiation process. The $\Delta\lambda$ has a decisive effect on the intensity, number, and distribution of maxima and minima in spectra. An increase in this variable results in a shift of the maxima and minima. The differential peaks reach their maxima when their half-peak width is equal to $\Delta\lambda$. However, the ability of the method to enhance weak narrow peaks and to resolve overlapping peaks in differential spectra will be lost when the $\Delta\lambda$ becomes larger. The random noise level may remain constant but

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[24] Strang, C. R.; Levine, S. P. *Am. Ind. Hyg. Assoc. J.* **1989**, *50*, 78–84.

Table I. Minimum Detectable Concentration for Selected Compounds

			minimum detectable concn[a] (ppm)					
				differential technique at $\Delta\lambda$[d]				
compound	TLVs[b] (ppm)	peak region (cm^{-1})	traditional method[c]	2 cm^{-1}	4 cm^{-1}	6 cm^{-1}	10 cm^{-1}	14 cm^{-1}
acetone	750	1225–1200	0.039	0.152	0.147	0.183	0.238	0.237
benzene	10 A2[e]	3053–3043	0.065	0.394	0.357	0.336	0.326	0.362
chlorobenzene	10	817–797	0.003	0.010	0.007	0.007	0.009	0.011
carbon tetrachloride	5 A2	771–753	0.059	0.279	0.242	0.233	0.245	0.267
3-chloropropene	10	2975–2958	0.010	0.037	0.034	0.036	0.052	0.062
o-chlorotoluene	50	698–690	0.027	0.048	0.062	0.076	0.107	0.120
cyclopentane	600	709–701	0.025	0.076	0.122	0.103	0.110	0.120
1,1-dichloroethane	200	744–728	0.026	0.110	0.088	0.079	0.090	0.101
1,2-dichloroethane	10	798–790	0.026	0.031	0.045	0.061	0.084	0.105
1,1-dichloroethylene	5	1143–1137	0.016	0.081	0.082	0.073	0.083	0.087
1,4-dioxane	25	2872–2859	0.012	0.029	0.031	0.035	0.053	0.063
ethyl acetate	400	3025–2992	0.043	0.291	0.302	0.296	0.300	0.148
ethylbenzene	100	2978–2972	0.033	0.182	0.145	0.127	0.144	0.159
ethyl ether	400	1160–1138	0.014	0.103	0.079	0.068	0.071	0.076
Freon 11	C 1000[f]	865–825	0.003	0.013	0.010	0.010	0.011	0.012
hexane	50	3003–2967	0.014	0.107	0.093	0.085	0.095	0.099
isopropyl alcohol	400	1157–1148	0.075	0.746	0.589	0.495	0.478	0.473
methylene chloride	50 A2	757–730	0.017	0.105	0.080	0.068	0.070	0.074
methyl ethyl ketone	200	1171–1171	0.057	0.598	0.492	0.445	0.441	0.406
methyl isobutyl ketone	50	1176–1168	0.053	0.428	0.333	0.287	0.297	0.306
styrene	50	750–740	0.015	0.025	0.033	0.040	0.058	0.063
1,1,1-trichloroethane	350	746–697	0.008	0.033	0.027	0.025	0.028	0.031
1,1,2-trichlroethane	10	760–718	0.017	0.086	0.068	0.060	0.064	0.069
trichloroethylene	50	853–848	0.016	0.049	0.058	0.053	0.061	0.063
toluene	100	735–721	0.022	0.050	0.057	0.060	0.087	0.102
vinyl chloride	5 A2	949–936	0.046	0.079	0.099	0.115	0.169	0.211

[a] Path length for the minimum detectable concentration data was 10 m. [b] Threshold limit value, time-weighted average concentration. See ref 25 for details. [c] Perfect background spectrum is available for each sample spectrum. [d] Wavelength interval introduced into the background spectra. [e] A2, suspected human carcinogens. [f] Ceiling limit.

