Technical Briefs: Report on a Microprocessor-Based Infrared Analyzer

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Introduction

The Miran 1B infrared analyzer (IR) is a single beam, microprocessor-based spectrometer, preprogrammed for the measurement of many substances in the workplace and also user programmable to measure additional gases and vapors of interest. The microprocessor controls the spectrometer, averages the measurement signal, and calculates absorbence values. Analysis results can be displayed on a digital readout in either parts per million (ppm) or absorbence units. It is Foxboro's newest line of portable ambient air analyzers [Foxboro Company, Foxboro, MA 02035]. Recently, a limited laboratory appraisal on the Miran 1B was conducted to determine its abilities to measure carbon dioxide, carbon monoxide, ethylene oxide, and nitrous oxide.

Test concentrations were generated in the laboratory for four compounds of current interest to some of the field studies groups at the National Institute for Occupational Safety and Health (NIOSH). The Miran 1B was used to analyze these test environments. All measurements were at ambient temperatures and at a relative humidity of less than 25 percent. While not a comprehensive assessment of this instrument, this paper reports data collected from limited experimentation and allows for comparison of experiences with other portable infrared analyzers.

Generation of Test Concentrations

Carbon dioxide (CO_2) and carbon monoxide (CO) were generated in a dynamic generation system by dilution of cylinder gases of known, verified concentrations as described by Woodfin.[1] Cylinders of CO_2

(greater than 99%) and CO (5000 ppm $\pm$ 5%) in nitrogen were metered through a low volume mass flow meter into a mixing chamber. There they were combined with dilution air from a pure air generator or from the laboratory compressed air system, metered through a high volume mass flow meter. All flow meters were calibrated versus a bubble meter. In the generation of CO_2 and CO, the dilution air was passed through an ascarite sorbent to remove residual CO_2 prior to the mixing chamber.

Reference samples of ethylene oxide (EtO) and nitrous oxide (N_2O) were prepared by addition of known amounts of a mixture of EtO in Freon 12® (27:83 V/V) or N_2O (greater than 99%) to an inert plastic bag containing a known amount of clean air. This procedure also is described by Woodfin.[1]

Analyte concentrations were confirmed at several levels by independent methods. The CO_2 supply cylinder concentration and samples from the generation system were measured by a Perkin Elmer Model 900 thermal conductivity detector gas chromatograph; however, only levels above approximately 1500 ppm could be quantitated. CO was measured by an electrochemical detector (Ecolyzer Hipster) which was calibrated by a commercial standard purchased from an independent source. EtO concentrations were monitored by a Photovac Model 10S50 photoionization detector gas chromatograph, also calibrated with a separate commercially obtained source of analyte. Reference N_2O concentrations were not verified and were assumed to be correct as generated. Residual amounts of CO and CO_2 in the dilution air were determined by comparing the difference in response of the infrared analyzer for the dilution air compared with dry nitrogen.

Measurements were made either in a "factory-calibrated" mode using an analytical wavelength and response curve programmed into the instrument's memory by the manufacturer or a "user-calibrated" mode. The user calibration is done with a closed loop calibration system consisting of a circulating pump, tubing, and a septum. The tubing allows for circulation of chamber air via the pump in a closed loop. The analyte in the gas cell can be adjusted
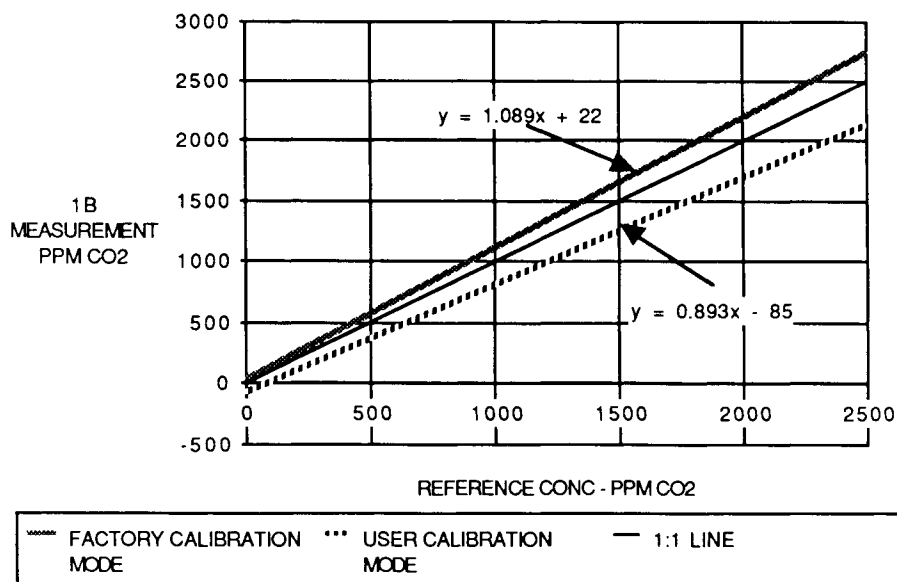

FIGURE 1. CO_2 reference vs. Miran 1B measurement.

to the desired concentration by injection of sample through the septum. The microprocessor allows the instrument response (absorbence) to be entered into instrument memory as a function of analyte concentration at up to five levels. The instrument then calculates a second degree regression line, forced through zero, which enables it to calculate concentration from absorbence measurements of samples.

