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Comparison of the Fourier Transform Infrared (FTIR) Spectrophotometer and the Miniature Infrared Analyzer (MIRAN®) for the Determination of Trichloroethylene (TCE) in the Presence of Freon®-113 in Workplace Air*

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Results obtained using the Fourier transform infrared spectrophotometer (FTIR) and the Miniature Infrared Analyzer (MIRAN®) for samples of workplace air containing trichloroethylene (TCE) were evaluated through comparison with results obtained when using a gas chromatograph (GC). The effects of instrument resolution, relative humidity, and sample storage stability were studied. Relative humidity was found to have no effect on the performance of the FTIR over the range studied. The effect of changing resolution is complex but is explained. The linear range of the FTIR is more than adequate for the concentrations encountered in the samples reported in this study. Interference from Freon® caused the TCE values to be high when the MIRAN was operated in the single-wavelength mode.

Many methods have been employed in monitoring hazardous gases and vapors in the workplace.(1) Several of these methods have been validated or evaluated by the National Institute for Occupational Safety and Health (NIOSH).(2) Gas chromatography (GC) is the most common method of analysis for air samples and for solutions eluted from adsorbent samplers.(2) GC is widely used because of its broad applicability, high accuracy, and precision. One of the few drawbacks of GC is that it is not normally a real-time method.

Within the past decade, there have been a number of important advances in the applicability of infrared (IR) instrumentation to the analysis of gaseous, liquid, and solid samples.(3-12) A number of IR instruments have been developed including filter, Fourier transform (FT), optical null and ratio recording grating, and tuned laser diode spectrophotometers. Most of these are computer controlled. The MIRAN® has seen the widest use in industrial hygiene air monitoring applications because it is moderately priced, fast, and convenient to operate.

The MIRAN may provide correct analysis results for certain gases or vapors in an atmosphere in which it is known that the target analyte can be determined without interference from other species in the sample.(13,14) Under some circumstances, results may not meet the ± 25% accuracy criterion set by the NIOSH Standards Completion Program.(15,16) If a MIRAN 980/981 is used, with its P-matrix, multiple wavelength capability, then precalibration to compensate for interferences is frequently possible.(17)

Unfortunately, for most applications, there are little data available in the peer reviewed literature which demonstrates that either the MIRAN or any other instrument has been validated for use in quantitative determination of analytes in either simple or complex mixtures of contaminants in either workplace air or air samples prepared in the laboratory.(1,2,9)

Recently, considerable effort has been expended to evaluate the Fourier transform infrared spectrophotometer (FTIR) for workplace air monitoring.(3-8) The use of least squares fit (LSF) software for spectral data interpretation(18) has shown itself to be particularly valuable in this respect. However, the FTIR is not yet a tool that is easily transportable or useable by the industrial hygienist.

In this study, air samples taken in Tedlar® bags in the workplace were analyzed in the laboratory by FTIR and MIRAN, and the resulting data were compared to those obtained via GC analysis of the same samples over a range of concentrations from 0.5 to 165 ppm (v/v).

The objective was to determine, in the simplest of situations, whether or not the IR methods were accurate and the cause(s) of inaccuracies that might be present. This exercise was necessary because the samples analyzed in previous studies(3-8) were almost all mixtures prepared for the purpose of analysis rather than actual workplace samples.

EXPERIMENTAL MATERIALS AND METHODS

Samples were collected in 20-L Tedlar bags using SKC Model 222-3,4 sampling pumps equipped with internal Teflon® tubing (SKC, Pittsburgh, Pa.) Samples were taken by industrial hy-

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gienists from the NIOSH Division of Surveillance, Hazard Evaluation and Field Studies, Hazard Evaluation and Technical Assistance Branch, Industrial Hygiene Section, and were in the Michigan laboratory within 24 hr of sampling. The volume of air in the bags ranged from 10 to 16 L.

All calibrations, and all standards prepared in Tedlar bags, were compared to ± 2% certified trichloroethylene (TCE) gas standards (Scott Specialty Gas Co., Troy, Mich.) which were available at 10- and 50-ppm concentrations.