Table II. Analysis of Four Components in Electronically Synthesized Mixture Spectra Evaluated at Different Wavelength Intervals

		concn (ppm) and relative deviation[a] (%)					
		exp value at different $\Delta\lambda$ (cm^{-1})					
compound	true value[b]	2 cm^{-1}	4 cm^{-1}	6 cm^{-1}	8 cm^{-1}	10 cm^{-1}	12 cm^{-1}
1,4-dioxane	5.35	5.36(0.19)	5.43(1.50)	5.50(2.80)	5.57(4.11)	5.64(5.42)	5.67(5.9)
hexane	4.99	4.98(−0.20)	5.01(0.40)	4.98(−0.20)	4.96(−0.60)	4.93(−1.20)	4.94(−1.00)
Freon 11	1.18	1.30(10.2)	1.30(10.2)	1.31(11.0)	1.34(13.6)	1.35(14.4)	1.36(15.3)
trichloroethylene	4.82	4.23(−12.2)	4.55(−5.60)	4.54(−5.81)	4.36(−9.54)	4.32(−10.4)	4.31(−10.6)
SSD		0.36	0.094	0.12	0.29	0.37	0.40

[a] Relative deviation (RD) is defined as (exp − true)/true × 100. [b] True value was determined by GC.

spectral artifacts observed in the differential spectra increase along with the larger value of $\Delta\lambda$. This may result in higher MDCs and introduce analytical bias. The MDC of vinyl chloride in Table I, for example, was 46 ppb at a 10-m path length in the absorbance spectrum. The MDCs in the differential spectra were 79, 99, and 115 ppb with $\Delta\lambda$ at 2, 4, and 6 cm^{-1}, respectively.

These data showed that the choice of optimal $\Delta\lambda$ depends on both peak width and the noise level in the differential mode. However, the presence of overlapping peaks of mixtures along with sloping single-beam background often makes the choice of $\Delta\lambda$ quite difficult. Depending on the width and the location of peaks, a different $\Delta\lambda$ may be chosen to obtain the optimal MDC for each compound. When a mixture spectrum was encountered, however, varying peak widths and overlaps of peaks in the mixture would lead to a compromised $\Delta\lambda$. Usually, a smaller $\Delta\lambda$ is chosen for the mixture spectra since a larger $\Delta\lambda$ does not significantly improve results for components with wide peak widths, but only leads to a higher noise level. It is always desirable to have the largest possible SNR to obtain the most precise results and the lowest MDC.

The study shows that the differential method is sufficiently sensitive to detect concentrations of all studied compounds well below their current recommended workplace air standards[25] even though the SNR in differential spectra is degraded. In addition, the use of differential spectra will enhance the selectivity of the system, which is especially valuable for accurate analysis of mixture spectra.[26–29]

Analysis of Digitally Synthesized Mixture Spectra (Closed Path Gas Cell). A synthesized mixture spectrum was generated by means of mathematically adding the spectra of 1,4-dioxane, hexane, Freon-11, and trichloroethylene. In addition, water and carbon dioxide spectra were added into the synthesized spectrum. Differential spectra were generated at $\Delta\lambda$ = 2–14 cm^{-1}. LSF was used for quantitative analysis.

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(25) Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices: 1991–1992. American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, OH, 1991.

(26) Hawthorne, A. R.; Thorngate, J. H. *Appl. Spectrosc.* **1979**, *33*, 301.

(27) Reid, A. F.; Garside, B. K.; Shewchun, J. H.; El-Sherbiny, M.; Ballik, E. A. *Appl. Opt.* **1978**, *17*, 433.

(28) Lawrence, A. H. *Anal. Chem.* **1984**, *56*, 1731–1734.

(29) Meal, L. *Anal. Chem.* **1983**, *55*, 2448–2450.

Table III. Paired Comparison of Quantitative Results from Traditional Method and Differential Method

	concn (ppm/m)								
	level one			level two			level three		
	TM[a]	DM[b]	RD[c] (%)	TM	DM	RD (%)	TM	DM	RD (%)
set one									
toluene	4.40	4.42	0.45	0.687	0.872	26.93	0.0886	0.0780	−11.96
1,1,1-trichloroethane	4.94	4.95	0.20	0.875	0.859	−1.83	0.111	0.148	33.33
1,4-dioxane	4.69	4.81	2.56	0.750	0.794	5.87	0.137	0.138	0.73
acetone	4.25	4.02	−5.41	0.616	0.670	8.77	0.121	0.099	−18.18
1,2-dichlroethane	4.90	4.87	−0.61	0.714	0.816	14.29	0.097	0.134	38.14
set two									
o-chlorotoluene	1.92	1.97	2.60	0.927	0.998	7.66	0.107	0.051	−52.34
chlorobenzene	2.19	2.49	13.70	1.33	1.24	−6.77	0.187	0.187	0.00
set three									
vinyl chloride	5.02	4.96	−1.20	1.07	1.28	19.63	0.103	0.188	82.52
benzene	5.09	5.10	0.20	1.06	1.01	−4.72	0.047	0.135	187.23
methylene chloride	5.06	4.88	−3.56	1.07	0.923	−13.74	0.180	0.111	−38.33
1,1-dichloroethylene	4.94	5.02	1.62	1.09	1.16	6.42	0.111	0.159	43.24
trichloroethylene	4.89	4.83	−1.23	1.03	0.963	−6.50	0.101	0.138	36.63
av diff		0.014			0.0308			0.0149	
SD		0.1384			0.1087			0.0499	
t value		0.338			0.981			1.037	
p value		>0.05			>0.05			>0.05	

