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EVALUATION OF POTENTIAL VOC SCREENING INSTRUMENTS

by

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Arthur D. Little, Inc.
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Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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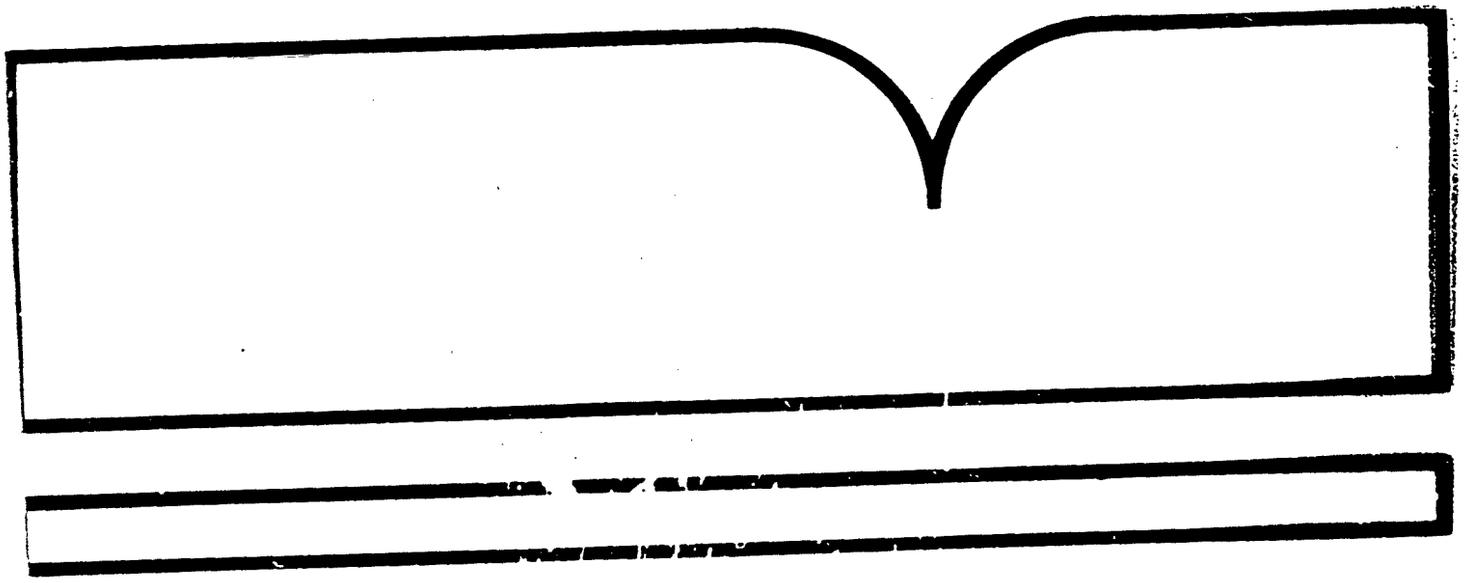

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16. ABSTRACT The report describes the evaluation of potential fugitive source emission screening instruments for analysis of volatile organic compounds (VOCs). An initial review of available portable VOC detection instruments indicated that detectors operating on several principles (i.e., flame ionization, catalytic combustion, photoionization, infrared absorption, and thermal conductivity) might be useful for VOC analysis. However, flame ionization and catalytic combustion devices evaluated previously showed poor sensitivity for highly substituted aliphatic and aromatic organic compounds. Instruments utilizing photoionization and infrared may be able to meet necessary criteria for practical and accurate VOC analysis of highly substituted organics. Therefore, three commercially available instruments (i.e., HNU PI-101, AID 580, and Foxboro Miran 80) were modified and evaluated for 32 such compounds in concentrations of 100-10,000 ppmv. Results show that photoionization may be suitable for general VOC screening, but a reliable instrument/dilution system does not exist. Infrared absorption will apparently not provide suitable general VOC screening, but may be useful for analyzing some classes of organic compounds.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Photochemical Reactions	Pollution Control	13B	
Analyzing		Stationary Sources	14B	07E
Organic Compounds	Infrared Radiation	Volatile Organic Compounds (VOCs)	07C	20F
Volatility	Electromagnetic Absorption		20M	
Selection		Screening Instruments	14G	20C
Photoionization	Processing	Fugitive Emissions	07B	13H
	Leakage			

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TABLE OF CONTENTS

LIST OF TABLES AND FIGURES

LIST OF TABLES AND FIGURES (Continued)

ABSTRACT

This report describes the evaluation of potential fugitive source emission screening instruments for analysis of volatile organic compounds (VOC). An initial review of available portable VOC detection instruments indicated that detectors operating on several principles, i.e., flame ionization, catalytic combustion, photoionization, infrared absorption and thermal conductivity, might be useful for VOC analysis. However, flame ionization and catalytic combustion devices evaluated previously have shown poor sensitivity for highly substituted aliphatic and aromatic organic compounds. Instruments operating on the photoionization and infrared principles may be able to meet necessary criteria for practical and accurate VOC analysis of highly substituted organics. Therefore, three commercially available instruments were selected, modified, and evaluated for 32 such compounds in the concentration range of 100 ppmv to 10,000 ppmv. The results indicate that the photoionization principle may be suitable for general VOC screening but a reliable instrument/dilution system does not exist at present. The infrared absorption principle will apparently not provide a suitable general VOC screening device but may be useful for analysis of some classes of organic compounds.

1. INTRODUCTION

The U.S. Environmental Protection Agency has issued performance standards and guidelines[1] to limit emissions of volatile organic compounds (VOC) from several stationary source categories such as surface coating operations. These guidelines apply to industries which emit significant quantities of air pollutants. It has become apparent that sources other than classical point sources may also emit large amounts of VOCs into the workplace and surrounding atmosphere. The EPA's Office of Air Quality Planning and Standards (OAQPS) is, therefore, evaluating the need for the control of fugitive emissions of VOCs from such sources as valves, pumps and drains. As described in EPA Method 21, Determination of Volatile Organic Compound Leaks,[2] technically and economically feasible devices suitable for monitoring such leaks include only a few portable detectors. These devices can be placed near possible points of emissions and will respond to releases of the organic compounds. Specific instruments suitable for this purpose include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption and photoionization detectors.

Unfortunately, due to the chemical complexity of many fugitive VOCs and the lack of universal sensitivity of these detectors, the detectors previously evaluated cannot adequately measure the concentration of all chemicals likely to be released. This fact has been documented[3] for two commercially available detectors using flame ionization (FID) and catalytic combustion principles. Among 168 compounds tested, 23 showed sufficiently poor response that the actual and measured concentrations differed by a factor of greater than five (Table 1). The classes of compounds which show the poorest agreement with the actual concentration generally incorporate functional groups such as halides, hydroxyl (alcohols), carbonyl (aldehydes, ketones) and carboxylate (acid) and include both substituted aromatic hydrocarbons and low molecular weight, highly substituted aliphatic compounds.

Additional portable devices which respond accurately to these compounds are needed for VOC screening. Instruments other than flame ionization or catalytic oxidation detectors which might meet this goal operate on the principles of infrared absorption, photoionization and thermal conductivity.[4]

The first step in this task was to select and procure one or more units of those detectors which meet the specifications of Method 21. The VOC instrument must be rugged, reliable, relatively inexpensive, portable and easy to operate. Of course, it must respond to the organic compounds of interest and be able to measure the leak definition concentration specified in the regulations. According to Method 21, the instrument must be intrinsically safe for operation in explosive atmospheres as defined by the applicable National Electric Code. At this time, there are few detectors which are "approved" for such an environment (Table 2).

TABLE 1

COMPOUNDS WITH RESPONSE FACTORS
EQUAL TO OR GREATER THAN FIVE

OCPDB[a] ID No.	Compound Names	FID Response Factor[b]
120	Acetophenone	10.98
—	Acetyl-1-propanol, 3-	10.87
490	Benzoyl Chloride	6.40
790	Carbon Disulfide	571.92
810	Carbon Tetrachloride	21.28
830	Chloro-Acetaldehyde	13.40
—	Dichloro-1-propanol, 2,3-	61.51
—	Dichloro-2-propanol, 1,3-	29.34
—	Diisopropyl Benzene, 1,3-	9.43
—	Dimethyl Styrene, 2,4-	37.09
2060	Formic Acid	34.87
1221	Freon 12	9.65
2073	Furfural	7.96
2105	Glycidol	8.42
—	Hydroxyacetone	8.70
2500	Methanol	5.69
—	Methyl-2,4-pentanediol, 2-	96.34
2690	Methylstyrene, α-	10.24
1660	Monoethanolamine	28.04
2770	Nitrobenzene	29.77
2910	Phenol	11.75
—	Phenyl-2-propanol,2-	89.56
3291	Tetrachloroethane,1,1,2,2	6.06

[a]Organic Chemical Producers Data Base

[b]Response Factor = $\frac{\text{Actual Concentration}}{\text{Measured Concentration}}$

Source: Reference 3

TABLE 2

PORTABLE VOC DETECTION INSTRUMENT CERTIFICATION

Manufacturer	Model No.	Certification
Bacharach Instrument Co., Santa Clara, California	L TLV Sniffer	Intrinsically safe, Class I, Division 1, Groups C & D Intrinsically safe, Class I, Division 1, Groups C & D, and Class I, Division 2, Groups A & B
Century Systems, Arkansas City, Kansas	OVA-128 OVA-108	Intrinsically safe, Class I, Division 1, Groups A, B, C & D Intrinsically safe, Class I, Division 1, Groups A, B, C & D
HNU Systems, Inc. Newton Upper Falls, Massachusetts	PI-101	Intrinsically safe, Class I, Division 2, Groups A, B, C & D
Mine Safety Appliance Co., Pittsburgh, Pennsylvania	40	Intrinsically safe, Class I, Division 1, Group D, and Class I, Division 2, Groups A, B, & C
Survey and Analysis, Inc. Northboro, Massachusetts	OnMark Model 5	Intrinsically safe, Class I, Division 1, Groups A, B, C & D

Source: Reference 4

The second step in this task was to set up a laboratory system capable of mixing known volumes of vapors with air and delivering the mixtures of known concentration to the detectors. Tedlar bags and a volumetric mixing system were selected for sample preparation since they provide adequate accuracy/precision and require little cost or time to set up.

