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Evaluation of the Applicability of Fourier Transform Infrared (FTIR) Spectroscopy for Quantitation of the Components of Airborne Solvent Vapors in Air

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Monitoring of solvent vapors can be performed by a variety of methods. Recent studies by this research group have shown that Fourier transform infrared spectroscopy (FTIR) can be a useful method for monitoring mixtures of vapors in air. The use of FTIR for the quantitation of individual components in a simulated 12-component paint solvent mixture is demonstrated, and optimal conditions for instrument use are detailed. The limit of detection (LOD) for each component is well below the threshold limit value (TLV®), although there is a significant degradation of LOD in the mixture when compared to the values obtained for individual compounds. Accurate quantitation is obtained through the use of a least squares fit program.

Introduction

Techniques used in painting have been described at length in industrial hygiene texts(1,2) and in EPA studies.(3,4) The principle focal points of these documents are the question of paint solvent vapor emissions (the measurement of which is central to the control of worker exposures), the design and monitoring of emission control methods,(5,6) the recycling of process air to the workplace,(7) and the cleanup of solvent spills in emergency response operations.(8) The sampling and analysis of solvent vapors also is a central focus of both the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) methods manuals.(9,10)

Monitoring of solvent vapors can be performed by a variety of methods. These include gas chromatography (GC),(5-10) mass spectrometry (MS),(11) and infrared spectroscopy (IR).(12) Recent studies by this research group(13-16) have shown that Fourier transform infrared spectroscopy (FTIR) can be a useful, and in some cases a preferred, method for the monitoring of mixtures of vapors in air. These studies of the use of FTIR previously have demonstrated the utility of the method for monitoring gas and vapor emissions in the semiconductor device manufacturing workplace. As a result of these studies, optimal conditions were determined for monitoring gases and vapors in air in cases when only one contaminant at a time is present.

In this paper, the use of FTIR for the monitoring of computer-generated, simulated paint solvent mixtures is demonstrated, and optimal conditions for instrument use are detailed. This step in the research program is necessary prior to the study of FTIR for the analysis of real workplace air samples.

Experimental Materials and Methods

The data were collected using a Nicolet 20 SXC FTIR spectrometer equipped with a liquid nitrogen-cooled HgCdTe (MCT) detector and a Hanst 10-m long path cell. All data were collected using 128 co-added interferograms. Data were collected over the frequency range 5000-700 cm^{-1}, at a resolution of 0.30 cm^{-1}. For this study, the high resolution interferograms were saved for later use but were transformed to yield spectra with resolutions of 2.0 cm^{-1}. The data system was a Nicolet 620 equipped with 1 megabyte of RAM and a 50 megabyte disc drive. (The FTIR and data system were manufactured by Nicolet Instrument Co., Madison, Wisconsin.) All other experimental conditions were identical to those previously reported.(16) This includes the use of UHP nitrogen for background spectra; least squares fit (LSF) program for quantitation; and the generation of spectra of gas standards at various concentrations using Scott ± 2% gas standards around 50-ppm initial concentration (Scott Specialty Gas, Troy, Mich.), and the use of an orbital welded, electropolished stainless-steel gas mixing system.(14) Calibrations were performed using standards which were diluted in 25°C air containing approx 300 ppm CO_2 and 30%-45% relative humidity. Stainless-steel tubing, vacuum fittings, and valves were used throughout. The pressure/vacuum gauge used was calibrated at the General Motors Technical Center, Warren, Michigan.

Paint solvent composition and concentration information was supplied by automotive industry experts and represents typical values found in automotive paint topcoat operations.(17) The computer-generated spectra of paint solvent

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TABLE I
Solvents, Limits of Detection, and Absorptivity for Compounds Taken One at a Time and in a Mixture, at a Resolution of 2 cm^{-1}