Results

Carbon Dioxide

Figure 1 presents a plot of generated CO_2 concentrations versus readings of CO_2 concentrations obtained from the Miran 1B analyzer. The light solid line indicates a linear regression fit of data using the calibration parameters programmed into the instrument by the manufacturer (factory calibration). The dotted line indicates a linear regression fit of data using the calibration parameters entered by the user (user calibration). A 1:1 (perfect fit) line, as would be predicted by Beer's law, also is shown. The fit of the lines to the data is presented in Table I.

TABLE I. Carbon Dioxide Data Produced for Fit of Lines

	Factory Calibration	User Calibration
Slope	1.089	0.893
Intercept	22	−85
Correlation coefficient	0.991	0.965
Coefficient of variation	6.6	14.6
Number of measurements	26	43

Carbon Monoxide

An air stream containing 100 ppm CO and no CO_2 was generated and verified by electrochemical detector. The IR was zeroed on room air (assumed to contain 300 ppm CO_2), and replicate measurements were then made in both the factory calibration and user calibration modes. The instrument was re-zeroed on dry nitrogen (free of CO_2), and the measurements were repeated. The arithmetic means and coefficients of variation of n samples are shown in Table II. The data indicate that the instrument assumes the presence of constant levels of CO_2 in CO samples and tends to read low when that material is absent.

Ethylene Oxide

Six concentrations of EtO in air, ranging from 6 to 50 ppm, were generated, and replicate measurements were made (n =

5 to 9) at each concentration using the Miran 1B as calibrated from the factory (runs A and D) or as calibrated by the user (balance). Baseline was established with room air in both instances. Figure 2 shows a plot of the readings obtained from the Miran 1B as compared to the readings obtained by the gas chromatograph.

Nitrous Oxide

Three concentrations (10, 25, and 250 ppm) of N_2O in air were generated. Replicate measurements were made (n = 3 or 6) of each using the Miran 1B as calibrated from the factory and baseline established with room air. The high readings were obtained using the high concentration range calibration; the medium and low measurements were made using the low concentration range calibration. The mean and coefficient of variation for n samples at the indicated concentrations are presented in Table III.

Conclusions and Observations

Excluding the EtO data, the measurements made by the Miran 1B were usually within the ± 25 percent criterion established by the NIOSH Standards Completion Program,[3] although comprehensive comparison with this criterion was not conducted. EtO measurements ranged from 78 percent below to 18 percent above the reference

TABLE II. Carbon Monoxide Data

	Mode	Mean	C.V.	n
Room air zero	Factory calibration	89.0 ppm	3%	5
	User calibration	79.8	1%	5
Nitrogen zero	Factory calibration	96.7	1%	3
	User calibration	106	1%	3

values. The reproducibility of measurements, as indicated by the coefficients of variation (C.V.), was usually very good (often less than 5%). Even in the data for EtO, precision was good for the three higher runs (average C.V. = 5.6%) although not so for the three lower runs (average C.V. = 89%). The standard deviation for all six runs was similar.

The greater error of measurements made in the user calibration mode as compared with the measurements made in the factory calibration mode was unexpected. Experience with other models of IR analyzers

TABLE III. Nitrous Oxide Data

Reference Concentration	Mean	C.V.	n
10 ppm	11 ppm	4%	6
25 ppm	24 ppm	0%	6
250 ppm	261 ppm	2%	3

by the same manufacturer and also with other instruments indicates better data from on-site calibrations than from precalibrated instruments. We feel that much of the error encountered in conducting a user calibration of the Miran 1B may have been due to the user's unfamiliarity with the instrument and that the ability to perform this function should improve with experience.
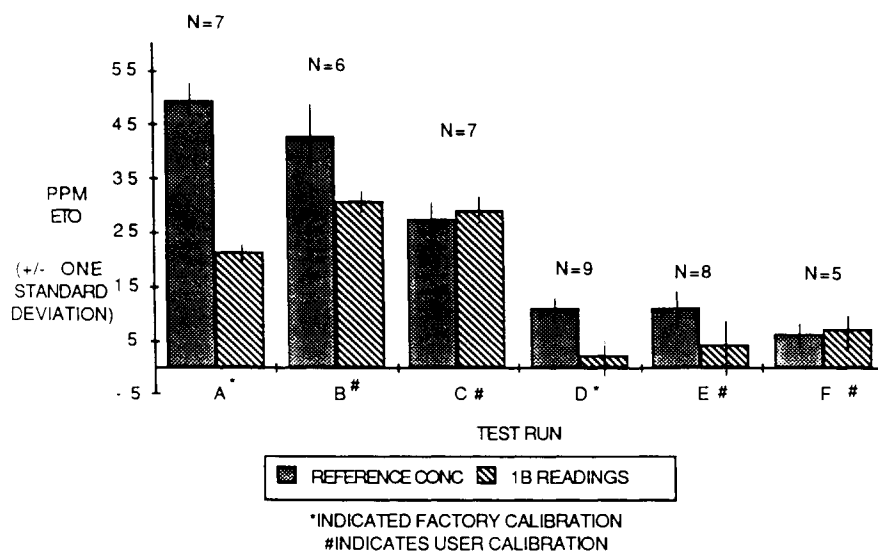