The third step in this task was evaluation of the detectors for response to the compounds of interest. The response factors were determined at several concentrations over the range of 100 ppmv to 10,000 ppmv. Measurements were limited to concentrations approaching about 90% of the saturation concentration or 75% of the lower explosive limit (LEL). In order to permit statistically valid interpretation of the measured response factors, five replicate measurements at three concentrations were conducted. Data analysis included calculations of mean response factors and confidence intervals.

2. INSTRUMENT SELECTION

A. General Rationale

A recent summary of available portable VOC detection devices[4] lists a number of instruments operating on the following principles:

Flame Ionization (FID)

Photoionization (PID)

Infrared Absorption (IR)

Thermal Conductivity (TC)

Hot Wire/Catalyst Combustion (Combustion).

The majority of available instruments operate on one of three principles, i.e., FID, IR or Combustion (Tables 3, 4, 5). As noted above and in previous work,[3] two specific FID and Combustion devices show poor sensitivity to several substituted organic compounds. Due to this observation and with the understanding that other FID or Combustion detectors available from different manufacturers probably do not differ significantly in construction or sensitivity, alternative VOC screening devices were evaluated. These were selected from instruments operating on other detection principles, including photoionization, IR and thermal conductivity. Photoionization or thermal conductivity detectors are highlighted in Tables 3 and 5, respectively, while infrared detectors are listed in Table 4.

The selection of potential VOC detectors from this list depends on several criteria which are outlined in EPA Method 21. That is, an instrument suitable for screening should have the following characteristics:

(1) Fast response (<30 seconds);

(2) Measurement range 100 to 10,000 ppmv;

(3) Similar responsiveness to a variety of organic vapors;

(4) Portable;

(5) Rugged;

(6) Reliable;

(7) Inexpensive;

(8) Easy to operate; and

(9) Intrinsically safe (as per National Electric Code).

Each of the first three characteristics is of primary importance in providing a practical instrument for VOC screening. Fast response time is necessary for rapid screening of a large number of fugitive sources. The specified measurement range is required by the need to limit significant leaks of volatile organic compounds. Equal molar sensitivity

TABLE 3

PORTABLE IONIZATION DETECTORS

Manufacturer	Model No.	Pollutant(s) Detected	Principle of Operation	Cost $	Weight lb	Range ppm	Accuracy %	Sensitivity	Precision %	Response Time s	Noise	Ambient Temperature °C	Drift[a]
Analytical Instrument Development, Inc., Avondale, Pennsylvania	550[b] and 551	Nonmethane total hydrocarbons	FID	3711	16.5	0-200 and 0-2000 for Model 550; 0-200 and 0-10,000 for Model 551	±3	0.1 ppm on a scale of 0-200 ppm	±3	5	Less than 0.1 ppm on a scale of 0-200 ppm	0-40	
	555[c]	Total hydrocarbons	FID	3987	20.5	0-10,000, 0-2000, and 0-100	±3	1 ppm on a scale of 0-2000 ppm	±3	5	1 ppm on a scale of 0-2000 ppm	0-40	
	511-12[d]	Total hydrocarbons and individual compounds with GC	FID/GC	4968	41			0.05 ppm as propane				5-45	
Bendix, Environmental and Process Instruments Division Lewisburg, West Virginia	8401[e]	Total hydrocarbons	FID	3195	40	1-1000	±2	0.01 ppm	±2	8	±1%	5-40	z = ±1% (24) s = ±1% (24)
Century Systems, Inc. Arkansas City, Kansas	OVA-118	Total hydrocarbons	FID	3500	12	0-10 and 0-100	±2	0.2 ppm methane	±2	2		-20 to 40	s = ±1% (1)
	OVA-128[f]	Total hydrocarbons	FID/GC	4200	12	0-1000	±2	0.2 ppm methane				-20 to 40	s = ±1% (1)
	OVA-98	Total hydrocarbons	FID	3500	12	0-10,000	±2	0.5 ppm methane	±2	2		-20 to 40	s = ±1% (1)
	OVA-108[g]	Total hydrocarbons	FID/GC	4200	12	0-10,000	±2	0.5 ppm methane				-20 to 40	s = ±1% (1)
General Electric Instrument Products Lynn, Massachusetts	TVM-1	Halogenated compounds	Ion capture[h]	4060	23	9 ranges: 0-1 through 0-10,000	±10	0.1 ppm		120		0-55	Negligible
Heath Consultants, Inc. Stoughton, Massachusetts	Detecto PAK II[i]	Total hydrocarbons	FID	2950	8	0-10 0-100 0-1000	j ±4 j	2 ppm 2 ppm 5 ppm		15		0-50	z = ±1% (7) s = ±4% (7)

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TABLE 3 (Continued)

Manufacturer	Model No.	Pollutant(s) Detected	Principle of Operation	Cost $	Weight lb.	Range ppm	Accuracy %	Sensitivity	Precision %	Response Time s	Noise	Ambient Temperature °C	Drift[a]
HNU Systems, Inc. Newton Upper Falls, Massachusetts	PI-101[i]	Chlorinated hydrocarbons, aromatics, aldehydes, ketones, any substance which adsorption of UV light results in ionization	Photoionization	3395	<9	0-20, 0-200 and 0-2000	-7 -7	1 ppm		5		-18 to 50	z = 1% (7) s = 3% (6) for a range of 0-20 ppm; no drift for other ranges
Melroy Labs, Springfield, Virginia	HC-500	Total hydrocarbons	FID		40	0-10, 0-50, 0-100, and 0-1000	±1 on low scale	0.1 ppm CH_4	±1	45	±0.05 ppm CH_4	10-40	z = 0.2 ppm (24) s = 0.2 ppm (24) for a range of 0-10 ppm
Mine Safety Appliances Co. Pittsburgh, Pennsylvania	Total HC analyzer	Total hydrocarbons	FID	3830	35	0-4 and 0-12,000	±1			1	±0.5	4-45	s = 0.5% (24)
Survey and Analysis, Inc. Northborough, Massachusetts	Snifty Model A-500[i]	Total hydrocarbons	FID	1695 for basic unit, 2295 for entire portability package	17	0-10 0-100 0-1000 0-10,000	-55 -35 -3 +20	2 ppm		4		0-50	z = ±20% (7) s = ±12% (7) z = 0 s = ±4% (7) z = ±0.7% (7) s = 0 z = ±0.7% (7) s = 0

[a] The letters "z" and "s" indicate zero drift and span drift. The numbers of hours over which drift occurs is given in parenthesis.

[b] A charcoal tube is used to adsorb organics, except methane, and a range of 0-10 ppm is available with the recorder. The instrument can be used as alarm by setting in 0-1000 range. This is a screening and leak detection device.

[c] The following features are available: a range of 0-100 ppm with recorder only; internal power, oxygen, and hydrogen supplies; a heated probe; and a battery-operated recorder with a range of 0-100 mV d.c.

[d] Capabilities equal or exceed those of Models 550 and 555.

[e] Capabilities to detect higher concentrations require further investigation. This may be suitable for ambient air measurement only.

[f] Optional GC.

[g] Optional GC.

[h] A heated platinum wire embedded in rubidium combusts incoming gases. Combustion of halogenated materials causes electrons to flow from the rubidium. The electrical flow measured is proportional to the amount of halogenated materials present.

[i] Performance characteristics as measured by NIOSH. Reference 6, Section 3.

[j] Inaccurate.

Source: Reference 4

TABLE 4

PORTABLE INFRARED INSTRUMENTS

Manufacturer	Model No.	Pollutant(s) Detected	Principle of Operation	Cost $	Weight lb.	Range ppm	Accuracy %	Sensitivity	Precision %	Response Time s	Noise %	Ambient Temperature °C	Drift[a]
Anarad, Inc., Santa Barbara, California	AR-400[b]	Individual species absorbing IR	IR	2395 for an analyzer measuring single gas 3745 for an analyzer measuring three gases (Model 403)			±1		<±1	5		0-49	z = ±1% (24) s = ±1% (24)
Astro Resources Corp., Houston, Texas	5000[c]	Individual hydrocarbons	IR		25	Specified by customer, up to 100%	±1		±1			-40 to 55	z = <±1% s = <±1%
Chrysler Huntsville Electronics Division, Huntsville, Alabama	III-C[d]	Total hydrocarbons	IR		20	0-300 and 0-2000	±2		±2	6		-1 to 46	
	Mopar[d]	Total hydrocarbons	IR		20	0-300 and 0-2000	±2		±2	6		-1 to 46	
	Atlas[d]	Total hydrocarbons	IR		30	0-300 and 0-2000	±2		±2	6		-1 to 46	
Foxboro Analytical, Wilks Infrared Center, S. Norwalk, Connecticut	Miran -104[e]	Any species absorbing IR between 2.5 and 14.5 μm in wavelength	IR	Not sold in U.S. but price may be similar to Miran-1A	24	ppm to percent	±5	[illegible]		1, 4, 10 and 40		0-46	z = ±0.3% (8)
	Miran-1A	Any species absorbing IR between 2.5 and 14.5 μm in wavelength	IR	6600	32	<ppm to percent	3-4		1-2	1, 4, 10 and 40	0.3	0-40	z = ±0.2% (8)
Gas Tech, Inc. Mountain View, California	Halide Detector	Halogenated hydrocarbons	Enhancement of radiation from a spark by halogens	1125	13	0-100 and 0-10,000				5			Never explosion proof

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TABLE 4 (Continued)

Manufacturer	Model No.	Pollutant(s) Detected	Principle of Operation	Cost $	Weight lb	Range ppm	Accuracy %	Sensitivity	Precision %	Response Time s	Noise %	Ambient Temperature °C	Drift[a]
Infrared Industries, Inc. Santa Barbara, California	IR-711	Alkane hydrocarbons 3.2 μm	IR (solid state detector)	1250	9	0-100% LEL and 0-1000 ppm	±5		±5	120		0-50	z = ±5% (8)
	IR-702[f]	Any species absorbing IR	IR	2895	34	IR 702, IR 703 and IR 705 are available with analog or digital scales; analog scales range from 0-100% to 0-200 ppm; digital scales range from 0-100% to 0.1%	±1			5		0-50	z = ±1% (24) s = ±1% (24)
	IR-703[f]	Any species absorbing IR	IR	2395	34								
	IR-705[f]	Any species absorbing IR	IR	2950	34								
Mine Safety Appliance Co. Pittsburgh, Pennsylvania	LIRA 303[g]	Hydrocarbon species that absorb IR	IR	2970	37	0-100% LEL and 0-1000 ppm			±1	5	<1	4-45	z = <±1% (24) s = <±1% (24)

[a]The letters "z" and "s" indicate zero drift and span drift. The number of hours over which drift occurs is given in parentheses.