Solvent	TLV® (ppm-v/v)	LOD (ppm-v/v) Individual	LOD (ppm-v/v) In Mixture	Absorptivity ($\times 10^{-4}$)
Toluene	100	0.067^{A}	0.2	6.2
o-Xylene	100	0.047	0.1	8.5
m-Xylene	100	0.04	0.1	5.2
p-Xylene	100	0.08	0.1	4.8
Ethylbenzene	100	0.029	0.5	4.1
Solvesso® 100	100^{B}	C	C	C
n-Butylacetate	150	0.005	0.2	20
i-Butylacetate	150	0.005	D	22
2-Ethoxyethylacetate	5	0.004	0.2	14
Methylethylketone	200	0.023^{A}	D	2.4
Methylpropylketone	200	0.03	D	2.4
Methylisobutylketone	50	0.026	0.2	6.9
Methylamylketone	50	0.04	0.2	2.5
Methanol	200	C	C	C
n-Propanol	200	0.07	0.05	2.6
n-Butanol	50	0.01	0.2	4.8
i-Butanol	100	C	C	C
Ethoxyethanol	5	0.012^{E}	0.2	6.4^{E}

[A] Linear to the LOD. All compounds not marked with [A] are linear only to 0.5 ppm. Below that point, questions of wall adsorption must be addressed (References 12 and 18).

[B] No TLV for Solvesso, which is a mixture of alkylbenzenes. This is the TLV for ethylbenzene.

[C] Included in the mixture but not measured because of the lack of a certified reference standard.

[D] Not included in the mixture.

[E] Measured in a different study (Reference 16).

mixtures were configured from the electronic addition of the spectra of the individual compounds.

Results and Discussion

For the purpose of this study, a 12-component mixture was chosen to represent typical solvent vapor compositions in a paint spray booth (Table I). This mixture includes esters, alcohols, ketones, and aromatics. The highest concentration is that of the sum of the mixed xylene isomers, which totals about 7 ppm. Concentrations of 1–2 ppm commonly are found in the workplace for each of the following solvents: toluene, ethylbenzene, n- and i-butyl acetate, methylamyl ketone (MAK), methylisobutyl ketone (MIBK), and n-butanol.(17) Concentrations of approximately 0.5 ppm typically are found for n-propanol, i-butanol, ethoxy ethanol, and 2-ethoxyethyl acetate. In addition, there is about 0.5 ppm of Solvesso®. Benzene was not included in this study because it is no longer a common constituent of paint solvent.

It is recognized that the composition and concentration of the solvents in each paint and each color of each paint varies, sometimes substantially.(6) This solvent mixture, however, was chosen to be investigated for the factors that affect the performance of the FTIR so that future work could be performed using actual workplace vapor samples.

Compounds used in this study are listed in Table I (arranged according to functional groups) along with their TLVs®, the limits of detection (LOD) determined in this study, and the sensitivity (instrument response per unit concentration of analyte) of the instrument for each compound.

The LOD is given for two situations. First, the LOD is given for each individual compound taken alone in air. In this case there is no possibility of interference from other solvent vapors. While this is not realistic in terms of actual painting operation workplace situations, it serves to give a point of comparison for LODs obtained for mixtures.

Second, the LOD is given for the simulated paint solvent mixture. These LODs were determined for each compound in the mixture by keeping the spectra representing a 2-ppm concentration of all compounds constant, except one for one component. That single component was decreased in concentration until the LOD was reached. This procedure was repeated sequentially for each component of the mixture.

Although there are several definitions for LOD in the literature,(19–21) the operational LOD achieved when using the LSF program was chosen for use in this and for previous studies.(15,22-24) LOD data given in the third column of the table are for analytes taken one at a time in the presence of ambient air without interfering organic vapors. In every case the LOD for individual compounds is much lower than the TLV for that compound.

The LOD could be, but will not necessarily be, higher if potentially interfering species are present. This was tested directly using the simulated paint solvent mixture. The LODs determined in the mixture are given in the fourth column of the table. In the case of the mixture, the LOD is still much lower than the TLV for each compound. The LOD in mixtures, however, is significantly higher than the LOD for individual compounds. The range of this degradation of LOD is from only 20% for p-xylene to a high of a factor of approximately 50 for n-butylacetate and 2-ethoxyethylacetate. Thus, the LOD for each compound must be determined for each mixture, except in cases in which the LOD is so far below the TLV or other relevant standard or guideline that there is no danger of a false negative result.