[a] Traditional method for obtaining absorbance spectra with a perfect background. [b] Differential method for obtaining absorbance spectra at $\Delta\lambda = 2$ cm^{-1}. [c] Relative deviation (RD) is defined as (DM − TM)/TM × 100.

Table IV. *Correlation Analysis of Traditional and Differential Methods for Analysis of Mixture Spectra Collected in a Chamber Using the RS-FTIR*

	concn range (ppm/m)	R^2[a]	X_{coeff}[b]	avg diff[c]	SD[d]
mixture I					
acetone	0.023–2.696	0.9999	0.953	0.072	0.051
methyl ethyl ketone	0.000–1.850	0.9999	0.945	0.026	0.041
chloroform	0.004–0.707	1.0000	0.962	0.014	0.011
1,1,1-trichloroethane	0.006–1.732	1.0000	0.970	0.018	0.014
methylene chloride	0.011–1.732	1.0000	0.995	0.008	0.004
mixture II					
carbon tetrachloride	0.094–1.136	0.9946	1.046	0.029	0.032
toluene	0.239–0.730	0.6684	0.718	0.150	0.092
2-propanol	0.000–0.945	0.9603	1.055	−0.118	0.075
acetone	0.358–3.416	0.9701	0.989	0.100	0.182
1,1,1-trichloroethane	0.083–1.189	0.9934	1.000	0.009	0.031
mixture II					
toluene	0.004–2.012	0.9999	1.069	−0.222	0.055
2-propanol	0.000–1.417	0.9998	0.948	0.042	0.035
1,4-dioxane	0.011–1.798	1.0000	1.006	−0.007	0.004
trichloroethylene	0.005–0.957	0.9999	1.045	−0.026	0.019
mixture IV					
ethylbenzene	0.004–0.301	0.9680	0.942	0.006	0.017
o-xylene	0.019–0.312	0.9972	0.855	0.027	0.016
1,2-dichloroethane	0.057–1.536	0.9986	0.908	0.085	0.050
ethanol	0.012–0.601	0.9997	1.024	−0.004	0.002
amyl acetate	0.040–0.601	0.9992	0.972	0.012	0.005

[a] Squared correlation coefficient with intercept forced through zero. [b] Slope. [c] Average difference betwee two methods. [d] Standard deviation of the difference.

From Table II, we can see that the discrepancy between the true value and the experimental value obtained from differential spectra was very small with relative deviation from the true values ranging from 0.05% to 3.54%.

Two IR regions, 3027–2815 and 970–815 cm^{-1}, were selected for quantitative analysis of the mixture spectra. Overlapping peaks of Freon-11 and trichloroethylene around 870–815 cm^{-1} may explain why Freon-11 results were consistently higher while trichloroethylene concentrations were lower than the true values in all results. However, the differences between true and experimental values for these two compounds were rather small. Comparison among sums of squared deviation (SSD) at each $\Delta\lambda$ might reflect the effect of wavelength interval on the outcome. SSD was observed to be optimal for this mixture when $\Delta\lambda$ was 4 cm^{-1} and gradually increased when the $\Delta\lambda$ became larger. This indicated that the optimal $\Delta\lambda$ may be frequency dependent. However, this $\Delta\lambda$ may not be optimal for other mixtures.

Analysis of Actual Mixture Spectra (Closed Path Gas Cell). Three sets of mixtures, each of which had three different concentrations, were collected using a 10-m gas cell. The concentrations of components in the samples were confirmed by using GC. The background spectra for obtaining absorbance spectra were collected when nitrogen gas was filled into the gas cell before samples were introduced. Differential spectra were generated from each sample single-beam spectrum with $\Delta\lambda = 2$ cm^{-1}. Quantitative analyses were performed on both absorbance and differential spectra. The comparison of results obtained from absorbance spectra and differential absorbance spectra is listed in Table III.