[b]Available in single and dual component versions.

[c]Factory-calibrated for gas to be detected in application.

[d]Autoexhaust analyzers; solid state detectors.

[e]Miran-101 and Miran-103 do not have built-in, multiparameter capabilities. Their measurement range is from 0 to 1000 ppm for most species.

[f]IR-702, IR-703 and IR-705 are usually bench- or panel-mounted instruments. IR-702 is a dual component instrument; and IR-703 and IR-705 are single-component instruments.

[g]Can be calibrated to measure a single gas or a mixture if the instrument is panel-mounted.

Source: Reference 4.

TABLE 5

PORTABLE COMBUSTIBLES ANALYZERS

Manufacturer	Model No.	Pollutant(s) Detected	Principle of Operation	Cost $	Weight lb	Range ppm	Accuracy %	Sensitivity	Precision %	Response Time s	Ambient Temperature °C	Drift[a]
Bacharach Instrument Co. Santa Clara, California	G	Combustible gases	Catalytic combustion	253	4	0-100% LEL					0-50	
	L			160	4	0-100% LEL						
	H[b]			279	5	0-100% LEL						
	TLV Sniffer[c]		Catalytic combustion	896	5	0-100, 0-1000 & 0-10,000 ppm	±3	2 ppm	±3			
Biomarine Industries, Inc. Malvern, Pennsylvania	922	Combustible gases and vapors	Catalytic combustion	495	1.5	0-100% LEL	±5% LEL			5	-15 to 40	
	900, 900R and 900RS	Combustible gases and vapors	Catalytic combustion	685, 695 and 715	3	0-100% LEL	±5% LEL			5	-15 to 40	
Control Instruments Corp. Fairfield, New Jersey	FFAP[d]	Flammable gases and vapors	Thermal combustion		28	0-100% LEL	±3		±1	<10	0-52	a = <±5% (1 yr) a = <±5% (1 yr)
Gas Tech, Inc. Mountain View, California	1177	Combustible gases	Catalytic combustion	525	6	0-100% LEL	±5		±2	4	0-40	
	1238	Combustible gases	Catalytic combustion	695	7	0-100% LEL & 0-500 ppm	±2		±2	10	-20 to 50	
International Sensor Technology Santa Ana, California	AG5100	Combustible gases and vapors	Change in resistance within detector	1200 for ppm scale; 825 for LEL scale		LEL and ppm	±5		±5	10 on LEL scale and 60 on ppm scale		Negligible in a 3-month period
Mine Safety Appliance Co. Pittsburgh, Pennsylvania	20[e]	Combustible gases	Catalytic combustion	374	6	0-100% LEL						
	30[f]	Combustible gases	Catalytic combustion	374		0-100% LEL						
	40[g]	Combustible gases	Catalytic combustion	374		0-10% and 0-100% LEL						

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TABLE 5 (Continued)

Manufacturer	Model No.	Pollutant(s) Detected	Principle of Operation	Cost $	Weight lb	Range ppm	Accuracy %	Sensitivity	Precision %	Response Time s	Ambient Temperature °C	Drift[a]
Survey and Analysis, Inc. Northboro, Massachusetts	OnMark Model 5[h]	Combustible gases and vapors	Thermal conductivity	285	<5	0-5 and 0-100%	±3		±3	<10	0-50	z = ±4% (2 mo)
Teledyne Analytical Instruments, San Gabriel, California	980	Total combustibles and oxygen	Catalytic combustion		17	Scale: 0-5% methane; others are available	±2	0.5% of full scale		20	0-50	

[a]The letters "z" and "s" indicate zero drift and span drift given as percent of scale over the time specified in parentheses.

[b]Catalytic combustion (hotwire) in low range and thermal conductivity in high range.

[c]The ranges of TLV can be multiplied by 10 with a dilution probe.

[d]The FFAP uses a propane flame to combust sample gas and is fully portable.

[e]Can be factory calibrated for five gases, such as pentane.

[f]Calibrated to measure natural gas and petroleum vapors in air mixtures.

[g]Factory calibrated for pentane.

[h]Filament for the 0-100% scale are thermal sensors heated to 300° to 400°F, and filaments for the 0-5% scale are catalytic sensors heated to 1200° to 1300°F.

Source: Reference 4

to compounds of widely differing functional character is not achievable with currently evaluated instruments but is a desirable goal. The other characteristics such as portability and instrinsic safety are also important but none should be considered individually critical to the acceptance of a potential detector.

Assuming that characteristics of fast response and appropriate measurement range are available in potential VOC detectors, the ability of the devices to meet the criterion of similar responsiveness needs to be reviewed prior to final instrument selection. Thus, the efficacy of various operating principles to meet this criterion is discussed below.

(1) Photoionization

Photoionization detectors utilize ultraviolet radiation to ionize a small fraction of molecules introduced into an ionization chamber. The ionization process is initiated by absorption of a photon of sufficient energy, i.e., greater than the ionization potential, to remove an electron from its ground state to infinity. A free electron and positively charged ion are thus formed:

$$R + h\nu \rightarrow R^+ + e^-$$

If the energy of the UV lamp is less than the ionization potential of the compound, no ionization takes place. Ions formed in the detector/ionization chamber may reach the electrodes under the influence of an electric field and produce a small current. The number of ions which reach the electrode is proportional to the concentration, although only a very small fraction ($\sim$0.01%) of the molecules in the ionization chamber are ionized by incident radiation. Depending on the character of the electrons, e.g., sigma vs pi electrons, the yield of ions (photoionization efficiency) may vary as a function of the energy of incident photons (Figure 1). At present, UV sources are available for commercial instruments which emit photons of approximately 9 eV, 10 eV or 12 eV. Based on the ionization potentials of organic compounds,[5] it is apparent that certain classes of compounds, e.g., aromatics and aliphatics greater than carbon number C7, can be ionized by a 10 eV lamp while many substituted aliphatics require photons of at least 11 eV (Figure 2). This observation leads to the conclusion that with sufficient energy most organic compounds can be ionized and detected. A practical upper energy limit for VOC analysis is about 12 eV since the major components of air such as nitrogen, carbon monoxide, carbon dioxide and water have ionization potentials above this level. As well as the ionization potential, the photoionization efficiency is important since this parameter determines sensitivity of the technique to different compounds. A recent report[6] indicates that the molar sensitivity of aliphatic and oxygenated aliphatic compounds is several times less than that of aromatic compounds if incident radiation is about 10.2 eV. In fact, for aliphatic hydrocarbons of carbon number less than C8, the relative sensitivity is less than one-tenth that for benzene. If incident radiation is about 11.7 eV, the relative sensitivity of aliphatic

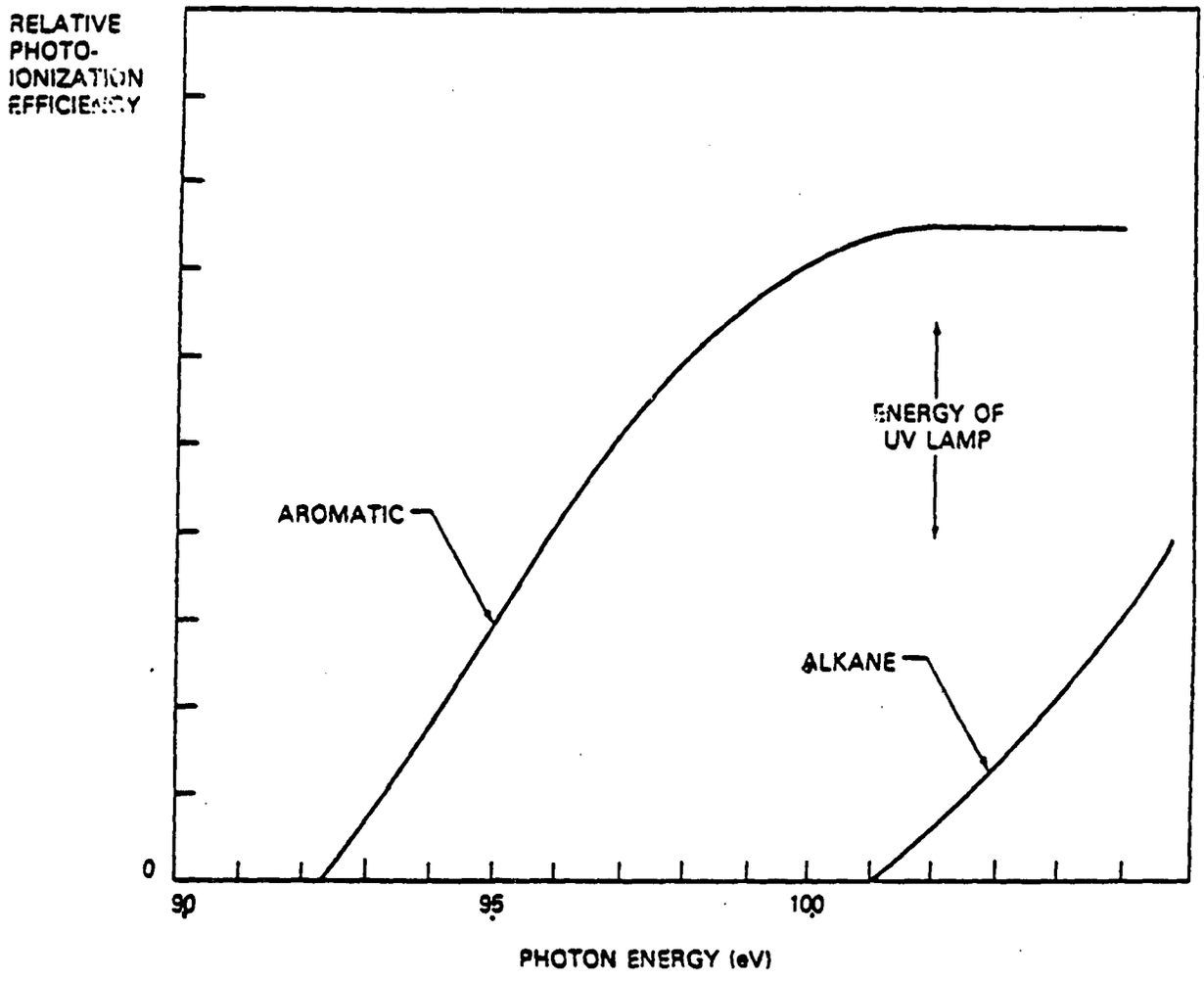

Figure 1. Photoionization efficiency curves as a function of photon energy for an aromatic hydrocarbon and an alkane (source: Ref. 5).