The 1,1,2-trichloro-1,2,2-trifluoroethane (Freon®-113) standards were prepared by injecting microliter quantities of neat (100%) Freon (obtained from M. Puskar, Abbott Laboratories, Chicago, Ill.) into the gas dilution manifold (Figure 1) that had first been evacuated to <1 torr pressure. The increase in pressure within the manifold caused by the Freon injection was then measured with a precision pressure gauge. An identical procedure was used to humidify standards and samples. The operation of the manifold has been described in detail in other publications.(4,5)

The IR system gas cells were evacuated to <1 torr and purged with high purity nitrogen three times prior to sample introduction; flushed at approximately 100 torr with sample air two times; and then filled with sample at 740 torr. All assays were performed at 740 torr.

Method I (FTIR)

Spectra were acquired using an engineering prototype of the Nicolet 20 SXB instrument (Madison, Wis.), equipped with a 10-m gas cell and a mercury cadmium telluride (HgCdTe [MCT])/indium antimonide (InSb) sandwich detector (liquid nitrogen cooled) and LSF software, as previously described.(3-8) For each sample 32 co-added interferograms were taken at a resolution of 2 cm^{-1}. Background ratios were obtained versus nitrogen.

The reference spectra of TCE that were used for calibration of the FTIR were obtained by filling the gas cell with both 10- and 50-ppm standard gases at 740 mmHg, then scanning as described above. The lower concentration of TCE for calibration was obtained by reducing the pressure of the TCE standard in the gas cell to a value calculated to give the desired dilution, then refilling the cell with nitrogen or air to a pressure of 740 torr. Multiple dilutions were used to calibrate the FTIR over the range of concentrations studied. The pressure was always kept to a maximum of 740 torr to facilitate sample transfer and handling.

A series of TCE standard gases from 1 to 200 ppm were also prepared by adding a known amount of TCE liquid into a Tedlar bag filled with a known volume of air. These standards were compared to and normalized against concentrations measured from Scott certified gas cylinder standards of TCE at 10 and 50 ppm. These standards were transferred into the gas cells in order from the lowest to the highest concentration and then were analyzed by GC, FTIR, and MIRAN.

TCE and Freon-113 were quantitated using the 760-1150 cm^{-1} region of the spectrum. All spectra were analyzed using LSF software supplied by Nicolet Analytical Instrument Company.(18)

Method II (MIRAN)

IR spectra were obtained using the MIRAN-Foxboro 980-A (Foxboro Co., Foxboro, Mass.), which was equipped with a microcomputer and a 20-m variable pathlength gas cell. The 980 was operated in the single-wavelength mode, which simulates the operation of a MIRAN 1A/1B.

The MIRAN and FTIR gas cells were connected as shown in Figure 1. All standard dilutions and purges were accomplished using high purity nitrogen (99.9995%) as a diluent and purge gas.

There are three absorption maxima that can be selected for the quantitation of TCE in air. However, the 10.58-μm (944 cm^{-1}) peak overlaps with Freon-113, and the 12.78-μm (782.8 cm^{-1}) peak is inappropriate because of its low intensity and overlap with water peaks. The peak at 11.77 μm (849 cm^{-1}) is relatively free from either Freon-113 or water peaks, so it was used as the analytical wavelength. The portion of the spectral baseline at 4.0 μm (2500 cm^{-1}) was used as the reference wavelength to compensate for baseline shifts caused by detector and source drifting when analyses were performed without compensation for relative humidity changes. Compensation for changes in humidity was performed at the analytical wavelength for each target analyte by calculating the changes in absorbance that were caused by humidity changes.

Calibration was performed in the same manner as the FTIR. The data collected from the samples were in the absorbance mode, and the TCE concentrations were calculated by hand using the calibration curve.

The automatic P-matrix calibration capability of the instrument was not used. Instead, all calculations were performed using the absorbance data, assuming a single absorbance wavelength for the TCE.

