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# A Transportable, Remote Sensing, Infrared Air-Monitoring System*

*H.K. Xiao*[a,b]
*S.P. Levine*[a]†
*W.F. Herget*[c]
*J.B. D'Arcy*[a,d]
*R. Spear*[e]
*T. Pritchett*[f]

[a]The University of Michigan, School of Public Health, Ann Arbor, MI 48109-2029; [b]Beijing Medical University, School of Public Health, Beijing 100083, Peoples Republic of China; [c] Nicolet Analytical, 5225-1 Verona, Madison, WI 53711; [d]General Motors Corp., Research Laboratories, Biomedical Science Department, Warren, MI 48090; [e]University of California, School of Public Health, Berkeley, CA 94720; [f]U.S. Environmental Protection Agency, Environmental Response Team, 2890 Woodbridge, Edison, NJ 08837-3679

*A transportable, remote sensing instrument has been built that is capable of performing real-time quantitative analysis of gas and vapor contaminants of workplace air. The emphasis in this system is on simplicity and sensitivity for use over pathlengths of up to 40 m. A method was developed to overcome the effect of nonanalyte species present in the background spectrum on the quantitation of analytes in the sample spectrum. In addition, results demonstrated that instrument response was proportional to the beam pathlength under homogeneous concentration conditions. The application of software capable of qualitative analysis was also demonstrated.*

In the early 1970s, papers appeared in the literature on the investigation of remote sensing of airborne emissions (ROSE).[1] ROSE methods held out the promise of monitoring systems that could "look across" environmental sampling sites, or the workplace, and "see" the air contaminants,[2] as well as see air contaminants coming out of smokestacks.[3]

The first ROSE Fourier transform infrared (FTIR) air-monitoring system was described in the peer-reviewed literature in 1979[4] and then again in the "open" (nonpeer-reviewed) literature in 1982.[5] However, the literature revealed two major weaknesses of this technology. First, these instruments filled up a converted "library-on-wheels" vehicle, making the technique mobile but certainly not portable, and secondly, the data analysis was off-line and depended on an experienced spectroscopist's interpretation.

From the mid-1970s into the 1980s, the use of FTIR, without remote sensing, but instead with the use of a closed gas cell into which the sample was pumped, was explored for environmental air,[6] automotive exhaust,[7] and workplace air samples.[8] By using the classical least squares fit (LSF) data analysis methods of Haaland,[9,10] the FTIR with a closed gas cell proved to be an applicable method for the quantitative analysis of complex air samples of known composition.[11–14]

In the late 1980s, the use of ROSE-FTIR was first revealed as a technique for remote sensing of chemical warfare agents in the air over a battlefield.[15,16] In the last few years, several groups have begun experimentations with ROSE-FTIR[17] and differential absorption laser (DIAL) systems for the remote sensing of pollutants at hazardous waste sites as fenceline emergency chemical-release monitors.

The first such study at a hazardous waste site, a joint effort in 1987 between the Environmental Protection Agency/Environmental Response Team (EPA/ERT) and the University of Michigan, resulted in the definition of questions of instrument stability under field conditions and problems with aiming of the beam over long (km) distances.[18] EPA reports specifically focused on the applicability of ROSE technology to hazardous waste site investigations.[17,19,20] However, the ROSE systems used in these studies have had certain drawbacks: some, such as the high-resolution system used by Spartz et al.[17] have been large, needing full-sized step vans or 42-ft mobile homes for transportation.

Another problem that has slowed the application of ROSE systems is the difficulty in selecting an appropriate background spectrum. FTIRs are single-beam instruments; for them to be successful in identifying and quantifying contaminants in air, a valid IR background spectrum must be obtained from analyte

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†Author to whom inquiries should be sent.

and nonanalyte interference-free air. For the purpose of this discussion, *analyte* means an air contaminant for which the hygienist wishes to obtain air concentration information; a *nonanalyte* is also an air contaminant, but one of no importance to the hygienist in the monitoring being carried out; *interference* is a nonanalyte that may cause erroneous results in the quantitative analysis of the analyte.

One approach used has been to equip the instrument with an internal long-path gas cell filled with interference-free air, or purified nitrogen, in order to obtain a background spectrum.[18] With this arrangement, the beam would be diverted to the internal cell for the background spectrum. Such a background would contain information about the spectrometer optics, IR source, and detector. However, the background measured with the internal cell does not take into account variations in background caused by beam alignment and performance of remote instrument modules. Additional drawbacks to the use of an internal gas cell are that the size and cost of the instrument are increased.

To solve this problem, a background spectral database may be used to match a sample spectrum. In this case, there is an assumption that the background spectra are free of contaminants that could interfere with the analysis. However, this is not always the case for background spectra obtained in the workplace. Workplace air samples, even those taken upwind of the process or work station to be monitored, may contain air contaminants that may interfere with the analysis of air samples. This may be a significant problem if the instrument is not equipped with an internal cell and a background spectrum is obtained by using the ROSE beam from air that may be neither analyte-free nor nonanalyte-free. This is true even when using LSF if spectral features of those nonanalytes overlap with those of the analytes or cause significant changes in the baseline in the analytical region. Because, in a workplace or in the environment, it is usually not possible to control the concentrations of all nonanalytes with spectrally absorbing features, this problem must be overcome if LSF is to be utilized.