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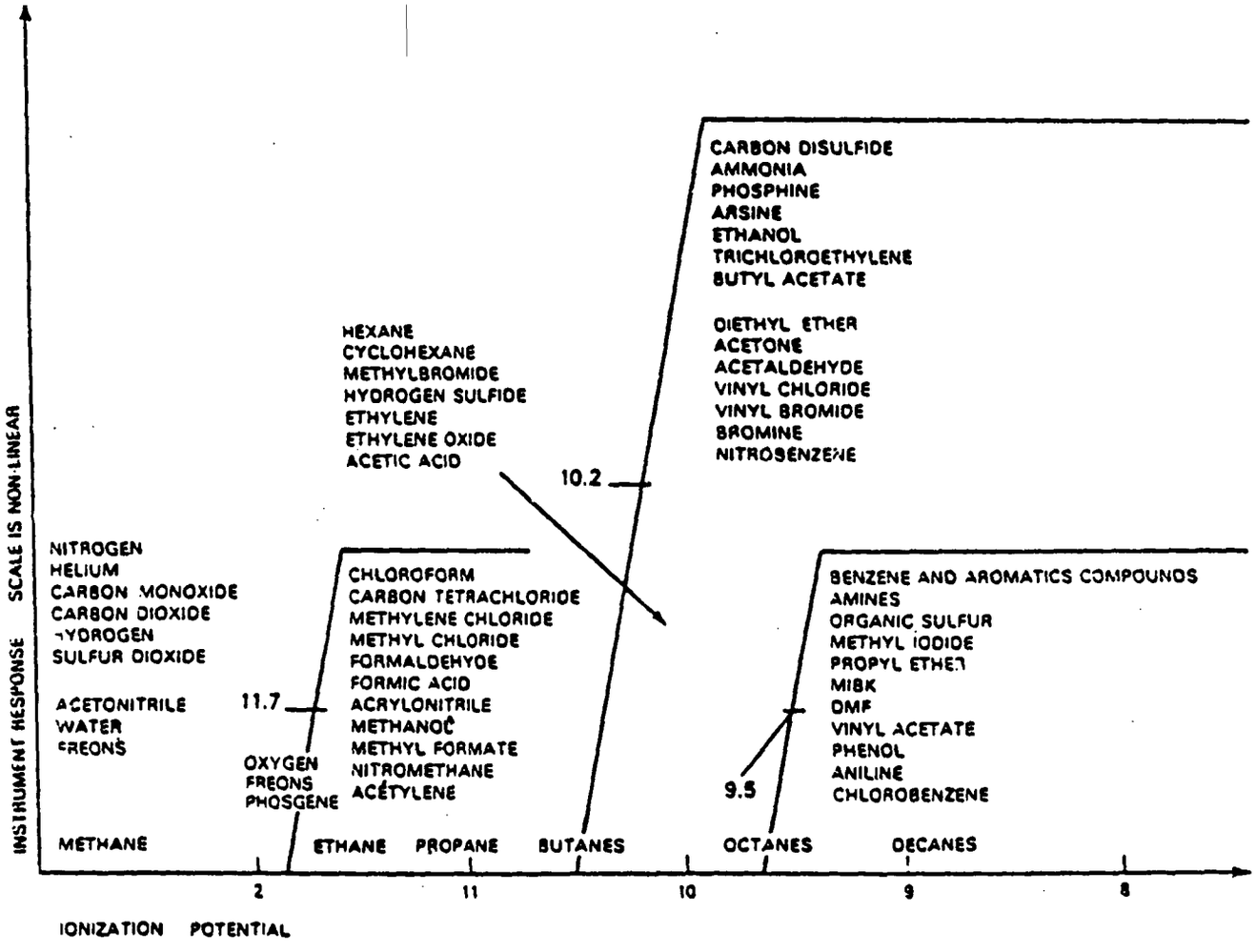

Figure 2. Instrument response vs. ionization potential for several classes of compounds (Ref. 5).

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and aromatic compounds is similar[7] and perhaps within a factor of two. Based on this assumption, a commercially available photoionization instrument with a lamp of about 12 eV may provide a generally applicable VOC detection technique.

(2) Infrared Detection

Typical nondispersive infrared devices operate by passing infrared radiation through two separate absorption cells: a reference cell and a sample cell. The sealed reference cell is filled with nonabsorbing gas, such as nitrogen or argon. The sample cell is physically identical to the reference cell and receives a continuous stream of gas being analyzed. Subsequently, the net radiation in the two beams are passed into and absorbed in matched selective detectors (e.g., Luft detector) containing the vapor to be detected. When organic vapors are present in the sample cell, energy is absorbed, and the temperature and pressure in the corresponding detector is reduced relative to that in the detector on the reference side of the analyzer. A diaphragm between the two detectors is displaced and the amount of displacement is detected, electronically amplified, and an output signal proportional to concentration produced. In other NDIR systems, narrow bandwidth filters which pass energy which corresponds to that absorbed by the compound of interest are used along with simple solid state IR detectors. In both cases, interference from compounds with overlapping absorption bands is possible. More importantly, the maximum absorbing wavelength for different organic species in the sample gas may not correspond to the maximum absorbing wavelength of the calibration compound used in the detector. Within reason, several different calibration compounds could be used in the detector to improve responsiveness for several compounds. Alternatively, by selection of a single narrow bandwidth filter with a wavelength corresponding to a general aliphatic C-H stretch, many aliphatic hydrocarbons might be detected quite uniformly. Based on the maximum absorption wavelength of aromatic hydrocarbons, a separate filter or cell would be needed for this class of compounds. In practice, the specificity of the detection principle has precluded the manufacture of an NDIR device suitable as a general (i.e., both aliphatic and aromatic) organic vapor detector.

An alternative IR detection scheme involves dispersive infrared analysis in which the specific wavelength absorbed by the organic vapor of interest is passed through a single sample cell. In this case, selectivity is provided by a monochromatic light source rather than a selective detector. Such a device is inherently more selective than an NDIR and thus may be less appropriate as a VOC screening device. However, by successive, rapid monitoring of IR absorption at several selected wavelengths corresponding to the maximum absorption wavelengths for several organic functional groups, e.g., aliphatic CH, aromatic CH, C-Cl, C=O, it may be possible to identify and quantify a wide variety of organic vapors in a fugitive emission source.

(3) Thermal Conductivity

Thermal conductivity (TC) of gases and vapors provides a physical method used extensively in gas chromatography where mixtures of compounds are resolved into individual components and quantified. The detector responds proportionally to a change in thermal conductivity of the trace gas in a background (helium, for example). The physical property of thermal conductivity is not specific to any class of compounds. In fact, the conductivity of many gases with the exception of hydrogen and helium is quite similar as shown below:

Gas	Thermal Conductivity [10^{-5} Cal/Sec-cm^2/(°C/cm)]
Air	7.5
Hydrogen	53.4
Helium	41.6
Nitrogen	7.5
Oxygen	7.6
Carbon Dioxide	5.3
Methane	10.9
Ethane	7.3
Propane	6.3

As molecular weight increases, the thermal conductivity decreases somewhat, but for organic compounds of interest in fugitive sources the thermal conductivity does not differ from that of air by more than a factor of two.[8] Thus, the concentrations of organic contaminants in air must be very large (e.g., 1-100%) in order for the vapor to be detected against the air matrix which has a similar thermal conductivity. This severely limits the usefulness of TC detectors for VOC screening. Two additional problems exist for TC detectors in this application. First, inorganic gases (e.g., CO_2, H_2O, HCl) which may be present in fugitive sources will be detected along with any organic vapors. Second, most thermal conductivity detectors consist of heated wires which are subject to degradation by oxidizing or humid atmospheres or by the presence of chlorinated hydrocarbons. Thus, the practical application of TC detectors to VOC screening is in doubt.

(4) Other Detection Schemes

Two other detection principles, implicitly limited in response only to chlorinated organic compounds, may be appropriate for this compound class. They include electron capture, which is used commonly in gas chromatography, and enhancement of radiation from halogens by a spark source. Each scheme depends on a unique property of halogens: electronegativity and electron energy levels, respectively. Their

application for organic detection is very limited and their practical use for VOC screening is in doubt.

B. Unit Selection

On the basis of the factors discussed above, both the IR and photoionization principles might be suitable for general VOC screening. However, a comparison of the specifications of commercially available instruments (Tables 3, 4) operating by these principles and the criteria of Method 21 lead to a rather unfortunate conclusion: no commercial instruments of these types are available for VOC screening. In terms of a desire to expand the list of potential detectors, such a finding is unsatisfactory.

What criteria led to this finding? The most obvious answer is the requirement for an intrinsically safe device. No IR or PID devices are certified for use in Class I, Division 1 environments (Table 2). One PID device is certified for use in Class I, Division 2. It should be noted, however, that in the future other devices may be modified so as to meet Class I, Division 1 certification. Alternatively, the use of an instrument only in less hazardous environments may not be considered as particularly restrictive. For these reasons, the criterion of intrinsic safety was given lesser significance and not used to rule out potential devices for screening in this program.

The other criteria listed previously were ranked in approximately descending order of importance. Thus, a response time of less than 30 seconds was given the highest importance. In fact, fast response time is very important to practical measurement of VOC leaks and several instruments with faster than 30-second response time are available. Thus, it was decided that this criterion must be met by any instrument to be evaluated. The criteria of portability, ruggedness and ease of operation are also important but were not chosen as absolute selection criteria. Portability can be evaluated subjectively and devices operated with automobile batteries placed on a small cart may be considered to have adquate portability. Devices operated with AC power are less practical in many industrial environments.