Methods III and IV (GC)

Assays were performed on a Hewlett-Packard Model 5890 gas chromatograph equipped with 2.0 m Carbopack C/0.1% SP 1000 packed 1/8 in. o.d. stainless-steel column, HP 3392A integrator, and a FID (Hewlett-Packard, Avondale, Pa.). GC conditions were as follows: temperatures (°C)—column, 90°C; injector, 220°C; detector, 250°C and nitrogen carrier gas flow rate—40 mL/min.

For calibration of the gas chromatograph and for quantitation of the TCE in air samples by GC, 1 mL of gas was drawn

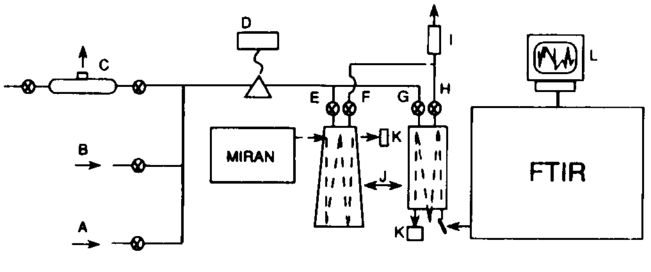

Figure 1—Schematic of the FTIR and MIRAN® inlet and gas cell systems: (A, B) sample, standard gas, and nitrogen inlets; (C) glass chamber where gas was drawn then injected into GC; (D) Pressure gauge; (E, F) MIRAN gas inlet and outlet; (G, H) FTIR gas inlet and outlet; (I) vacuum system; (J) multireflection, longpath gas cells; (K) IR detectors; (L) computer.

either from the IR gas cell manifold (Method III, or GC- manifold) or directly from the Tedlar bag (Method IV, or GC-direct) using 1.0 mL gastight syringes. This sample was injected into the gas chromatograph, which was fitted with a six-port valve (Valco, Houston, Tex.) equipped with a 100-μL gas sampling loop. Quantitation was accomplished by comparing chromatographic area of the samples with those of prepared standards.

Analysis of the Data

Both the Friedman test and the Student *t*-test were used.(19-21) The Friedman (nonparametric) test was applied to the results obtained from the five methods for analysis of TCE in air in order to test the null hypothesis that the samples had been drawn from the same population.

RESULTS AND DISCUSSION

Stability of the Sample in the Tedlar Bag

Prior to discussing instrument performance with workplace samples collected in gas sampling bags, the integrity of the samples must be ensured. The storage stability for samples of organic vapors in sampling bags has been previously investigated.(22-24) In this instance, the stability of the TCE, the principal target analyte, in the bags was of primary importance. It was found that 10 ppm TCE is stable in Tedlar bags at about 20% relative humidity over a period of at least 6 days. The recovery of TCE on Day 6 was 96% of that on Day 1. The recovery of the three spiked sample bags over the entire test period was 99% (± 3% at the 95% confidence level). Thus, sample integrity was assured.

Storage stability for Freon-113 in the Tedlar bags was not tested. However, since the boiling point of TCE is 87° C, and the boiling point of Freon-113 is 47.7° C, and TCE is stable in Tedlar bags, it is a reasonable assumption that Freon-113 would also be stable over the time period of this study.

Linearity of Results

As noted in the "methods" section, calibration of instruments was accomplished using both dilutions of gas cylinder standards performed in the manifold and standards prepared in gas sampling bags. The reason for using both of these calibration methods was to allow the calibration to be performed from high to low, and then from low to high, concentrations. (The manifold is only capable of providing standards from high to low concentration.) Nonlinearities have been observed with less volatile substances in previous tests.(7)

As shown in Figure 2, in the 1-200 ppm range, gas chromatography shows a linear relationship for the response versus concentration curve. For the gas chromatography, this was true for measurements of both peak height and area. For FTIR, a linear relationship exists between concentration and response up to 100 ppm, with a very slight decrease in response above that point (Figure 2).

However, for the MIRAN, when the concentration of TCE is greater than about 50 ppm, the relationship of absorbance at 11.77 μm (849.5 cm^{-1}) versus concentration is no longer linear (Figure 2). The manufacturer of the MIRAN recommends that a short IR pathlength must be used with high concentrations in order to keep the absorbance below approximately 0.5. Thus, the upper end of the linear range of absorbance that can be used with the MIRAN is lower than that of the FTIR.