The response of an infrared instrument to an analyte usually is quoted in terms of absorptivity. Thus, an indication of the relative size of a peak is to be found in Table I under the column *Absorptivity.* This is given in units of absorbance per ppm per meter of pathlength × 10^{-4}. This is determined at the maximum absorbance wavelength for the peak chosen for quantitation.

It is likely that a peak with a large absorbance value will be characterized by a low LOD, but this is not necessarily a direct relationship. This is because spectral interferences and noise also play a large part in determining the value of the LOD. It is expected that the value of the absorptivity when measured at any concentration and pathlength will be constant so long as Beer's law is obeyed. (Sensitivity, absorptivity, and LOD are not the same, despite confusion of these three terms in common usage.)

Figure 1 shows the spectrum of the 12-component mixture used in this study in air containing about 300 ppm CO$_2$ and 45% humidity. The spectrum shown has all of the components present at 2-ppm concentration.

Figure 2, Tracing A, shows a close-up of the region of the mixture spectrum around 3000 cm^{-1}, the region where C-H bonds absorb infrared radiation. Thus, in this region, overlapping peaks are expected for all C-H-containing organic compounds. Tracings B–D show the details of that region of the spectrum for the 3 compounds that are quantitated in that region: ethyl benzene (B), methylisobutyl ketone (C), and n-butanol (D).

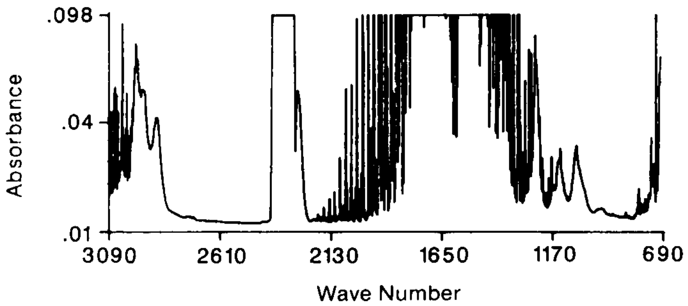

Figure 1—The spectrum of the 12-component mixture given in Table I (all components at 2-ppm concentration in air, spectrum taken at 2 cm^{-1} resolution).

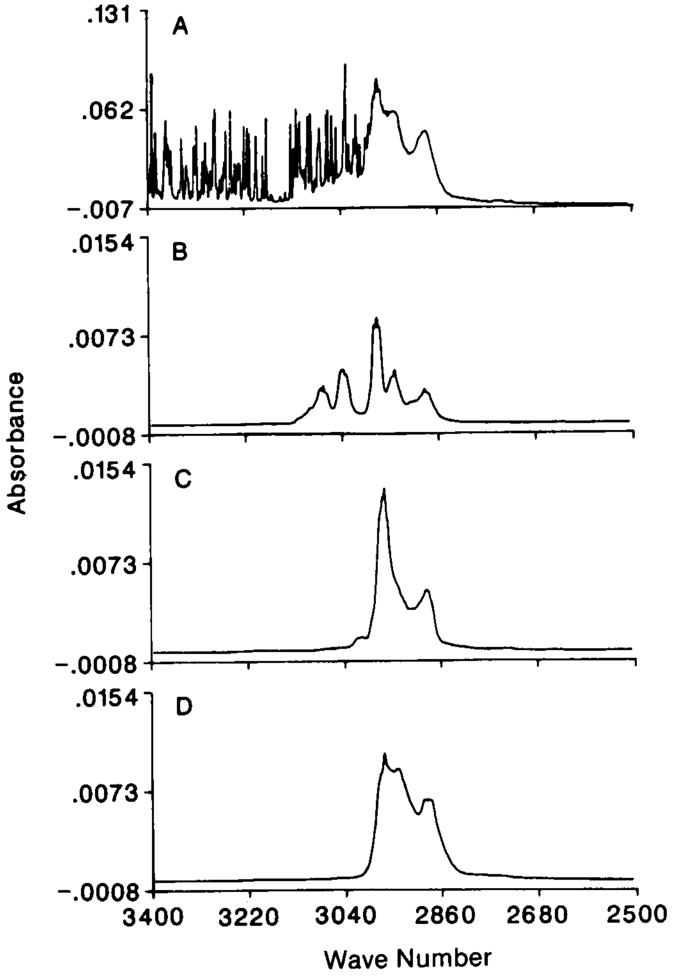

Figure 2—The portion of the spectrum containing the C-H absorption peaks (2-ppm concentration, 2 cm^{-1} resolution): (A) all 12 components in air, (B) ethylbenzene, (C) MIBK, and (D) n-butanol.