Because of the lack of applications of ROSE systems to monitor contaminants in the workplace, it is not surprising that even the most recent edition of the American Conference of Governmental Industrial Hygienists' *Air Sampling Instruments*[21] does not mention remote sensing instruments. Recently, a paper was published that described how a remote sensing instrument might be used in a workplace where the concentrations and concentration gradients of air contaminants would be constant over the time scale required to completely "crisscross" the workplace with beams.[22]

The ROSE-FTIR instrument described in this study is theoretically capable of performing data acquisition for approximately one complete quantitative analysis per second. If the beam were moved around the workplace with a digital stepper motor-controlled aiming mirror, the most important paths within an entire workplace or emergency response site could be traversed in under a minute.

However, in practice, each beam configuration, data acquisition, and analysis sequence will take 1–2 min rather than 1–2 sec. This is because, in actual use, the instrument noise is reduced in proportion to the square root of the number of scans. For example, the instrument response is eight times less noisy if 64 scans are acquired and co-added to give one result versus the result that would be obtained with one scan.

An aspect of the use of remote sensing systems in practice relates to the relevance of the beam measurement to industrial hygiene data requirements. In essence, the ROSE-FTIR measurement gives the spatial average concentration of one or more contaminants along the beam path, temporally averaged over the time required to achieve an acceptable signal/noise ratio. For use in the leak detection/alarm mode, the beam, with its flexibility in tailoring the path-to-source geometry, would appear to have clear advantages over fixed-position area monitors. The long-term potential of tomographic applications, on the other hand, is technically appealing, but it is not clear to what extent practical industrial hygiene needs would be met by a knowledge of the average concentration field.

In this paper, the design and applications of a small, transportable ROSE-FTIR system designed specifically for use in the workplace are described.

An LSF method is presented that is designed to overcome the problem of background spectra contaminated by nonanalytes. The results support the conclusion that the ROSE-FTIR method is appropriate for the direct quantification of multicomponent mixtures of airborne gases and vapors at the ppm concentration level.

## DESCRIPTION OF REMOTE SENSING INFRARED AIR-MONITORING SYSTEM

The prototype system, which is called the "Baby-ROSE," is contained in three modules: an IR source/optical bench, an IR receiver/detector, and a portable MS-DOS computer. The IR source/optical bench weighs 16 kg and measures approximately 20 cm × 48 cm × 36 cm. The IR source is an air-cooled globar operating at 1300 K. The interferometer is designated as a Model ST-1, which is a simplified version of the Nicolet 5-DX system that was used on the Army XM-21 battlefield ROSE-FTIR.[15] It contains a "porch swing" interferometer capable of up to 2 $cm^{-1}$ resolution at scan speeds as high as 2 scans/sec.

A He-Ne laser of 3 mW power is used for two purposes: (1) to track the moving mirror in the interferometer and (2) to help with aiming the IR beam across the workplace. To aid in the accurate aiming of the IR beam, which is invisible to the naked eye, the visible He-Ne laser beam emerges from the source/optical bench module in a manner that is coaxial with the IR beam. The laser beam has an intensity of 260 $mW/cm^2$ at 1 m distance from the instrument, so protective glasses are not needed. Additionally, the software has a routine that allows easy aiming of the beam with the capability of a real-time visual and audio output to aid the instrument operator in alignment.

The receiver/detector module consists of an 8-in. diameter Cassagrain telescope equipped with first-surface, aluminum-coated mirrors and a 3-in. diameter convex spherical secondary mirror. The IR detector is liquid nitrogen–cooled HgCdTe (MCT) with an image area of 1 $mm^2$. The receiver/detector is mounted on an aluminum plate and also weighs 16 kg. Dimensions of this module are 28 cm × 38 cm × 36 cm with a 30-cm × 25-cm extension on the telescope cover. The electrical requirement for the complete instrument is <10 A of 115 V electrical service.

Mirrors may be used to direct the IR beam around the workplace. These mirrors are 1-ft$^2$, square, first-surface, aluminum-coated mirrors. The source/optical bench module and the IR receiver/detector module may be mounted on tripods.

The computer is a Dell Computer (Austin, Tex.) 310 20-Mhz 80386 system with an 80387 coprocessor, a 150-Mb hard drive, 4 Mb of RAM, a Dell VGA-Plus color card for use with a NEC Multisync II color monitor, a Nicolet Instrument (Madison, Wis.) Fourier transform coprocessor board, and a Nicolet analog/digital controller board. Software is Nicolet PC/IR, modified for use with a ROSE system. As noted above, the system software was modified to produce a visual and audio output that indicated the accuracy of the aim of the IR beam from the IR source module to the detector module.

Diagrams of the Baby-ROSE in two configurations, a straight line and an "M," are shown in Figures 1 and 2. The actual configurations used would be a function of the shape of each individual work station or emergency response site.