Tables 3 and 4 and additional manufacturers' literature were reviewed using the modified criteria described above. A list of potential VOC detectors was developed (Table 6). This list includes instruments which operate on photoionization and IR principles and which meet most of the Method 21 criteria. It is obvious that not all of the IR instruments that meet most of the criteria are included. Since the goal of this study is to evaluate the usefulness of the IR principle rather than all available IR devices, only selected IR devices suitable on the basis of the criteria for VOC screening were included.

The list, therefore, includes a dispersive IR device and NDIR devices with or without solid state detectors. The NDIR devices may be useful for a specific group of organics, i.e., aliphatic hydrocarbons. Also included are two devices operating on other detection principles, i.e., ion capture and UV spark. These instruments are only useful for a

TABLE 6

POTENTIAL VOC DETECTORS[4]

Instrument	Principle	Range (ppm)	Response(s)	Wgt (lbs)	Pump	Power	Intrinsically Safe
HNU Systems, Inc. (PI-101)	Photo-ionization	0-20, 0-200, 0-2000	5	9	Yes	Battery	Yes
General Electric (TVM 1)	Ion Capture (Halogenated	0-1 → 0-10,000	120	23	Yes	No	No
Gas Tech, Inc. (Halide)	UV Spark (Halogenated)	0-100, 0-10,000	5	13	Yes	AC	No
Foxboro, Inc. Miran 1A/80	IR	ppm → %	1-40	32	Yes	Car Battery (37 lbs)	No
103	IR	ppm → %	1-40				
ANARAD, Inc. AR-400 <5μ	IR	100-10,000 ppm	5	24	Yes	AC	No
Infrared Industries IR-711 <5μ	IR Solid State	1000 ppm, 100% LEL	5-120	9	Yes	Battery	Yes
AID, Inc. (580)	Photo-ionization	0-200 0-2000	2	8	Yes	Battery	Pending

specific class of organics, i.e., halogenated hydrocarbons, but were included due to the widespread industrial use of these solvents.

The final instruments selected for evaluation were as follows:

Instrument	Manufacturer	Principle of Operation
Model 580	AID, Inc.	Photoionization
PI 101	HNU Systems, Inc.	Photoionization
Miran 80	Foxboro/Wilks, Inc.	Dispersive Infrared

The rationale for the selection of these instruments is based on both suitability and availability. As noted previously, photoionization may be a particularly suitable VOC detector for aliphatic, aromatic, and substituted organic vapors. Either of the two commercially available, portable instruments meet most Method 21 criteria and may be suitable for evaluation. Both photoionization instruments were selected on the basis of the following considerations:

1. Each was supplied free of charge;

2. Each was modified by the manufacturer with a dilution probe (see discussion in Section 2c);

3. The location of HNU Systems, Inc. provided the potential for rapid modification/repair; and

4. Negligible additional time would be expended in evaluating both devices due to similarity of design.

The Miran instrument is the one available infrared device which permits a selection of wavelength as opposed to selection of a test compound in a reference cell. This option permits the rapid (a few seconds) assessment of the suitability of several wavelengths for the measurement of the substituted organics of interest. Specific examples are an aliphatic C-H stretch, aromatic C-H stretch or a C=O stretch. Other portable IR devices utilize a filter at one specific wavelength band corresponding, for example, to an aliphatic C-H stretch. Thus, they have an inherent selectivity against aromatic or substituted species. Since all three classes of compounds are of interest, the latter devices are not preferred as VOC screening devices. It is possible that one wavelength may be suitable for analysis of a wide variety of organic vapors. If that is the case, other IR instruments could potentially be used for VOC leak detection. In summary, the Miran 80 (with associated microprocessor) permits the most rapid and cost-effective assessment of the IR principle as a general VOC detector. Other IR devices were, therefore, not evaluated.

The halocarbon specific detectors, i.e., General Electric TVM-1 and Gas Tech Halide Detector, were not selected for evaluation despite

the potential usefulness of such a device in environments subject to halocarbon solvent combination. Neither the GE TVM-1 nor an equivalent model is now sold. The Gas Tech device could not be modified to meet the intrinsic safety requirements of Method 21 due to the presence of a spark in the detector section.

No other instruments appeared to have a reasonable expectation of meeting the Method 21 criteria and of providing a significantly different performance than those devices evaluated previously or selected for evaluation in this study.

C. Unit Modification

Both photoionization devices operate with a maximum quoted linear range of 0-2000 ppmv. In fact, the linear range is frequently reported to be only about 1500 ppmv. Since the maximum concentration of concern in VOC screening is 10,000 ppmv, dilution of sample air is necessary for both instruments to operate in the linear range. Both HNU Systems, Inc. and AID, Inc. provided their instruments with dilution systems designed in their respective laboratories. The HNU Systems, Inc. design (Figure 3) consisted of (1) a fine bore restrictor which limited the flow of sample air, and (2) a charcoal tube which passed an excess (10x) of hydrocarbon-free air (methane is not removed but does not respond in the detector). The sample stream is thus diluted about 1 to 10. The AID, Inc. design (Figure 4) consisted of a pump and needle valve which diverted 90% of the incoming sample air through a charcoal tube and 10% to the normal exhaust point. The hydrocarbon-free (except for methane) sample air is combined with the incoming sample stream and thus a continuous tenfold dilution is provided.

Problems were observed with these dilution systems and the UV lamps provided with both instruments. The absolute accuracy of the dilution ratios is in some doubt since independent flow rates were difficult to measure. The UV lamps provided with both instruments were subject to degradation during the life of the study. In fact, the 11.8 eV lamp supplied with the AID, Inc. device failed during the study and, unfortunately, a replacement could not be obtained in time to collect useful data with this instrument. The 11.7 eV lamp supplied with the HNU Systems, Inc. device failed during the study and a replacement was provided. The difference in energy output from the two HNU Systems, Inc. lamps was large (i.e., a factor of three to ten depending on the age of the lamp). This variation affected the linear range of the instrument and created problems in obtaining consistent results. In some cases with the new lamp, saturation of the detector occurred even with the dilution probe attached to the instruments. The test results reported in Section 5 must, therefore, be carefully interpreted and conclusions narrowly drawn.

The Miran 80 operates over the concentration range from ppm to percent. The wide dynamic range is provided by a cell in which the pathlength of IR radiation can be changed by optical folding of the incident beam.

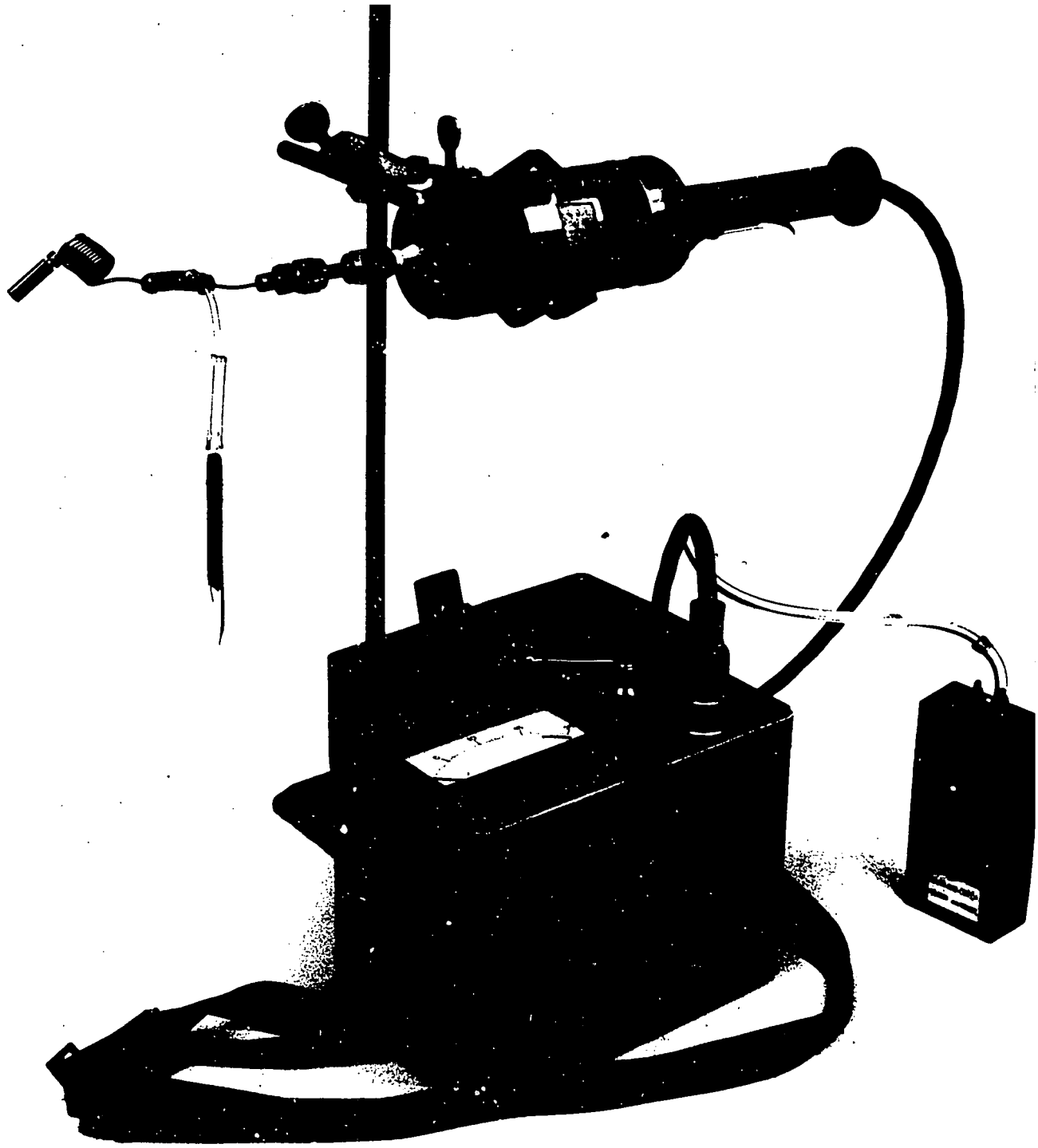

Figure 3. HNU Systems, Inc. dilution probe.