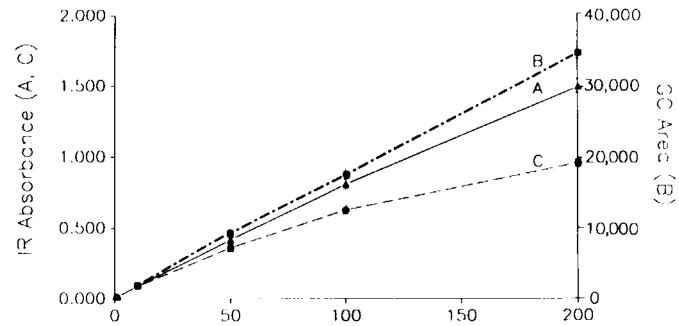

Figure 2—Calibration curves for trichloroethylene in air obtained for the FTIR (A) and MIRAN® (C) and compared to that obtained for the GC (B).

An optimal absorbance level of 0.434 for the quantitative analysis of traditional IR in presence of photometric error is well known. However, in the FTIR, photometric error is no longer a limiting factor, and the photometric noise has been reduced to such an extent that it is usually negligible in an analysis.(25)

While any MIRAN or FTIR can be equipped with a variable pathlength gas cell, this type of cell is more expensive and has a lower optical throughput than a fixed pathlength cell. Equally important is the fact that changes in pathlength must be accompanied by recalibration to ensure that accurate results are obtained.

Precision

To evaluate the analytical precision of the methods tested for gas analyses, 12 replicate TCE samples from gas cylinder standards at 10 ppm and 50 ppm were measured by FTIR, MIRAN, and gas chromatography. The procedure followed was the same as analysis of samples. The relative standard deviation (RSD) of the results obtained from FTIR, MIRAN, and GC for the standard containing 10 ppm of TCE in air was 1.14%, 0.53%, and 5.07%, respectively; at the 50-ppm concentration level, it was 1.12%, 0.36%, and 3.53%, respectively.

This demonstrates that the results obtained with the MIRAN are very reproducible, and the reproducibility of the results obtained with the FTIR is also acceptable. Repeatable results are only obtained for the FTIR if a new background spectrum is used for spectral ratioing at least twice daily. This could be a problem in a plant or hazardous waste site environment in which a clean background spectrum may be difficult to obtain. In such cases a stored, clean ambient air background sample could be stored for automatic reanalysis, or the spectrum of such a sample could be electronically archived for use as needed.

The RSD of results obtained when using the gas chromatograph was slightly higher than that obtained when using the two IR techniques. This may be caused either by inconsistent injection or by peak area integration techniques.

Resolution

The MIRAN is usually operated in a mode in which the resolution of the spectrum is approximately 1% of the wavelength. Expressed in wavenumbers (cm^{-1}), this means that at 700 cm^{-1}, the resolution is 7 cm^{-1}, and at 1300 cm^{-1}, the resolution is 13 cm^{-1} (700–1300 cm^{-1} is the usual range of wavelengths used to identify and quantify most organic vapors in air).

In contrast to this, the FTIR used in this study can acquire interferograms with a resolution of 0.5 cm^{-1}. These interferograms can be processed to yield spectra of poorer resolution. In this study, results at resolutions of 2, 4, 8, and 16 cm^{-1} were tabulated and compared (Table I). In this way the FTIR results can be evaluated at resolutions approximately equivalent to those used by the MIRAN.

When the results of the TCE analysis at the four resolutions are compared as a whole, no significant differences are indicated by the *t*-test. However, two sources of inaccuracy must be evaluated: first, the results obtained for Samples 10 and 15 show a trend to reducing concentration with reducing resolution. This can be explained by a reduction in linear range of the method at lower resolution, which manifests itself as apparent deviations from Beer's Law at high absorbances associated with these high concentrations.

Second, results from Samples 5 and 6 also show a decreasing trend of reported concentration of TCE with lower resolution. This effect is not subtle. In the case of these two samples, significant concentrations of Freon-113 are also present.