The mixtures at high concentration levels were prepared in dry nitrogen. The effects of water and carbon dioxide on quantitative results, therefore, were negligible. From Table III, we can see that the level of high concentration ranges from 2 to 5 ppm/m. Since the spectra of high-concentration mixtures were prepared in nitrogen, most of the fingerprint region can be used for quantitative analysis. Results obtained from analysis of two types of mixture spectra agreed very well.

The mixtures at medium- and low-concentration levels were diluted in ambient, unpurified air that was similar in nature to the situation where remote measurements were carried out in the workplace and environment. At the medium-concentration level, the concentration ranged from 0.68 to 1 ppm/m. Since the mixtures were prepared in air, water absorption had a significant effect on the outcome due to overlap with analytical peaks of the components. This effect became more apparent at the low-level concentration category (Table III, level three), which was 10 times lower than that in the medium level (level two). Besides the effect of water, overlap of peaks in the mixture spectra also played an important role in discrepancies between the two methods. The effect became significant when the concentration of components was at the ppb level. This was clearly shown in the low-concentration-level mixtures (level three).

Table V. Comparison among Three Different Methods for Analysis of a Five-Component Mixture Measured by the RS-FTIR in a Ventilation Chamber

	concn (ppm/m)														
	ethylbenzene			*o*-xylene			1,2-dichloroethane			ethanol			amyl acetate		
sample	Met1[a]	Met2[b]	Met3[c]	Met1	Met2	Met3	Met1	Met2	Met3	Met1	Met2	Met3	Met1	Met2	Met3
1	0.87	0.42	0.91	0.92	1.30	0.83	5.26	2.19	4.92	0.99	0.69	1.01	1.61	ND[d]	1.56
2	1.14	1.17	1.22	1.27	1.34	1.14	6.37	2.35	5.95	1.19	0.88	1.21	2.41	ND	2.31
3	1.36	1.42	1.36	1.53	1.38	1.33	7.29	2.46	6.77	1.34	1.01	1.37	2.99	0.27	2.88
4	1.54	1.40	1.52	1.75	1.42	1.48	8.23	2.56	7.42	1.46	1.10	1.49	3.40	0.48	3.33
5	1.62	1.52	1.64	1.85	1.44	1.57	8.77	2.62	7.99	1.57	1.19	1.59	3.73	0.66	3.62
6	2.04	1.75	1.78	2.11	1.49	1.76	10.33	2.79	9.24	1.78	1.37	1.83	4.11	0.85	4.04
7	2.15	1.86	1.87	2.23	1.51	1.89	10.97	2.85	9.81	1.87	1.44	1.92	4.29	0.96	4.22
8	1.57	1.48	1.45	1.66	1.42	1.44	8.26	2.56	7.53	1.40	1.07	1.45	3.36	0.47	3.19
9	0.32	ND	0.36	0.38	1.20	0.33	1.81	1.78	1.64	0.31	0.11	0.33	0.86	ND	0.82
10	0.03	ND	0.07	0.13	1.10	0.13	0.40	1.60	0.39	0.08	ND	0.08	0.28	ND	0.25

[a] Method 1: background spectra were collected 5 min before collection of sample spectra. [b] Method 2: background spectra were collected 2 days before collection of sample spectra. [c] Method 3: background spectra were generated from each sample spectrum by using the differential technique. [d] ND, not detected.

Table III shows that the relative difference between the two methods became larger than the concentration was near the MDC. The Student *t* test was performed to test whether or not the differential method statistically differs from the traditional method. Although the discrepancy increased with reduced concentration, the Student *t* test showed that there was no significant difference between those two methods. It was interesting to see that the relative difference of the value obtained for toluene and 1,4-dioxane in set one and chlorobenzene in set two was higher at the medium concentration than at the low concentration. There was no clear explanation of this.

Analysis of Field Mixture (Open Path, Pilot-Scale Chamber). Initial remote measurements were carried out in the environmental chamber where four sets of chemical mixtures were generated. The RS-FTIR collected sample spectra when the concentrations of the mixtures reached equilibrium. Then the vapor generator was stopped, and fresh air was introduced into the chamber to dilute the concentration until the concentrations were below the limit of detection of the RS-FTIR. Sample spectra at different concentration levels were taken during this ventilation period. Optimal background spectra were collected under the same conditions in the absence of analytes.

The concentrations of mixture components along the beam path were calculated from both the absorbance spectra and the differential spectra. The concentrations in the mixtures ranged from 0.04 to 2.7 ppm/m along the beam path. The correlation between these two methods on the quantitative analysis of these four mixtures was determined and is shown in Table IV. The test was done for each component in the four mixtures.