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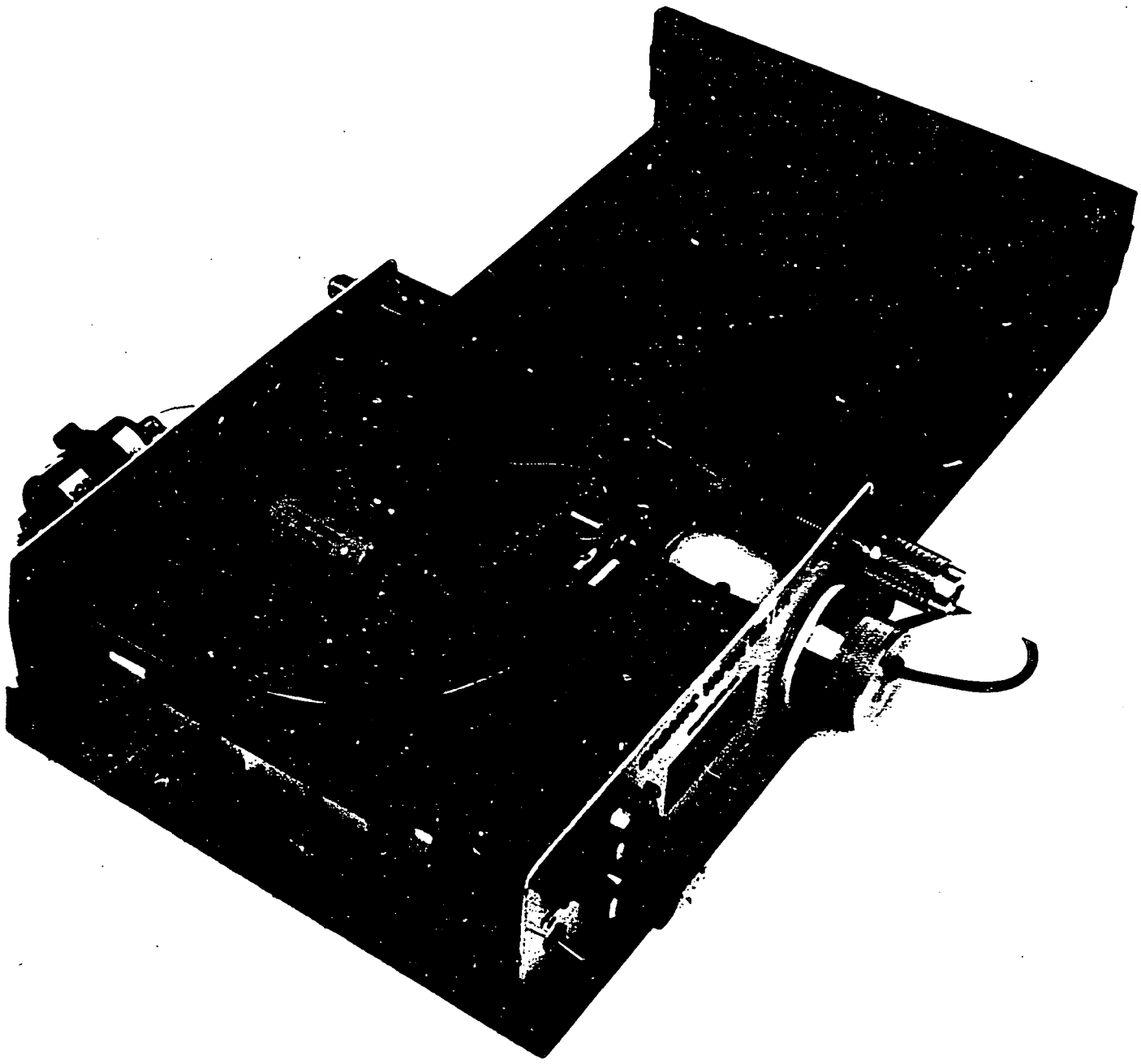

Figure 4. AID, Inc. dilution system.

At the concentration range of interest, i.e., 100 ppmv to 10,000 ppmv, the incident beam traversed a distance of about 0.75 m. At this pathlength, the full-scale absorbance for vapors of interest at a concentration of 10,000 ppmv was about one absorbance unit. Once the cell pathlength was set, no other modifications of operating conditions were required.

3. COMPOUND SELECTION

As noted in the Introduction, 168 compounds had previously been tested for response factor on two commercially available VOC detectors.[3] Twenty-three showed sufficiently poor response that the actual and measured concentrations differed by a factor of greater than five (Table 1). The classes of compounds showing poor agreement were generally highly substituted aliphatic and aromatic compounds and those compounds incorporating functional groups such as carbonyl and hydroxyl groups.

These 23 compounds were selected for testing on the alternative VOC screening devices to be evaluated in this study. Several other compounds (Table 7), which were not evaluated in the previous work, were added to the list.

These compounds (Tables 1 and 7) include only a portion of those commonly used in chemical production. At the request of OAQPS, other industrial compounds which have a vapor pressure greater than 0.3 kPa but which were not considered previously have been tabulated (Table 8). This extensive list of 76 compounds includes many species for which an FID or catalytic combustion detector would respond well. However, others are highly substituted compounds which will probably not give adequate response on these two detectors. Selected substituted compounds from Table 8 were included in the detector evaluation.

The selection criteria required a response to several questions:

1. Are substituent groups present or absent? If absent, don't test,

2. Are the compounds similar (functionally and/or isomerically) to others previously evaluated? If they are, don't test,

3. Are response factors on an FID instrument likely to exceed five? If not, don't test, and

4. Do the compounds pose a serious health hazard to laboratory personnel? If they do, cautiously consider evaluation.

As a result of the responses, the compounds were separated into two groups: compounds that should and those that need not be analyzed. Within the first group, the compounds were prioritized on the basis of (1) their similarity to other vapors to be analyzed (for example, positional isomers of compounds selected for testing were given lower priority), and (2) their health hazard (extremely toxic compounds with little commercial application or likelihood of release and which require complex/expensive handling were given lower priority).

The compounds selected for evaluation in this program are listed in Table 9. They are listed in the approximate order of testing.

TABLE 7

ADDITIONAL COMPOUNDS TO TEST

OCPDB[a] ID No.	Compound Name
1660	Ethanol
--	Formaldehyde
1235, 1236	Ethylene Dichloride (Dichloroethylene)
—	Chlorinated Ethanes (C_2H_5Cl, etc.)
—	Chlorinated Methanes (CH_3Cl, etc.)

[a]Organic Chemical Producers Data Base

TABLE 8

SYNTHETIC ORGANIC COMPOUNDS WITH VAPOR PRESSURE

GREATER THAN 0.3 kPa (20°C) AND NOT TESTED PREVIOUSLY

Compound	Vapor Pressure (kPa)
Acetal	2.7
Acetaldehyde	98.6
Acrolein	29.7
Acrylic esters: methyl acrylate	8.7
Allyl chloride	40.8
Amyl acetate	0.5
Amyl amine	2.0
Amyl chloride	2.2
Amyl mercaptans: 1-pentanethiol	1.5
2-methyl-2-butanethiol	5.0
2-methyl-1-butanethiol	2.0
3-methyl-1-butanethiol	2.1
Aniline hydrochloride	4.0
Benzyl benzoate	0.5
Chlorobenzoyl chloride	2.6
Chlorodifluoromethane	G
Chlorodifluoromethane	G
Chloroprene	23.1
Chlorotrifluoromethane	G
Cyanoacetic acid	2.9
Cyanogen chloride	G
Cyclooctadiene (1,5-)	3.3
Dichlorodifluoromethane	G
Dichloropropene (isomers)	70.3
Diethylamine	24.0
Difluoroethane	G
Diketene	1.6
Dimethylamine	G
Dimethyl ether	G
Dimethyl sulfide	48.8
Dioxolane	9.3
Ethyl bromide	51.4
Ethyl chloride	G
Ethylene chlorohydrin	0.7
Ethylene dibromide	1.5
Ethylene glycoldimethyl ether	7.8
monoethyl ether	0.6
monoethyl ether acetate	0.3
monomethyl ether	1.2
monomethyl ether acetate	0.3
monopropylether	0.5
Ethyl orthoformate	0.4
Glycerol dichlorohydrin	0.9

SOURCE: REFERENCE 3

TABLE 8 (continued)

Compound	Vapor Pressure (kPa)
Hydrogen cyanide	66.6
Isoamylene	G
Isobutanol	1.0
Isobutyl acetate	1.9
Isobutyraldehyde	18.3
Isopentane	76.5
Isopropylamine	29.3
Ketene	G
Methallyl chloride (isomers)	70.3
Methylamine	G
Methyl bromide	G
Methylene chloride	46.1
Methyl isobutyl carbinol	0.4
Methyl isobutyl carbinol	2.1
Neopentanoic acid	1.1
Nonene	0.5
Paraldehyde	3.4
Pentene	70.3
Perchloroethylene	1.8
Perchloromethyl mercaptan	0.6
o-Phenylene diamine	1.18
Phosgene	G
Propylamine	33.0
Propylchloride	37.3
Propylene chlorohydrin	0.7
Propylene dichloride	5.3
Quinone	5.0
Tetramethyllead	3.0
Toluene sulfonic acids	70.3
Toluene sulfonylchlorides	70.3
Trichlorofluoromethane	79.5
Trichlorotrifluoroethane	31.8
Trimethylamine	G

SOURCE: Vapor pressure distribution of synthetic organic chemicals. Weber, R.C.; P. Parker and M. Bowser. IERL, Cincinnati, Draft Report, November 1980.

G - Gas; VP >101.3 kPa.