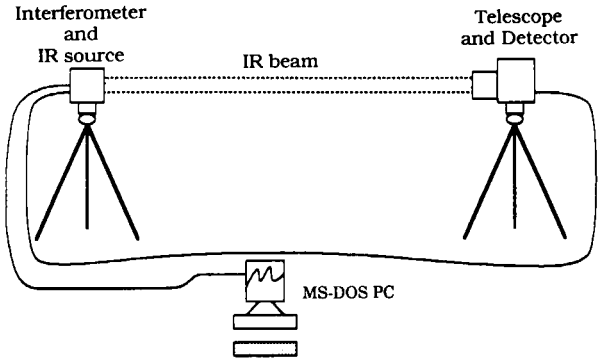


*FIGURE 1. Baby-ROSE with the beam in a straight-line configuration. Note that the visible "aiming" laser beam is coaxial with the IR beam.*

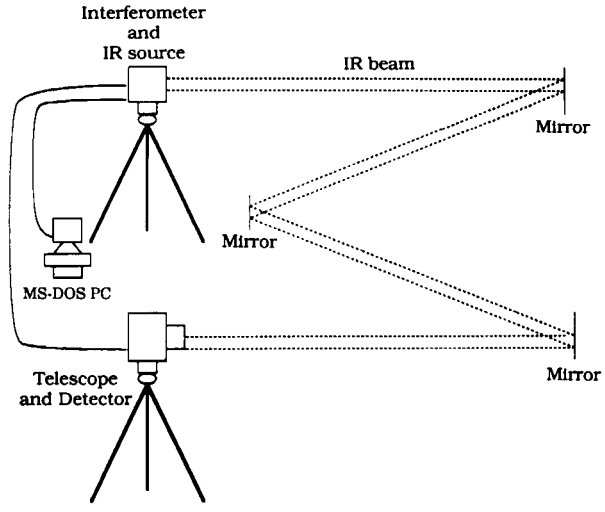


*FIGURE 2. Baby-ROSE, using three mirrors, with the beam in an "M" configuration*

The IR beam that emerges from the source module is roughly elliptical in cross section, with an initial height of 3.8 cm and a width of 2.5 cm, and has a beam divergence of 2.5 cm/m. Thus, if the beam path exceeds 7 m, some of the IR beam will not be captured by the receiver telescope. At all pathlengths greater than 3 m, the center of the beam is blocked by the secondary mirror in the receiver telescope.

## *Spectra*

### *Response versus Pathlength*

For the test of the response of the ROSE system to acetone at various beam pathlengths, the acetone was evaporated into the inlet plenum of an exposure room and diluted to the 10-ppm concentration level with a flow of humidified ambient air. The IR beam of the ROSE system was directed into the room, and the spectrum of the unknown vapor mixture was acquired at a resolution of 2 $cm^{-1}$. Background spectra were obtained from the ambient air in this exposure chamber prior to the evaporation of the solvent. The concentration was confirmed with a total hydrocarbon (THC) monitor equipped with a flame ionization detector (FID).

### *Baseline Correction*

For the test of the baseline correction software, two mixture spectra, with vapor concentrations of five and six components, respectively, at 1, 5, and 10 ppm each, were synthesized by electrically adding library spectra, instrument noise, and water and $CO_2$ in concentrations normally seen in workplace air sample spectra. (The components included in these spectra are listed below.) The library spectra, noise, and water and $CO_2$ spectra had been collected for previous studies[13,14] at a resolution of 0.5 $cm^{-1}$ and then deresolved to a resolution of 2 $cm^{-1}$ for this study. Reference standard spectra used for quantitative analysis were different from those with which the mixture spectra were synthesized.

Background spectra were also synthesized. These spectra either contained the spectrum of the vapor of one of seven compounds or the spectrum of the mixture of all seven compounds. The concentration of each component (listed below) in the background spectrum ranged from 5 to 0.5 ppm. For the calibration of the LSF system, the positive spectra of library standards were used for the analyte mixtures, and the negative spectra of library standards were used for the interferences.

### *Identification of Unknowns*

For the test of the iterative LSF software's ability to identify the components of a mixture of air contaminants, a five-component mixture of organic vapors was generated by evaporating a commercial liquid paint stripper into the inlet plenum of an exposure room and diluting the vapors to the 1–10 ppm concentration level with a flow of humidified ambient air. The IR beam of the ROSE system was directed into the room, and the spectrum of the unknown vapor mixture was acquired at a resolution of 2 $cm^{-1}$. Background spectra were obtained from the ambient air in this exposure chamber prior to the evaporation of the solvent.

## RESULTS AND DISCUSSION

### *Instrument Response versus Beam Pathlength*

Data shown in Table I demonstrate that the instrument response is linear with increases in beam pathlength. The same results were obtained when the pathlength of the IR beam was between 3.7 and 13.6 m. Replicate measurements, which were

**TABLE I. Concentration of Acetone in a Large Room Measured with the ROSE-FTIR at Different Beam Pathlengths**

| Pathlength[A] (m) | N[C] | Concentration[B] By ROSE-FTIR (ppm) | RSD[D] (%) | By THC-FID (ppm) | RSD[D] (%) |
|---|---|---|---|---|---|
| 3.7 | 10 | 10.0 | 3.2 | 10.3 | 7.3 |
| 4.0 | 12 | 10.1[E] | 1.62 | 11.2 | 6.5 |
| 6.8 | 10 | 10.9 | 0.78 | 10.1 | 7.2 |
| 12.0 | 6 | 10.0[E] | 0.58 | 10.9 | 5.6 |
| 13.6 | 10 | 9.3 | 0.73 | 9.4 | 1.2 |

[A]Distance that the IR beam traveled from the source to the detector.