At 2 cm^{-1} resolution, the peaks caused by these two components can be easily resolved. As the resolution was degraded, the peaks appear to be merged. This is illustrated in Figure 3, which is the spectrum of TCE (Tracing A), Freon-113 (Tracing B), and Sample 5 (Tracing C) at the 2 cm^{-1} resolution used in FTIR procedures, and Sample 5 at 8 and 16 cm^{-1} (Tracings D and E, respectively), the resolutions closest to typical values used by the MIRAN.

When the resolution was degraded, the data points collected

TABLE I
Effect of Resolution on the Results Obtained when Using FTIR to Analyze Workplace Air Samples

	Trichloroethylene (ppm)			
Sample No.	**2 cm^{-1}**	**4 cm^{-1}**	**8 cm^{-1}**	**16 cm^{-1}**
1	0.55	0.53	0.52	0.50
2	1.44	1.42	1.41	1.39
3	1.06	1.06	1.05	1.04
4	0.48	0.45	0.44	0.42
5	0.54	0.00	0.00	0.00
6	1.19	0.25	0.21	0.00
7	2.60	2.63	2.63	2.63
8	3.55	3.58	3.58	3.58
9	3.50	3.52	3.52	3.52
10	165.80	165.28	152.02	130.04
11	1.85	1.21	1.21	1.20
12	1.20	1.85	1.84	1.84
13	0.83	0.83	0.82	0.82
14[A]	9.93	9.97	9.95	9.95
15[A]	49.27	49.22	48.80	47.43

[A] Numbers 14 and 15 are Scott certified standard gas of TCE at 10 and 50 ppm concentration, respectively.