TABLE 9

COMPOUNDS FOR EVALUATION

Carbon Disulfide
Carbon Tetrachloride
Chloro-Acetaldehyde
Dichloro-1-propanol, 2,3-
Dichloro-2-propanol, 1,3-
Diisopropyl Benzene, 1,3-
Dimethyl Styrene, 2,4-
Formic Acid
Freon 12
Methanol
Methylstyrene, α-
Tetrachloroethane, 1,1,2,2
Ethanol
Formaldehyde
Ethylene Dichloride (Dichloroethylene)
Chlorinated Ethanes (C_2H_5Cl, etc.)
Chlorinated Methanes (CH_3Cl, etc.)
Acetophenone
Benzoyl Chloride
Furfural
Monoethanolamine
Nitrobenzene
Phenol
Acetyl-1-propanol, 3-
Glycidol
Hydroxyacetone
Methyl-2,4-pentanediol, 2-
Phenyl-2-propanol, 2-
Aniline Hydrochloride
Difluoroethane
Diketene
Dimethylsulfide
Glyceroldichlorohydrin
Paraldehyde
Perchloromethylmercaptan
Propylene Chlorohydrin
Toluenesulfonic Acid
Toluene Sulfonylchloride
Ethyleneglycoldimethyl Ether
Ethyleneglycolmonoethyl Ether Acetate
1-Pentanethiol
Acetal
Chlorobenzoylchloride
Chlorodifluoromethane
Chlorotrifluoromethane
Trichlorofluoromethane
Trichlorotrifluoroethane
Cyanoacetic Acid
Neopentanoic Acid
Amylmercaptans
  2-methyl-2-butanethiol
  2-methyl-1-butanethiol
  3-methyl-1-butanethiol
Glycols
  Ethylene Glycolmonoethyl Ether
  Ethylene Glycolmonomethyl Ether
  Ethylene Glycolmonomethyl Ether Acetate
  Ethylene Glycolmonopropyl Ether
  Glycolmethyl Ether (Dioxolane)

4. EXPERIMENTAL PROCEDURES

A. Introduction

Determination of response factors required initial calibration of the VOC detectors with a gas or gases of known concentration. Methane had been used previously for calibration of FID and combustion analyzers.[3] However, the photoionization instruments do not respond to this compound and the multiple wavelength analysis by dispersive infrared spectrometry cannot be carried out by the use of methane as a single calibration gas.

Therefore, 1,2-dichloroethane was selected as the calibration gas for the photoionization detectors. This compound can be detected by the instruments and it has a response factor of about one (compared to methane) when analyzed on an FID instrument. As a result, data collected in this study may be comparable to data collected in a previous EPA study.[3]

Several calibration compounds were used for the IR evaluation since several wavelengths were scanned in the dispersive infrared instrument to determine if any wavelength gave similar response factors for all the compounds of interest. The wavelengths were selected to correspond to key functional groups of the test compounds to be analyzed. The wavelengths, functional groups and calibration compounds are listed in Table 10.

Once calibrated, the instruments were used to analyze the test compounds at three concentrations over the range of 100-10,000 ppmv. The response factor was determined by calculating the ratio of the actual concentration to the concentration indicated by the instrument. The following sections describe the procedures involved in calibration and operation of the instruments, preparation of test gas samples, and calculation of response factors.

B. Instrument Operation

Three instruments were selected for evaluation as VOC screening devices. Two instruments operated on the photoionization principle, i.e., AID, Inc. Model 580 and HNU Systems, Inc. Model PI-101. The other in instrument was the Foxboro/Wilks, Inc. Miran 80 which operates on the principle of dispersive infrared spectrophotometry. Details of the operation of each instrument are given in the appendices.

During the tests, the lamp in the Model 580 failed and a replacement could not be obtained. Therefore, only the PI-101 and Miran 80 were evaluated.

C. Preparation of Gas Standards/Samples

Gas mixtures tested in this study were prepared in Tedlar gas sampling bags of a nominal 25 liter volume. These bags provide a relatively

TABLE 10

CALIBRATION SCHEME FOR MIRAN-80

Wavelength (μm)	Functional Groups(s)	Calibration Compound
3.3	Aromatic & Unsaturated C-H	Toluene
3.4	Saturated C-H	Pentane
3.6	Aldehyde C-H	Butyraldehyde
4.0	Reference Wavelength	Air
5.7	Carbonyl C=O	Acetone
6.35	Aromatic C-C, conj C=C (also N-H, C-S)	Toluene
8.8	Ether C-O-C	Diisopropyl Ether
9.5	Alcohol C-O-H	Isopropanol
13.5	C-Cl	1,2-dichloroethane

inert surface to preclude adsorption, reaction, or permeation. They also permit visual inspection of the bag interior to provide an indication of sample condensation or reaction. The bags are equipped with two valves to facilitate flushing of sample gas and a septum to permit injection of sample liquid with a syringe.

Gas samples were prepared by the following procedure:

1. Flush and evacuate bag three times with hydrocarbon-free air (i.e., until no hydrocarbons are detected on each instrument).

2. Fill bag with 20.0 L of hydrocarbon-free air.

3. Inject a known volume of test compound into the bag.

4. Permit at least one hour equilibration to insure adequate evaporation and mixing.

5. Draw gas sample from bag with each instrument.

The hydrocarbon-free air was prepared by passing house compressed air through silica gel, charcoal and a high efficiency filter. A known volume (20.0 L) of air was introduced into the hose fitting of the Tedlar bags through a calibrated rotameter. The volume was calculated on the basis of rotameter flow rate (L/min) and duration of flow (min). The flow rate was corrected for system temperature and pressure although these corrections were negligible over the range of conditions observed. Known volumes of the test compounds (all liquids) were injected through the septa of the bags with Hamilton microliter syringes. The volumes injected were in the range of 10 to 100 µL. The mass of material injected was calculated from density data. Manual manipulation of the bag, visual observation and at least one hour equilibration period were used to ensure complete mixing.

The target concentrations prepared for each compound were 500, 1000, 5000 and 10,000 ppmv. In several cases, it was not possible to prepare the higher concentrations due to the low vapor pressure of the compound or due to safety reasons, that is, such a concentration would exceed the lower explosive limit. In these cases, a concentration of 100 ppm was often prepared. For each target concentration, the required volume of liquid was calculated and measured in a microliter syringe. The volume required to produce the test concentration was calculated according to the following equation:

$$V_L = (C)(V_A)(MW_L)(BP)/(62.36 \times 10^6)(\rho_L)(T)$$

where V_L is the volume of liquid compound in the syringe in milliliters,

C is the target concentration of compound "L" in parts per million by volume (ppmv),

V_A is the sample bag volume in liters (i.e., 20.0 L),

MW_L is the molecular weight of compound "L,"

BP is the barometric pressure in mm Hg,

62.36×10^6 is a combined constant with the unit (liters)(mm Hg)(g-mols)(°K). This constant incorporates the ideal gas volume of 22.4 liters per g-mol, standard temperature and pressure, and a factor of 10^6 to go from volume fraction to ppmv,

ρ_L is the liquid density in g/ml, and

T is the laboratory temperature in °K.

D. Calibration Protocol

Each instrument was initially calibrated (spanned) with a gas sample prepared in triplicate at a concentration of 10,000 ppmv. Calibration curves were then prepared by introducing samples of the calibration gas, prepared in triplicate at five concentrations over the range of 100 to 10,000 ppmv, into the instruments and recording the response. The PI-101 was calibrated with 1,2-dichloroethane while the Miran 80 was calibrated at individual analytical wavelengths with the compounds listed in Table 10.

During subsequent analysis of each test compound, the HNU PI-101 instrument was spanned with an 8040 ppmv 1,2-dichloroethane certified gas standard provided by Scott Specialty Gas, Inc. of Plumsteadville, Pennsylvania. This span was carried out just prior to analysis of each set of sample bags for each test compound.

The Foxboro/Wilks Miran instrument was electronically zeroed and spanned according to the manufacturer's instructions. This zero and span check was carried out prior to analysis of each set of sample bags for each test compound.

E. Instrument Sampling

The procedure used to obtain response data involved the following steps for each of five replicate sample bags for each of three target concentrations of each test compound:

1. Span and zero instruments.

2. Connect bag to photoionization instrument (PI-101).

3. Observe instrument response and record three instrument readings at equilibrium point.

4. Remove bag and permit instrument response to return to zero.

5. Repeat steps 1-4 with each sample bag.

6. Connect bag to infrared instrument (Miran 80); start pump.

7. Empty bag to approximately 10% of original volume; stop pump.

8. Record instrument response at each of eight analytical wavelengths and one reference wavelength.

9. Repeat steps 6-8 with each replicate sample bag at first target concentration.

10. Remove bag, start pump and rezero instrument on zero air (room air was adequate).

11. Repeat steps 6-10 for each target concentration.

F. Data Analysis

The response factor reported in the following test results section is the number that, when multiplied by the apparent concentration based on instrument response, yields the actual concentration as calculated to exist in the gas bag sample. That is:

$$\text{Response Factor (RF)} = \frac{\text{Actual Bag Concentration (C)}}{\text{Concentration Calculated from Instrument Response}}$$

Response factors were determined at three actual concentrations, i.e., generally 100, 500, 1000, 5000 or 10,000 ppmv. No attempt was made to fit the three response factors for each compound to a particular function. For some compounds, the response factor is nearly identical for each concentration whereas for others it differs dramatically and in a complex manner. The response factor for individual compounds is, therefore, not reported for an observed instrument response of 10,000 ppmv. Instead, the mean response factors calculated from up to five replicate data points at each of the three actual bag concentrations are reported along with the standard deviation. Also reported is the 95% confidence intervals for the response factors as calculated from Student's t-test.

5. TEST RESULTS

The response factors for the compounds tested in this instrument evaluation program are listed on the following tables. The response factors for all 16 compounds tested on the HNU Systems, Inc. Model PI-101 are reported in Table 11. The data are limited due to several factors including:

1. The low vapor pressure of many compounds of interest and thus the low concentration prepared in the sample bag and found in the dilutor outlet;

2. The failure of the dilution system to operate suitably;

3. The declining intensity of the UV lamp; and

4. Saturation of the instrument's detector.

The response factors for 32 individual compounds tested on the Miran are reported in Table 12. The response factors are reported only for those wavelengths where the detector was sufficiently sensitive to yield an absorbance value above the background noise. Where this is not the case, the response factor would be much greater than ten. The remainder of the 57 compounds listed in Table 9 were not tested for several reasons including:

1. Similarity with compounds tested, e.g., amylmercaptans with pentanethiols and glycols with ethyleneglycol-monoethylether acetate,

2. Low vapor pressure, e.g., phenyl-2-propanol,

3. Solid state, e.g., phenol,

4. Reactivity in Tedlar bags, e.g., toluene sulfonylchloride,

5. Poor availability of gaseous fluorinated methanes, and

6. Difficulties with operation of analyzer.

TABLE 11

RESPONSE FACTORS ON PI-101

Compound	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)*	Response Factor	95% Confidence Interval
Acetal	1000	925	13	(5)	1.1	1.1 - 1.0
	5000	7200	10	(5)	0.69	(0.69)
	10000	13200	100	(5)	0.76	(0.76)
Carbon Disulfide	1000	1990	71	(5)	0.50	0.57 - 0.45
	10000	12900	921	(5)	0.78	0.97 - 0.65
Carbon Tetrachloride	500	784	59	(5)	0.64	0.94 - 0.48
	1000	1070	72	(5)	0.94	1.2 - 0.77
	10000	6070	475	(5)	1.6	2.1 - 1.3
Chloroform	1000	756	11	(5)	1.3	1.4 - 1.3
	5000	2550	10	(5)	2.0	(2.0)
	10000	5250	10	(4)	1.9	(1.9)
Diketene	1000	148	7.6	(5)	6.8	7.9 - 5.9
	5000	318	13	(4)	16	18 - 14
	10000	460	7.1	(5)	22	23 - 21

*Number of replicates analyzed

TABLE 11 (Cont.)