[B]Concentration maintained at uniform and constant value across the beam path during experiments.

[C]Number of replicate measurements.

[D]Relative standard deviation (SD/conc).

[E]Concentration normalized to 10 ppm for purposes of comparison. Actual concentration was 8 ppm.

taken both with the ROSE-FTIR and with a total hydrocarbon (THC) analyzer equipped with a flame ionization detector (FID), demonstrated that the results obtained by using the beam were reproducible. This indicates that the measurement of the concentrations of acetone in ambient air with the ROSE system at different pathlengths obeyed the Beer-Lambert law (the instrument response, holding concentration constant, was directly proportional to the beam pathlength).

The instrument was designed for use with pathlengths of up to 40 m. If pathlengths longer than 40 m are required, a second reflecting telescope, mounted at the IR source, would be needed. This telescope would collimate the IR beam and reduce beam spreading. However, it also would increase instrument size, weight, and cost. The additional telescope would be needed, for example, for plant downwind fenceline air-monitoring applications. In that application, a sudden release of gases or vapors from a plant production process might be sensed and quantified by the beam along the downwind fenceline, and an alarm might be sounded.

### *Identification of Unknown Air Contaminants*

The ability to identify unknown gases and vapors in air is an important advantage of this system. In order to accomplish this task, iterative least squares fit (ILSF) software, developed by the authors, may be used. This ILSF method allows identification of unknown compounds in the air.[23]

Briefly, in order to perform quantitative analysis of spectral data by using LSF methods, the identity of the compounds in the mixture must be input into the program prior to analysis. When using ILSF, the identity of the compounds need not be known prior to analysis. However, the compounds in the mixture of unknowns must be present in the IR spectral library accessed by the ILSF program. To date, the ILSF program has been tested by using a maximum of 64 compounds in the spectral library and up to 11 components in the spectrum of the sample containing unknown species.

In order to obtain quantitative results from either LSF or from ILSF, both the identity and concentration of the spectra used for calibration must be input into the system.

A criticism of this requirement (that the spectra of the unknown air contaminants be present in a library of spectra accessible by the ILSF software) could be that this requirement means that the method does not really represent "identification of unknowns." However, this same criticism could be directed at the spectral library used in mass spectrometry, the list of retention times used in gas chromatography, or even the list of color changes used in colorimetric methods. Thus, virtually all commonly used qualitative analysis methods require some library-based information for their operation. Although identification of unknowns could be accomplished from "first principles" by using the mass spectral fragmentation pattern of the unknown, the retention time versus boiling point relationship for a homologous series that uses gas chromatography, the series of color change reactions used in colorimetry, or the functional group IR frequency correlation charts available to IR spectroscopists, these methods are far less powerful than library-based qualitative analysis.

An example of the use of this software is shown in the spectrum in Figure 3. This is the ppm–concentration level vapor from a commercial furniture stripper. This vapor mixture was introduced into an exposure chamber in which the FTIR system was operating. The fact that the investigator had no information about the identity of the components of the vapor had no bearing on the results, because once it was started, the ILSF program functioned with no operator interaction. However, as explained above, at the time of this specific experiment, the ILSF program

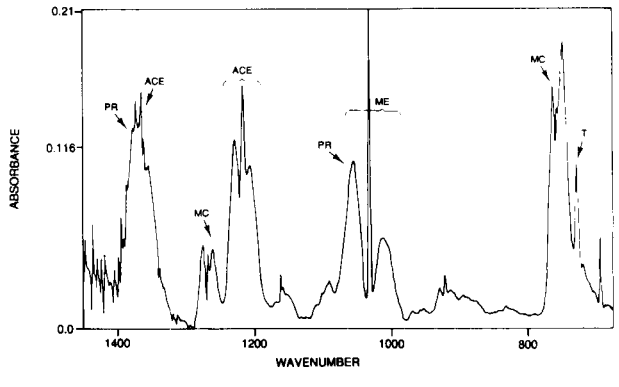


*FIGURE 3. Spectrum of the ppm–concentration level vapors of a commercial furniture stripper. Components of the mixture are MC = methylene chloride, ACE = acetone, PR = 2-propanol, ME = methanol, and T = toluene. Note that peaks and peak envelopes are strongly overlapped.*