FIGURE 2. Summary of EtO data.

The baseline was stable, with a zero drift of less than 0.5 percent of full scale in a 100-minute run at a path length of 0.75 meter and a wavelength of 4.720 micrometers (analytical wavelength for CO_2). The rise and fall time of the instrument (to 90% full scale) ranged from less than one minute with no tubing connected to the sample chamber inlet, to almost five minutes with a 4-foot by ⅟₁₆-inch (I.D.) Teflon® inlet line connected. This long response time is the result of a pressure drop caused by sampling with a small diameter tube at a flow rate of approximately 30 L/min. This tubing was used for convenience of connection to the generation system and is much more restrictive than the approximately 0.5-inch tubing supplied with the instrument.

Interference between CO and CO_2 was reasonable in spite of the proximity of their analytical wavelengths, 4.76 and 4.72 μm, respectively. A CO_2 concentration of 1000 ppm produced a response approximately equal to 100 ppm CO at 4.76 μm. Similar high but unquantitated concentrations of halothane and a mixture of EtO and Freon produced a positive response at the 4.68 μm analytical wavelength used for N_2O.

The analytical wavelength recommended for some substances in the instruction manual provided with the Miran 1B analyzer is slightly longer than in a wall chart,[2] also distributed by the manufacturer of this instrument, which lists recommended wavelengths, pathlength, and other information on a number of toxic gases and vapors. This disparity, approximately 0.4 μm for CO_2, 0.2 μm for N_2O, and less than 0.1 μm for CO, did not appear to cause any problems. In the process of developing a user calibration, the wavelength of maximum absorbence near the recommended wavelength was determined; in all cases, it was within a few hundredths of a micrometer of the wavelength preset in the factory calibration.

The microprocessor permits calibration of this instrument at a maximum of five analytical concentrations and forces the second degree regression curve of these data through zero. As indicated by the results presented here, this calibration method is usually sufficient. However, one situation was encountered which produced problems. That was when we attempted to measure concentrations of CO_2 up to the NIOSH time-weighted average recommended exposure level of 10,000 ppm (the criteria established by the Occupational Safety and Health Administration and the American Conference of Governmental Industrial Hygienists are both 5000 ppm). The large absorbence readings obtained at these concentrations produced a negative term in the calibration equation. It was determined that measurement of CO_2 concentrations much above 2000 ppm was not practical with this instrument unless a secondary analytical wavelength is available.

The Miran 1B is somewhat easier to use than the models 1A and 103. The instrument manual has a somewhat unusual format; however, once the user becomes familiar with that format, the instructions are relatively clear and straightforward although occasionally not as complete as these authors would like. Upon checking with the manufacturer, it was found that a maintenance manual is available for this instrument which would probably answer most remaining questions for anyone wanting to become more involved with this unit. The closed loop calibration system allows for easy user calibration or verification of factory calibration. At 28 pounds, this device is transportable but probably not something one would want to carry for extended periods. As with any IR instrument, the user must be aware of other contaminants in the environment to determine if overlapping absorption bands exist with the analyte of interest.

References

1. Woodfin, W.J.: Gas and Vapor Generation Systems for Laboratories. DHHS (NIOSH) Pub. No. 84-113 (August 1984).
2. The Foxboro Company: OSHA Concentration Limits for Gases, Incorporating Infrared Analytical Data for Compliance Testing and Other Applications. (October 1985).
3. Taylor, D.G.; Kupel, R.E.; Bryant, J.M.: Documentation of the NIOSH Validation Tests. DHEW (NIOSH) Pub. No. 77-185. NIOSH Technical Information, Cincinnati (April 1977).

Answers to "The Action Level"

1. b; 0.2 ng/m³
2. c
3. mass median aerodynamic diameter (MMAD) is decreased
4. b
5. d—the aerosol generator is specifically designed to produce 1.3 μm MMAD particles
6. humans, multiple mechanisms
7. Cr(VI) in the soluble fraction