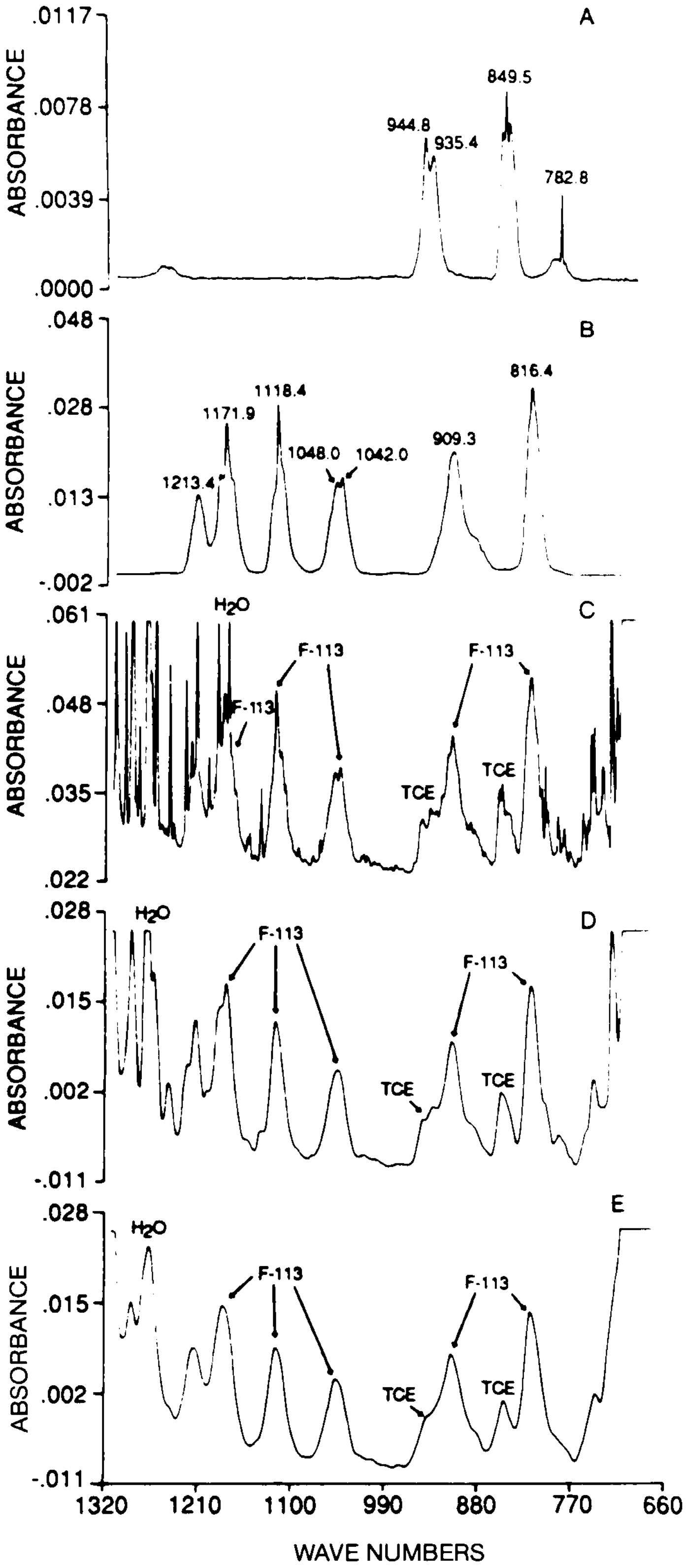

Figure 3—Illustration of the effect of decreasing resolution and peak overlap on the ability to define spectral details of TCE for a mixture of TCE and Freon®-113 in air. This figure also illustrates the effect of decreasing resolution on the apparent effect of water vapor. Tracings show infrared spectra as follows: (A) TCE (2 cm^{-1}); (B) Freon-113 (2 cm^{-1}); (C) Sample 5 (2 cm^{-1}); (D) Sample 5 (8 cm^{-1}); (E) Sample 5 (16 cm^{-1}).

to define the entire spectrum decreased, which led to the apparent merging of certain TCE and Freon-113 peaks. When the Freon peak is larger than that of the 944 cm^{-1} TCE peak, even the LSF algorithm attributes a significant portion of the small TCE peak to Freon-113 peak area at lower resolution. Therefore, in this case, better resolution is necessary in order to collect additional data points in the analytical window used by LSF.

Effect of Water Vapor

If not for the presence of peaks caused by water vapor, the mid-IR region of the spectrum could be used with minimal difficulty. Thus, it is likely that, in the absence of water peaks, IR methods probably would have been, for some time, the dominant methods of air monitoring in industrial hygiene.(9) Because of the intensity of water vapor peaks, only the regions of the spectrum between the main peak envelopes are normally used for air monitoring applications. Since minor water peaks extend throughout the spectrum, resolution of 2 cm^{-1} or better is frequently recommended for certain air monitoring applications.(4,5)

In the case of air monitoring for TCE or Freon-113 in the concentration range of the threshold limit value (TLV®)/10 or greater, the effect of water vapor at 2 cm^{-1} resolution or higher is still trivial, but it becomes important at lower concentrations of TCE. For TCE, as the resolution of the spectrum decreases to the range 4–8 cm^{-1}, the effect of water apparently decreases because of the decrease in apparent intensity of the water peaks. This reduction in water peak intensity will apparently be greater than that of the analyte peaks if the analyte is an organic vapor. This is because the peak widths of most organic vapors are far wider than those of water.

In Figure 3, Tracing C, water peaks are strong and sharp and overlap with two Freon-113 peaks at 1213 and 1172 cm^{-1}. This is a common phenomenon in the region between 1320–1100 cm^{-1} when data are gathered at 2 cm^{-1}. When at 8 or 16 cm^{-1} resolution, Tracings D and E, these water peaks are apparently unimportant compared to the Freon-113 peaks. (The spectrum shown is that of Sample 5.) However, some narrow (water) peaks will merge with adjacent, large Freon-113 peaks, thus increasing the difficulty of interpretation of the spectrum for the purpose of qualitative analysis. Also, this may lead to errors in quantitative analysis, especially based on the one-point (at the peak maximum) measurement method. This is true even in the 700–1300 cm^{-1} region normally used for such assays.