There was excellent agreement between these two methods. The correlation coefficients ranged from 0.9680 to 1.000 except for toluene in mixture II. The correlation coefficient of the two methods for toluene is 0.6684 in mixture II. However, in mixture III, the correlation coefficient for toluene is 0.9999. The main difference between these two mixtures was that the composition was different. Mixture II contained carbon tetrachloride, toluene, 2-isopropanol, acetone, and 1,1,1-trichloroethane, while mixture III only included toluene, 2-propanol, 1,4-dioxane, and trichloroethylene. Examining the IR spectra, a strong toluene peak was found in the region of 820–720 cm^{-1} and overlapped with one of the peaks of 1,1,1-trichloroethane. The nonlinear baseline due to the overlap in this region may lead to an error in analysis of both absorbance and differential spectra at low concentration.

In addition, three methods were used to process the interferograms from mixture IV. These results are shown in Table V. Methods one and two are the same except they used different background spectra for obtaining absorbance spectra. The background spectra used in method one were collected 5 min before collection of sample spectra, while the method two backgrounds were collected 2 days prior to the collection of the sample spectra. Method three was the differential technique that generated background spectra from each sample's own single-beam spectra with $\Delta\lambda = 2$ cm^{-1}.

Results of quantitative analysis of these spectra are shown in Table V. Differences among the three methods are small for analysis of ethylbenzene and *o*-xylene. However, the data showed that method two yielded results that were significantly different from those obtaining when methods one and three were used for analyses of 1,2-dichloroethane, ethanol, and amyl acetate. This was because the spectral baseline of method two in the quantitative region suffered from significant curvature and interfering broad features. This curved and irregular baseline changed the analytes' peak shapes, which led to inaccurate results.

Analysis of Real Environmental Samples (Open Path, Field Location). The field measurements of the RS-FTIR were conducted in a pharmaceutical plant. Different IR beam configurations were set up to cover all working areas.[5] The working environment during the measurement was hot and humid, which was the ideal, high-stress condition to test the whole hardware and software system for analysis of emissions in the workplace. It is important to stress that one of the most important aspects of this project was the evaluation of this method in the actual conditions encountered in the field, rather than only testing the method in the laboratory.

Along with various measurements of industrial emissions in the workplace, a point source of SF_6 was released during the data collection. The reasons for releasing SF_6 were as follows: (1) SF_6 was not used nor was a product in the manufacturing area; (2) it was stable and nontoxic; (3) it could be used to determine the effectiveness of the IR beam coverage for fugitive emissions; (4) SF_6 could be accurately determined since it had a unique, strong peak in the fingerprint region. Thus, analysis of SF_6 spectra taken under actual field conditions represented a valid test of the accuracy for the differential technique.

Absorbance and differential techniques, as discussed above, were used to obtain absorbance and differential spectra. A regression analysis was performed to compare these two methods for analysis of SF_6. There were 104 measurements of SF_6 during five runs. The SF_6 concentration along the beam ranged from 0.03 to 2 ppm/m over the 30-m path length. Results indicated that two methods were highly correlated.

The R^2 is 0.9875. The slope and intercept of the regression line are 1.059 and 0.281, respectively.

Since as many as 11 other compounds including organic solvents and ammonia were also present in these workplace air samples, mixture spectra were encountered which represented significant interference for the differential spectra. These mixtures did not represent a problem in the absorbance spectra since all components except the SF_6 could be subtracted using a background obtained immediately prior to the release of the SF_6 into the workplace air. Since the nonanalytes were not included in the calibration for differential spectra, the overlap of the SF_6 with other component peaks in differental spectra might explain some discrepancies between the two methods.

CONCLUSION

In conclusion, the differential technique provides a simple and alternative way to generate a background spectrum for remote-sensing measurement in the field, where a valid background measurement is not achievable. Since the background spectrum is generated from each sample single-beam spectrum, the possibility of analytes in the background that lead to inaccurate results in the traditional method is reduced or eliminated. The temporal variation in spectral intensity due to instability of the interferometer can be reduced by using the differential procedure. Although narrow peaks are enhanced in the differential spectrum, in general, the detection limit obtained when the differential technique is used is higher compared to that of traditional methods (which are not generally applicable in the field remote monitoring situations). The advantage of this approach over the hardware approach, such as modulation and electronic differentiation, is the elimination of electronic noise due to an electronic differentiator or a modulation oscillator.

The combined efficacy of this technique in background correction and least-squares fit in quantitative analysis provides a tool for the RS-FTIR system for accurate remote measurement of gases and vapors in the workplace and the environment.

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