All of the peaks are overlapping, but the peak shapes are different. Also, the absorbance of the peak in Tracing A (the composite of all of the absorbances in this region from all of the compounds in this mixture) is about a factor of 10 higher than those of the three components quantitated in this region.

Despite this, those three components (ethylbenzene, MIBK, and butanol) are quantitated with an accuracy of ± 1.0%, 4.0%, and 1.4%, respectively. The LODs of these three compounds in the paint solvent vapor mixture are 0.5, 0.2, and 0.2 ppm, respectively. This means that these three solvents can be quantitated accurately using a completely overlapped peak in the presence of interferences, each of which is present at 10 times the concentration of those three solvents. This was demonstrated previously for liquids but not for gases in a study by Haaland et al.(23)

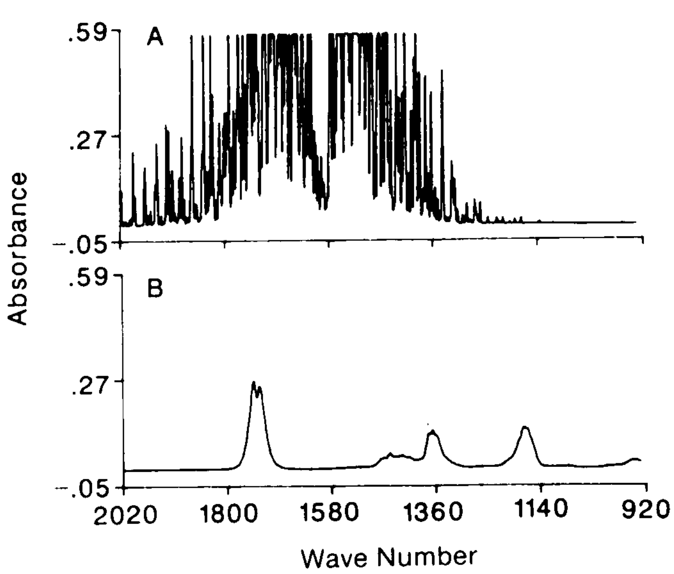

Figure 3—A portion of the ambient air spectrum containing water vapor peaks (Tracing A) and MEK peaks at 2-ppm concentration (Tracing B), both at 2 cm^{-1} resolution.

These data demonstrate the power of the LSF program. It is safe to say that these results could not be obtained without the LSF program, despite the high resolution capabilities of this instrument.

With the use of LSF, the 12-component mixture shown in Figures 1 and 2 was analyzed. All components returned values of better than within ± 4% of the true value, despite the strongly overlapped peaks used in some cases.

This was a fully-defined system, however. If components were present that were not defined in the LSF matrix, the results could have been in error. For example, if the LSF reference file contains only the spectrum of methylamyl ketone (MAK), but both MAK and methylethyl ketone (MEK) are present, the result for MAK will be a factor of 2 high (a 100% error). This effect of an underdefined LSF file varies according to the source of interference and thus must be determined individually for each case. Therefore, an LSF file cannot be established that is universal. This also was demonstrated by Haaland and Easterling(24) in a study of a 1:1:1 liquid xylene mixture in which a high error resulted when one of the xylene isomers was omitted.

The need to include water in the LSF file and to choose optimal peak windows with due regard for the spectrum of water vapor is illustrated in Figure 3. In Tracing A, a portion of the spectrum of water vapor is shown. In Tracing B, the spectrum of MEK is shown in that region. While the largest peak in the MEK spectrum (at 1686–1784 cm^{-1}) can be used, quantitation of MEK is limited to values above approximately 1 ppm because of the water vapor peaks. Therefore, the peak chosen for quantitation is the much smaller one at 1135–1220 cm^{-1}. The use of this smaller peak allows MEK to be quantitated accurately to values below 0.05 ppm. Note also the scale of MEK and water vapor absorbances. Thus, the regions covered by water vapor absorbance may be difficult to use for air monitoring of gases and vapors, although LSF can compensate for water interferences.