**TABLE II. Comparison of Quantitative Results Obtained by Using Three LSF Methods[A]**

| Analytes (across) / Interferents[E] (down) | Recovery (%) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Method 1[B] | | | | | Method 2[C] | | | | | Method 3[D] | | | | |
| | Tol[F] | Ben | Ace | VCM | MIBK | Tol | Ben | Ace | VCM | MIBK | Tol | Ben | Ace | VCM | MIBK |
| F11[F] | 140 | 128 | 161 | 429 | 103 | 103 | 97 | 101 | 92 | 101 | 100 | 101 | 102 | 119 | 99 |
| F12 | 192 | 37 | 169 | 0 | 80 | 46 | 92 | 160 | 235 | 81 | 102 | 102 | 98 | 96 | 104 |
| Ald | 98 | 117 | 106 | 97 | 107 | 93 | 112 | 117 | 113 | 103 | 101 | 94 | 98 | 101 | 98 |
| Hex | 699 | 210 | 119 | 126 | 0 | 131 | 7 | 94 | 37 | 111 | 103 | 97 | 99 | 99 | 105 |
| Ace | 100 | 100 | 7 | 100 | 100 | 105 | 110 | 0 | 108 | 97 | 100 | 100 | 7 | 100 | 100 |
| MCB | 38 | 110 | 107 | 111 | 108 | 0 | 300 | 101 | 76 | 112 | 90 | 102 | 101 | 102 | 101 |
| DCA | 64 | 113 | 87 | 78 | 103 | 61 | 121 | 92 | 84 | 102 | 79 | 114 | 92 | 87 | 102 |
| ALL[G] | 45 | 221 | 154 | 310 | 0 | [H] | | | | | 91 | 99 | 0 | 97 | 116 |
| Mean | 172 | 130 | 114 | 156 | 75 | 77[I] | 120[I] | 95[I] | 106[I] | 101[I] | 96 | 101 | 98[J] | 100 | 103 |
| RSD | 219 | 60 | 52 | 141 | 47 | 44 | 88 | 48 | 62 | 10 | 8 | 6 | 4 | 9 | 6 |
| Pooled mean (RSD) | 129 (122) | | | | | 100 (55)[I] | | | | | 100 (7)[J] | | | | |

[A]The concentrations of components in both sample and background spectra are 5 ppm.

[B]Traditional LSF quantitative method was used. There are two broad IR analytical windows: 3200–2700 $cm^{-1}$ and 1400–700 $cm^{-1}$.

[C]Traditional LSF quantitative method was used. The window(s) where the negative peak(s) were located were excluded from the broad IR analytical windows. Depending on the negative peak locations, the number of IR analytical windows = 1 to 4.

[D]New LSF quantitative method was used. The two broad IR analytical windows used were 3200–2700 $cm^{-1}$ and 1400–700 $cm^{-1}$.

[E]Seven single-beam background spectra containing one component were ratioed with a single-beam sample spectrum that contained five components.

[F]Tol = toluene; Ben = benzene; Ace = acetone; VCM = vinylchloride monomer; MIBK = methylisobutyl ketone; F11 = Freon-11; F12 = Freon-12; Ald = acetaldehyde; Hex = *n*-hexane; MCB = monochlorobenzene; DCA = 1,1-dichloroethane.

[G]A single-beam background spectrum containing seven components was ratioed with the single-beam sample spectrum.

[H]All regions are covered by interfering windows, so Method 2 cannot be used.

[I]Excluding the case where all seven interferents are present (Footnote H).

[J]Excluding the two cases where acetone is present as an analyte and an interferent. Values with acetone interferent are for Method 3: 75 (44) for acetone analyte and 95 (22) for the pooled mean (RSD).

had access to a 47-compound reference library that contained the spectra of the five components of the unknown mixture.

The ILSF analysis was performed off-line with a Nicolet 1280 minicomputer because the MS-DOS personal computer with which the ROSE-FTIR was equipped did not yet have the capability of running ILSF. Working from a choice of 47 possible compounds that might be present, the ILSF software correctly identified methylene chloride, acetone, 2-propanol, methanol, and toluene in the vapor, with no false positive or false negative results. The correctness of the identification of the components of this mixture was validated by the manufacturer of the liquid.

The manual identification of the vapors that constitute the components of this mixture would have been difficult, and library search software would not have worked. However, the ILSF software is not yet commercially available, and not all mixtures of vapors would have yielded results in which there were neither false positives nor false negatives.[23]

The ILSF program, written in FORTRAN and run on a Nicolet 1280 minicomputer, took 10 to 40 min to complete the analysis of the spectrum of one mixture. The same program written in Microsoft-C and run on a Dell 80386/387 MS-DOS computer took from 0.5 to 3 min to analyze a typical spectrum.

The time it took for the program to perform a spectral analysis is also a function of the size of the spectral library and of the similarity of the spectra of the unknown compounds in the mixture. Thus, if the spectra have regions of great dissimilarity, the program will reach a conclusion more quickly than when the components of the mixture are spectrally similar. This is because, for the latter case, the program will have to iterate, or repeat, the LSF calculations through more cycles.

### *Background Spectra Contaminated with Nonanalytes*

A potentially serious problem with open path measurement may occur when the background air spectrum is supposed to be free of interferences but actually contains nonanalytes that might interfere with accurate quantitation of the analytes through spectral overlap, causing spectral subtraction, or through baseline shifts.

This situation was actually encountered when the ROSE-FTIR was first tested in a chamber in which the air was filtered through charcoal, a molecular sieve, and potassium permanganate. The expectation was that the air would be free of organic vapors. In fact, this "clean" air contained substantial concentrations of Freon-11® and Freon-12®.

However, the method described here is not aimed at the situation where the background spectra might contain unknown and varying concentrations of analytes. This latter case is illustrated below.