This effect was investigated for TCE at 10 ppm in air (Figure 4). For the FTIR when used to monitor TCE at 2 cm^{-1} resolution, there is no measurable effect of relative humidity over the range that would be equivalent to 0–75% relative humidity at ambient pressure. This is true either with or without the spectrum of water added to the reference file of the LSF program.

For the MIRAN, operated in the single-wavelength mode, the positive bias of the results were as great as 15% at 75% relative humidity. This is apparently caused by a baseline shift compared to the baseline used for the calibration standard at 0% relative humidity.

If the effect of baseline shift is compensated as a function of the humidity at the analytical wavelength used for the TCE, then there is no significant shift of the results obtained with the MIRAN over the range of humidities studied. This correction for baseline shift must be performed for the MIRAN even in the absence of apparent water peaks in the area of interest, or significant errors may occur.

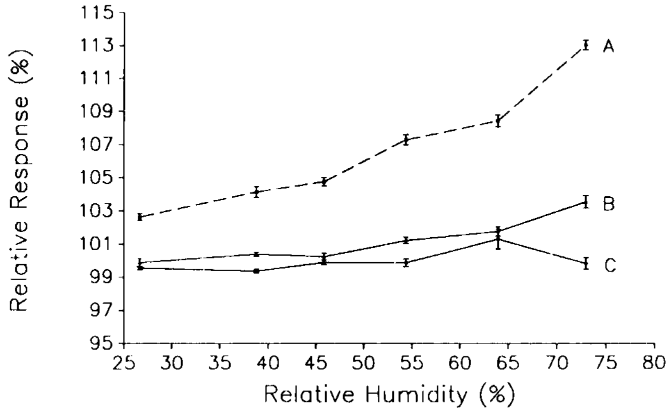

Figure 4—The effect of changes in relative humidity (RH) on results of the analysis of TCE in air samples using FTIR and MIRAN®. Tracing A: MIRAN calibrated at 0% RH and operated at the indicated RH; Tracing B: MIRAN calibrated as above but baseline shift caused by changes in RH compensated at the analytical wavelength of TCE; Tracing C: FTIR calibrated at 0% RH and operated at the indicated RH.

This inaccuracy could be compensated by either always calibrating the MIRAN at the same relative humidity by storing the values of the bias in a background register which would be accessed when the relative humidity of a sample is known prior to the calculation of the results. This use of a background library accessed for zero and calibration purposes has been pioneered by Kroutil(26) and Small et al.,(27) who have concluded that 3000 complete atmospheric background spectra taken at various temperatures and humidities are adequate for such purposes for FTIR-remote sensing applications on the battlefield.

For multiple wavelength MIRAN systems with P-matrix capability (such as the MIRAN 980 operated in the P-matrix mode), water can be incorporated as a component into the calibration in order to compensate for differences in humidity between samples.

Comparison of the FTIR, MIRAN, and GC

To assure that the three instruments actually analyzed the same samples, each sample was introduced into the sample manifold that distributed the vapor to the gas cells in an equivalent fashion (Figure 1). In addition, in order to assure that the gas chromatographic results were accurate, those assays were performed on the samples from the gas manifold as well as on samples taken directly from the Tedlar bag by syringe and injected into the GC.

Thus, in Table II, the results of five assay methods are given: (1) GC with injection of a sample taken from the manifold of the IR systems (GCM); (2) GC with direct injection of the samples from the sample bags (GCD); (3) FTIR; (4) MIRAN without compensation for atmospheric moisture (MIRAN1); and (5) MIRAN with compensation for moisture (MIRAN2). In addition, the concentration of Freon-113 in each sample is given.