In this study, the optimal wavelength windows for quantitation were chosen using the same criteria as was used for the previously reported study(16) of the use of FTIR for single compounds in air. These optimal windows are given in Table II. In all cases, while the optimal windows were used for single compounds in air, either the same or different windows or spectral regions were chosen for quantitation of the components of mixtures (Footnote A, Table II).

In all cases, one of the reference spectra included in the mixture was that of background air which included CO_2 and water vapor as major constituents. This constituent (air) of the mixture also must have a window defined for the computer to use in its calculations. This is perhaps the single most important reference spectrum and window that is included in the LSF calculation for a mixture of gases and vapors in air. Thus, since water overlaps with the peaks of many constituents, the LSF file for mixtures of solvents may include a region of the spectrum that includes water peaks, rather than just a narrow spectral window.

In the case in which the air window was defined as being from 723 to 3013 cm^{-1}, a very wide window, accuracy of the system degraded. For butyl acetate, MAK, MIBK, ethoxyethyl acetate, ethoxyethanol, and n-butanol, accuracy ranged from ± 6% to 31%, which is unacceptable. Accuracy of

TABLE II
Solvents, Optimal Spectral Region for Quantitation, and Minimum Resolution for Compounds in a Mixture

Solvent	Optimal Spectral Region (cm^{-1})[A]	Minimum Resolution (cm^{-1})[B]
Toluene	724-762	16
o-Xylene	724-762	16
m-Xylene	746-790	8
p-Xylene	772-819	16
Ethylbenzene	2849-2992[C]	[D]
n-Butylacetate	1201-1288	16
i-Butylacetate	1211-1270	8
2-Ethoxyethylacetate	1197-1294	16
Methylethylketone	1135-1220	16
Methylpropylketone	1138-1209	16
Methylisobutylketone	2850-2983	16
Methylamylketone	1145-1190	8
Methanol	[D]	[D]
n-Propanol	934-1112	8
n-Butanol	2826-3013	8
i-Butanol	[D]	[D]
Ethoxyethanol	1103-1162[C]	[D]

[A] Peak window given for quantitation of only one component in the solvent mixture. For simultaneous quantitation of multiple components, use peak regions that include these windows.

[B] See cautionary notes in the text related to the use of the minimum resolutions quoted on this table.

[C] Measured during the study cited in Reference 16.

[D] Not measured in this study.

analysis of all other components of the mixture was still better than ± 2%.

In the case in which two smaller air windows were defined (723-1300 cm^{-1} and 2800–3100 cm^{-1}), all results were accurate to better than ± 2%. This strategy allowed the LSF program to compensate more accurately for local baseline shifts and decreased the number of data points that had to be processed for the air reference file from 2400 data points per sample to 900. This also saves processing time. Without exception, in each air monitoring case, the optimal reference file and windows for the air spectrum must be tested.

In this case, in which LSF can be used to quantitate up to 16 compounds simultaneously, qualitative analysis is done simply by default. If the components of the mixture are divided into two groups, aromatic and nonaromatics, the system correctly identified when all components of either of the two groups were or were not present.

It is always advantageous to use the lowest possible resolution (lowest means poorest) for IR instrumentation that can be used without loss of sensitivity and specificity. The lowest value for each compound is given in the last column in Table II. All of the values are either 8 or 16 cm^{-1}. This may allow the use of low performance instrumentation which will keep the cost of the instrumentation to a minimum. This also will result in savings in computer storage space and data manipulation time.

The effect of resolution on the spectral signal is illustrated in Figure 4, which shows the portion of the spectrum of o-xylene that is used for quantitation. Tracings A–D are that portion of the spectrum at 2, 4, 8, and 16 cm^{-1} resolution, respectively. The figure shows the degradation of the peak detail and height with poorer resolution. Despite this degradation of peak shape, o-xylene still can be quantitated at a resolution of 16 cm^{-1}.