**TABLE III. Effect of Varying the Concentration of Components in Both Sample and Background Single-Beam Spectra on the Quantitative Results**

| Analytes (across) / Interferents[B] (down) | Recovery of Analytes in Sample Spectra | | | | | |
|---|---|---|---|---|---|---|
| | 10 ppm[A] | | 5 ppm[A] | | 1 ppm[A] | |
| | M1[C] | M3[D] | M1 | M3 | M1 | M3 |
| At 5 ppm | | | | | | |
| Mean[E] | 104 | 101 | 99 | 101 | 166 | 112 |
| RSD | 61 | 2 | 39 | 4 | 187 | 29 |
| At 1 ppm | | | | | | |
| Mean | 99 | 100 | 99 | 100 | 102 | 103 |
| RSD | 6 | 1 | 11 | 2 | 43 | 9 |
| At 0.5 ppm | | | | | | |
| Mean | 99 | 100 | 99 | 100 | 100 | 102 |
| RSD | 2 | 1 | 6 | 1 | 26 | 7 |

[A]Mean recovery of the six analytes in each sample spectrum at the indicated concentration.

[B]Seven single-beam spectra at 5-, 1-, and 0.5-ppm concentrations were used to represent the case where there are nonanalyte interferents in the spectrum of the background air.

[C]M1 is Method 1; see the description in Table I and the text.

[D]M3 is Method 3; see the description in Table I and the text.

[E]Mean was calculated from all results with each method. Details of results available upon request.

Other research groups have looked into the question of interference by nonanalytes in the spectra of mixtures of analytes. Osten and Kowalski[24] described an approach to detecting spectral features of nonanalytes even when their presence was unknown. Although this approach is quite useful, it was only tested on spectra with 20 data points each (a factor of 50 fewer data points than used in this study). In addition, the method was neither tested on infrared spectra nor on the spectra of gases. However, the conclusion reached in Osten and Kowalski's study is still valid and is encompassed in the approach detailed in this study: "...the identification of all sample components, both analytes and interferences, affecting the measured response is still a worthwhile goal for obtaining the most accurate analytical results."[24]

The electronically added spectra of two mixtures of air contaminants were used in this portion of the study. In each case, the mixture represented concentrations of 1, 5, and 10 ppm (v/v) of each contaminant in ambient air. The first mixture (I) consisted of equal concentrations of toluene, benzene, acetone, vinyl chloride monomer (VCM), and methyl isobutyl ketone (MIBK). The second mixture (II) consisted of equal concentrations of Freon-113® (trichlorotrifluoroethane), cyclopentane, isopropanol, methylene chloride, trichloroethylene (TCE), and methyl ethyl ketone (MEK). In each case, the LSF file was calibrated with the positive spectra of these compounds, as well as with water vapor, $CO_2$, and "ambient" air.

The nonanalytes in the background spectra consisted of Freon-11 (trichlorofluoromethane), Freon-12 (dichlorodifluoromethane), acetaldehyde, *n*-hexane, acetone, monochlorobenzene (MCB), and 1,1-dichloroethane (DCA). Thus, for this test, the spectra of those compounds were deliberately added to the background spectrum, rather than the usual practice of using an interference-free background spectrum. This would represent the case in which there was no location at the work site in which the air was actually "contaminant-free," so a contaminated background had to be used.

Electronically synthesized composite spectra can be an important tool in the evaluation of IR-based analytical methods. This is because the actual generation of complex spectra at several different concentrations, and ratios of concentrations of components, such as shown in Tables II and III, is a complex task. Therefore, prior to field testing of new IR methods, such an approach is commonly used. Furthermore, the approach is reasonable as long as different spectra of the analytes and interferences are used for the system calibration and the analysis steps.

For each analysis, the IR spectrum was obtained by means of ratioing the sample spectrum against the background spectrum. The word *ratioing* is common jargon in IR spectroscopy, and the procedure is almost always performed. The analytes in the sample and nonanalytes in the background result in an absorbance spectrum with peaks displayed in the positive and negative directions from the baseline, respectively.

The IR spectra of the mixtures of the air contaminants are shown in Figure 4. In Spectra A and C, air contaminant Mixtures I and II (respectively) are ratioed against "zero grade" background air obtained from a gas cylinder. Note that the baselines are relatively flat. In Spectra B and D, air contaminant Mixtures I and II (respectively) are ratioed against the background air that is contaminated with nonanalytes. Note that there are dips in each baseline. Those baseline nonlinearities were caused by Freon-11, Freon-12, and dichloroethane and are marked on the Spectrum B. The presence of these dips in the baseline, and changes in the shapes and sizes of peaks caused by background air that is contaminated, represent a serious challenge to the method.

When Mixture I was analyzed by using only the positive spectra of the analytes, results were not accurate. These inaccurate results were obtained when any of the nonanalytes were used individually or when all seven nonanalytes were included at the same time in the background spectrum. This is illustrated in Table II as Method 1. "Universal" (broad) spectral windows (regions of the spectrum) covering the C-H region (3200–2700 $cm^{-1}$) and the Fingerprint region (1400–700 $cm^{-1}$) were used.

The table illustrates the accuracy of the method by the closeness of approach of the results of the LSF calculation to the true concentration value. In all of the results shown in Table II, the concentrations of both the analytes and nonanalytes are 5 ppm. A perfect answer would be represented in this table as "100," representing 100% "recovery" of the analytes by the method.