In Table II, the data show that the measured concentration of TCE ranged from 0.5 to 170 ppm. The measured concentration of Freon-113 was from nondetectable to 7.7 ppm. All results

TABLE II
Tabulation of Results Using Chromatographic and Infrared Spectroscopic Methods for Analysis of Workplace Air Samples for Trichloroethylene and Freon®-113

Sample Number^{A}	Trichloroethylene (ppm)^{B} Gas Chromatography Manifold	Direct	Infrared Methods FTIR	MIRAN1^{C}	MIRAN2^{D}	Freon-113 (ppm)^{B} FTIR^{E}
1	0.47	0.60	0.55	1.34	0.72	0.45
2	1.52	1.07	1.44	1.86	1.24	0.33
3	1.16	1.13	1.06	1.83	1.20	0.16
4	0.44	0.40	0.48	1.24	0.61	0.48
5	0.63	0.67	0.55	1.46	0.91	7.21
6	1.15	1.27	1.19	2.16	1.55	7.74
7	2.69	2.80	2.60	3.39	2.77	ND^{F}
8	3.60	3.93	3.55	4.30	3.70	ND
9	3.78	3.80	3.50	4.27	3.64	ND
10	174.1	179.8	165.8	95.6	95.3	ND
11	2.30	1.13	1.85	2.44	1.81	ND
12	2.97	2.00	1.20	1.66	1.03	ND
13	1.06	0.95	0.83	1.49	0.90	ND

^{A}All samples were taken in Tedlar® bags as general area samples.

^{B}All the results are the average of three measurements.

^{C}Calibrated at 0% relative humidity.

^{D}Compensated for baseline shift caused by humidity.

^{E}Freon-113 analyzed by FTIR only.

^{F}Not detectable = ND < 0.12 ppm Freon-113, in the presence of 1 ppm of TCE.

given in the table represent the mean of three replicate analyses. These data were evaluated using both the Friedman and *t*-test methods. Analysis of these data using NIOSH Overall System Accuracy (OSA) calculations were not performed because such calculations usually require a greater number of samples and replicates than could be accomplished with the available samples.(15,28)

The single sample with a concentration of >100 ppm was not included in this statistical analysis, because it was out of the linear range of the MIRAN instrument under the conditions used for this test.

The principal reasons for the high value for the MIRAN results obtained for Samples 5 and 6 are the high levels of Freon-113 found in those samples. The spectra obtained with the FTIR of TCE (Tracing A) and Freon-113 (Tracing B), and that of Sample 5 (Tracing C) are shown in Figure 3 at 2 cm^{-1} resolution.

Note also, that for Samples 1, 4, 5, and 6, in which the concentrations of TCE and Freon-113 are approximately equal, the results obtained with the MIRAN, even after compensation for humidity, are always high. While this does not constitute proof, it does add credence to a cautionary note relating the use of the MIRAN in the single-wavelength mode for monitoring of target analytes in the presence of potential interferents.

If these samples had been analyzed in the multiple wavelength mode with the P-matrix capability of the MIRAN 980, the error in the TCE results caused by Freon interference may been reduced or eliminated.

If these samples had been analyzed using the FTIR without having Freon-113 included in the calibration set for the LSF software, the results might have shown a high bias because of interference from Freon-113. The degree of bias would have been a function of the location and width of the spectral window chosen for TCE analysis.

CONCLUSIONS

In this study, the FTIR and MIRAN methods were compared with the GC for analyses of trichloroethylene in workplace air. Some of the samples had Freon-113 vapor present as a potential interferent. Results obtained when using these methods were tested by the Friedman and paired *t*-test methods.

These results demonstrate the following conclusions for analysis of samples performed in the laboratory under the conditions and sample types described in this test.

(1) High TCE concentration values found in this test for the results obtained with the MIRAN, when the MIRAN was operated in the single wavelength mode, were caused by the presence of Freon-113.

(2) The linear range of the GC and FTIR is wider than that of the MIRAN. Therefore, when the concentration of certain analytes approaches the 50–150 ppm range, readjustment of the gas cell to a shorter pathlength is recommended for the MIRAN.

(3) A change in relative humidity can cause a shift of the baseline of the MIRAN. Especially, when the concentration of the analytes is low, the background used during the calibration of the MIRAN should be carefully chosen to match the relative humidity of samples.

(4) The precision of both the MIRAN and the FTIR were more than adequate for these assays.

(5) Degradation of resolution from 2 to 16 cm^{-1}, in this study, does not show significant effects on the results for most of the samples. However, when the sample contains potential interferents, the higher resolution is necessary in order to obtain accurate results.

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