Extreme caution must be used when using low resolution instrumentation, however, and when quantitating components of mixtures at these low resolutions. Preliminary work indicates that low resolution data may be more sensitive to the effects of underdetermined LSF files. Thus, a situation in which all components of a mixture are not defined by the instrument operator for the LSF file may result in significant errors in the quantitation of the components that are defined. This situation can arise either because of operator error or because there are airborne gases or vapors that are present that were not expected. Both of these situations can be expected to occur with sufficient frequency that it is prudent to use resolutions that are better than the minimum required resolutions listed in Table II.

In this study, most of the compounds' peaks are very broad, so lower resolution is sufficient for quantitative analysis. In cases in which compounds with narrow peaks are present, such as hydride and acid gases, better resolution generally is required.(14,15) Resolution effects have not been thoroughly investigated yet for multicomponent mixtures with both narrow and sharp peaks in air.

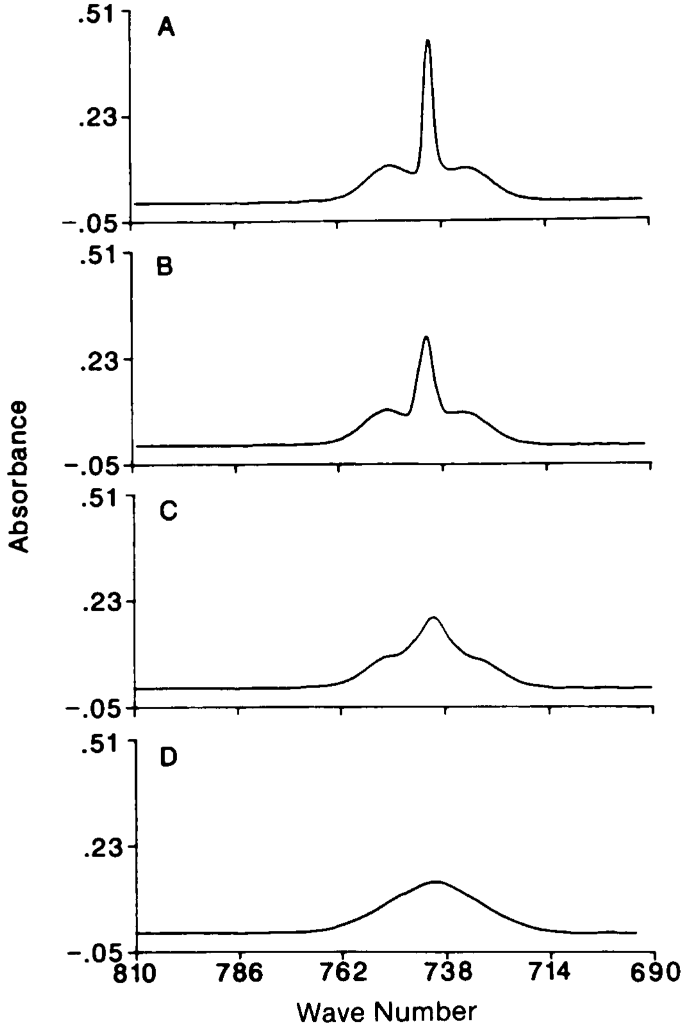

Figure 4—A portion of the spectrum of o-xylene (2-ppm concentration) at the following resolutions: A = 2 cm^{-1}; B = 4 cm^{-1}; C = 8 cm^{-1}; D = 16 cm^{-1}.

Conclusions

(1) FTIR shows promise for the quantitation of mixtures of components in paint spraybooth vapors. This study, however, does not encompass all possible mixtures. Thus, the FTIR should be validated for each application that is significantly different from this.

(2) Least squares fit (LSF) software can be used for the quantitation of strongly overlapped multicomponent mixtures.

(3) For mixtures of solvents with known composition, quantitation can be performed to levels far below the TLV.

(4) The issue of nonlinearity, presumably caused by wall adsorption effects, is still open for solvents at concentrations below about 0.5 ppm.(12,18)

(5) Additional operational parameters that must be considered include the questions of vapor phase versus aerosol-bound solvent concentration in the paint spray booth and the applicability of the use of remote sensing FTIR in place of the system (which uses a conventional gas cell) described in this study.

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