Method 2, shown on Table II, is the same as Method 1 except that it involves the use of separate spectral windows chosen by the instrument operator so that the LSF windows used for the analyte peaks avoided the use of wavelength regions occupied by the nonanalyte peaks. The degree to which this method works is a function of the degree of peak overlap. For example, the peaks caused by Freon-11 seldom overlap with those of the analytes, but the chlorobenzene spectrum interferes strongly with the determination of toluene. This accounts for the good results obtained when

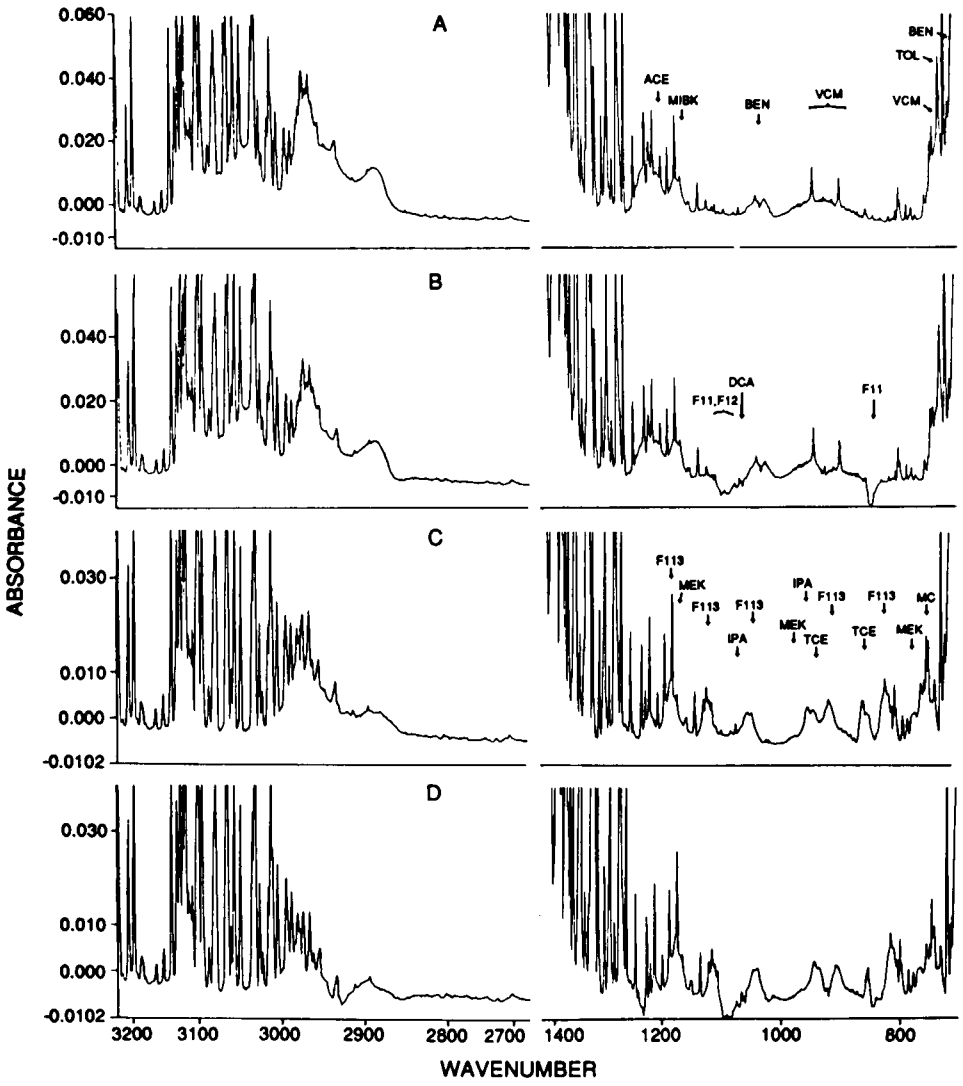


*FIGURE 4. Tracing A: spectrum of Mixture I with organic vapors present at 5 ppm in air, ratioed against contaminant-free air. Note that the C-H region of the spectrum is at the left and the "Fingerprint" region of the spectrum is on the right. Identities of peaks are as marked. Note scale of absorbances on y-axes. Tracing B: same as A except ratioed against air containing seven-component, nonanalyte mixture at 1 ppm. Note identities of negative peaks as marked. Tracing C: spectrum of Mixture II with organic vapors present at 1 ppm in air, ratioed against contaminant-free air. Tracing D: same as C except ratioed against air containing seven-component nonanalyte mixture at 1 ppm. Identities of negative peaks are the same as in B.*

using Method 2 in the presence of Freon-11 and the null result obtained for toluene in the presence of chlorobenzene (Table II).

Furthermore, in order to avoid analyte peak windows in which a nonanalyte peak falls, it may be necessary to choose a frequency window for an analyte that is suboptimal. This manipulation of peak windows is not easy, even for an experienced operator. Thus, when all seven nonanalytes are present in the spectrum of the background air, Method 2 cannot be used. Also, when an analyte is present in both the background and the sample spectra, the results are invariably low, as shown in Table II.

It is also interesting to note that, when there is contamination of the spectrum of the background by nonanalytes, there may be a positive bias in the results obtained for the analyte. This is caused by the effects of the nonanalytes in the background spectrum on the shape of the baseline in the ratioed absorbance spectrum.

In Method 3, the broad spectral windows (3200–2700 $cm^{-1}$, 1400–700 $cm^{-1}$) were used despite the fact that the nonanalyte peaks fell within these windows. The calibration of the LSF calculation for this analysis included positive peaks for the analytes and negative calibration spectra for the nonanalytes. Thus, the contribution by the negative spectra of the nonanalytes in the sample spectrum can be calculated by computing their concentrations with LSF analysis. Therefore, variations in the concentrations of the nonanalytes in the background spectra could be compensated directly by the LSF program.

This is illustrated in Table II, Method 3, for Mixture I at 5 ppm concentration. In this case, almost all of the recovery values for the target analytes were close to 100% recovery (mean = 99.7%, standard deviation = 7.1%).

These results demonstrate that Method 3 solves the problem of interferences in the background air except for the situation where the background spectra might contain unknown and varying concentrations of analytes. This is illustrated in the data in Table II, Method 3, in which both the background air and the sample air contained acetone at 5 ppm concentration. If this case is suspected (that the background air contains appreciable concentrations of analytes), then the instrument operator will have to make the added effort of finding sources of background air without the analyte.

Clearly, Method 1 suffers from baseline irregularities and spectral subtraction from nonanalytes present in the spectrum of the background. This situation can be expected to occur frequently when nonanalytes might be present in the background (clean) air spectrum collected by using a ROSE system in the workplace.

In Table III, a summary of the data set is shown for Mixture II, where the concentrations of the analytes are at 10, 5, and 1 ppm and the concentrations of nonanalytes are 5, 1, and 0.5 ppm. The results "cell" for 1 ppm each of analyte and nonanalyte (middle row, right-hand column on the table) shows, for Method 3, a mean = 103 and a relative standard deviation = 9%.

Although this method is not specifically designed to calculate the concentration of the nonanalytes in the background file, these values can be obtained from the LSF calculation. These results are illustrated in Table IV. Note that the null result for acetone in the presence of Mixture I is caused by the presence of acetone in both spectra. This indicates that two separate sample spectra of different composition can be taken and ratioed, and quantitative results can be obtained for either set of analytes with Method 3.

## FUTURE APPLICATIONS

The authors are currently investigating the use of beam measurements in exposure assessment applications. The preliminary hypothesis is that beam information may be useful in generating task-specific exposure data. The combination of a high data collection rate with flexible beam geometry may provide a real-time monitoring capability that will allow the hygienist to correlate short-term exposures with specific tasks and work practices.

A second application under investigation concerns the use of beam data to estimate group mean exposures in particular work areas. To be successful, this application will require clever beam placement along with specific ventilation conditions and emission source geometries.

Nevertheless, the path-averaged concentration data provided by ROSE systems provide a different capability than that available from fixed-position monitoring systems, particularly if a system can be developed where the beam is operated in a steerable mode, with rapid switching of beam position by using computer-controlled moveable mirrors. This capability, when accompanied by the high rate of data acquisition and processing, may present the hygienist with a powerful new tool for monitoring airborne contaminants.

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**TABLE IV. Quantitative Analysis of Components in Background Air as Determined by Method 3**

| | *Concentration of Components in Background (ppm)* | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *F11*[A] | | *F12* | | *Ald* | | *Hex* | | *Ace* | | *MCB* | | *DCA* | |
| | *b1* | *b2* | *b1* | *b2* | *b1* | *b2* | *b1* | *b2* | *b1* | *b2* | *b1* | *b2* | *b1* | *b2* |
| True Conc. | 5.0 | 1.0 | 5.0 | 1.0 | 5.0 | 1.0 | 5.0 | 1.0 | 5.0 | 1.0 | 5.0 | 1.0 | 5.0 | 1.0 |
| Mixture I[B] | | | | | | | | | | | | | | |
| At 10 ppm | 5.09 | 1.01 | 4.83 | 0.90 | 5.10 | 1.02 | 5.04 | 1.03 | 0.0 | 0.0 | 5.08 | 1.08 | 5.04 | 1.04 |
| At 5 ppm | 4.97 | 1.02 | 4.83 | 0.90 | 5.10 | 1.10 | 5.04 | 1.04 | 0.0 | 0.0 | 5.09 | 1.09 | 5.04 | 1.04 |
| At 1 ppm | 4.97 | 1.02 | 4.83 | 0.90 | 4.95 | 0.95 | 5.04 | 1.04 | 0.0 | 0.0 | 5.08 | 1.08 | 5.04 | 1.04 |
| Mixture II[C] | | | | | | | | | | | | | | |
| At 10 ppm | 5.10 | 1.00 | 4.91 | 0.91 | 7.64 | 3.65 | 5.14 | 1.14 | 5.28 | 1.28 | 3.94 | 0.0 | 7.38 | 3.38 |
| At 5 ppm | 5.11 | 1.01 | 4.93 | 0.94 | 7.56 | 3.56 | 5.11 | 1.10 | 5.07 | 1.07 | 3.99 | 0.0 | 6.22 | 2.23 |
| At 1 ppm | 5.02 | 1.02 | 4.94 | 0.96 | 7.42 | 3.43 | 5.06 | 1.06 | 4.89 | 0.90 | 4.10 | 0.07 | 5.23 | 1.23 |

[A]See Table II, footnote F, for abbreviations.

[B]Mixture I contains toluene, benzene, acetone, vinyl chloride, and methyl isobutyl ketone.

[C]Mixture II contains cyclopentane, isopropanol, methylene chloride, trichloroethylene, MEK, and F113.

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