RESPONSE FACTORS ON PI-101

Compound	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)	Response Factor	95% Confidence Interval
Dimethylsulfide	1000	1180	10	(4)	0.85	(0.85)
	5000	9200	10	(4)	0.54	(0.54)
	10000	11000	100	(5)	0.91	(0.91)
Ethanol	1000	360	20	(5)	2.8	3.4 - 2.4
	5000	1330	45	(5)	3.8	4.9 - 3.4
	10000	3630	250	(5)	2.8	3.4 - 2.3
Ethyleneglycoldimethyl Ether	1000	7620	250	(5)	1.3	1.4 - 1.2
Ethylene Dichloride (trans)	1000	1040	55	(4)	0.96	1.1 - 0.84
Methanol	1000	125	12	(5)	8.0	11 - 6.3
	5000	798	4.5	(5)	6.3	6.4 - 6.2
	10000	1060	54	(4)	9.4	11 - 8.3
Pentanethiol, 1-	1000	1260	69	(4)	0.79	0.96 - 0.68

TABLE 11 (Cont.)

RESPONSE FACTORS ON PI-101

Compound	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)	Response Factor	95% Confidence Interval
Perchloromethyl Mercaptan	5000	103	2.9	(5)	48	55 - 43
Toluene	1000	1180	120	(5)	0.85	1.2 - 0.67
Tetrachloroethane,1,1,2,2-	1000	736	5.5	(4)	1.4	1.4 - 1.3
	5000	1170	10	(4)	4.3	(4.3)
	10000	1880	10	(4)	5.3	(5.3)
Trichloroethane,1,1,	1000	1020	77	(5)	0.98	1.4 - 0.74
	5000	6170	66	(5)	0.81	0.84 - 0.79
	10000	9430	200	(5)	1.1	1.1 - 1.0
Trichlorotrifluoroethane 1,1,2-	5000	155	1	(5)	32	(32)
	10000	430	1	(5)	23	(23)

TABLE 12

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)*	Response Factor	95% Confidence Interval
Acetal	3.3	1000	9670	149	(4)	0.103	0.109 - 0.0986
		5000	28000	150	(4)	0.179	0.182 - 0.176
		10000	37600	386	(4)	0.266	0.275 - 0.258
	3.4	1000	1500	49.3	(4)	0.667	0.744 - 0.604
		5000	8480	64.5	(4)	0.590	0.604 - 0.576
		10000	22600	50	(4)	0.442	(0.442)
	3.6	1000	226	119	(4)	4.42	7.82 - 1.65
		5000	1420	79.4	(4)	3.52	4.28 - 2.99
		10000	2980	164	(4)	3.36	4.07 - 2.86
	5.7	1000	698	115	(3)	1.43	4.91 - 0.839
		5000	1150	129	(4)	4.35	6.76 - 3.20
		10000	1840	257	(4)	5.34	9.78 - 3.76
	8.8	1000	1890	75.7	(3)	0.529	0.639 - 0.451
		5000	9640	540	(5)	0.519	0.614 - 0.449
		10000	15800	141	(4)	0.633	0.651 - 0.615

*Number of replicates analyzed

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Acetal	9.5	1000	6690	672 (4)	0.149	0.220 - 0.113
		5000	23400	699 (5)	0.214	0.233 - 0.197
		10000	27200	54.8 (5)	0.368	0.370 - 0.366
Acetyl-1-propanol,3-	3.3	500	247	33.7 (5)	2.02	3.26 - 1.47
		1000	813	66.7 (5)	1.23	1.59 - 0.501
	9.5	100	39.2	12.9 (4)	2.55	3.78 - 1.25
		500	217	11.4 (5)	2.30	2.70 - 2.01
		1000	406	41.5 (5)	2.46	3.44 - 1.92
Benzoyl Chloride	6.35	100	970	80.1 (5)	0.0209	0.0215 - 0.0196
		500	5080	50.3 (5)	0.0984	0.101 - 0.0192
		1000	5420	270 (5)	0.185	0.214 - 0.162
Carbon Tetrachloride	5.7	500	115	5.13 (3)	4.35	5.38 - 3.65
		1000	232	42.9 (4)	4.31	10.5 - 2.71
		10000	390	45.7 (5)	25.6	38.0 - 19.3

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Carbon Tetrachloride	6.35	10000	7920	330 (5)	1.26	1.43 - 1.13
	9.5	10000	64	4.28 (3)	156	219 - 121
	13.5	500	1810	143 (5)	0.276	0.354 - 0.226
		1000	4300	309 (5)	0.233	0.291 - 0.194
		10000	33100	572 (5)	0.302	0.317 - 0.288
Chloro-Acetaldehyde	3.3	1000	116	92.3 (5)	8.62	14.71 - 2.68
		10000	3660	384 (4)	2.73	3.00 - 0.205
	3.4	10000	580	40.9 (4)	17.2	22.2 - 14.1
	3.6	1000	64.0	3.80 (5)	15.6	18.7 - 13.4
		10000	2020	127 (4)	4.95	6.00 - 4.21
	5.7	500	1870	13.0 (5)	0.267	0.273 - 0.262
		1000	2350	28.8 (5)	0.426	0.441 - 0.412
		10000	7620	356 (4)	1.31	1.54 - 1.14

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Chloro-Acetaldehyde	6.35	500	4840	55.9 (5)	0.103	0.107 - 0.100
		1000	5680	151 (5)	0.176	0.190 - 0.164
		10000	6760	813 (4)	1.48	2.40 - 1.07
	9.5	500	76	12.9 (5)	6.58	12.5 - 4.47
		1000	228	5.89 (5)	4.39	4.73 - 4.09
		10000	1880	64.3 (3)	5.32	6.27 - 4.64
	13.5	500	709	29.9 (4)	0.705	0.814 - 0.621
		1000	2300	82.9 (5)	0.435	0.483 - 0.395
		10000	21800	802 (3)	0.459	0.545 - 0.396
Chloroform	13.5	1000	6680	747 (5)	0.150	0.217 - 0.114
		5000	22200	1260 (5)	0.225	0.267 - 0.195
		10000	34200	2430 (4)	0.292	0.378 - 0.239
Dichloro-1-propanol, 2,3-	3.3	1200	64.9	22.6 (3)	18.5	29.7 - 7.40

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Dichloro-1-propanol,2,3-	9.5	100	85.2	12.2 (5)	1.17	1.95 - 0.840
		500	447	6.81 (3)	1.12	1.20 - 1.05
		1200	747	20.6 (4)	1.61	1.76 - 1.48
	13.5	500	1160	58.0 (4)	0.431	0.513 - 0.372
		1200	2230	154 (4)	0.538	0.690 - 0.441
Dichloro-2-propanol,1,3-	3.3	1200	227	10.1 (3)	5.29	6.54 - 4.44
	9.5	100	65.4	6.95 (5)	1.53	2.17 - 1.18
		500	304	22.3 (3)	1.64	2.40 - 1.25
		1200	653	35.2 (4)	1.84	2.22 - 1.57
	13.5	500	1070	70.9 (3)	0.467	0.653 - 0.364
		1200	2300	177 (3)	0.522	0.780 - 0.392
Diisopropyl Benzene,1,3-	3.3	100	133	30.8 (4)	0.774	2.94 - 0.446
		500	703	60.1 (5)	0.716	0.938 - 0.578
		1225	1270	108 (3)	0.965	1.52 - 0.706

TABLE 12 (Cont.

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Diisopropyl Benzene,1,3-	6.35	500	134	34 (3)	3.75	5.65 - 1.80
		1225	507	77.9 (3)	2.42	7.12 - 1.45
	5.7	100	311	8.04 (5)	0.331	0.359 - 0.309
		500	343	12.5 (4)	1.47	1.66 - 1.31
		1225	380	14.2 (3)	3.22	3.84 - 2.78
Diketene	3.3	5000	354	13.9 (3)	14.1	17.0 - 12.1
		10000	1240	197 (3)	8.06	25.5 - 4.79
	5.7	1000	2280	226 (5)	0.439	0.605 - 0.344
		5000	6390	171 (4)	0.782	0.855 - 0.721
		10000	8600	487 (4)	1.16	1.42 - 0.985
	9.5	1000	69.4	15.7 (4)	14.4	51.4 - 8.38
		5000	377	23.6 (5)	13.4	16.1 - 7.41
		10000	580	65.9 (4)	17.2	27.0 - 12.7

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Dimethyl Styrene,2,4-	3.3	500	146	23.1 (4)	3.43	6.91 - 2.28
		1170	567	27.0 (5)	2.06	2.38 - 1.82
	5.7	100	956	8.81 (5)	0.105	0.107 - 0.102
		500	964	4.55 (5)	0.520	0.527 - 0.513
		1170	978	7.56 (5)	1.20	1.22 - 1.17
	6.35	100	2540	73.0 (5)	0.394	0.0428 - 0.0365
		500	2710	50.7 (5)	0.185	0.195 - 0.184
		1170	3010	33.6 (5)	0.389	0.401 - 0.377
Dimethylsulfide	3.3	1000	2030	49.9 (4)	0.493	0.534 - 0.457
		5000	10100	394 (4)	0.495	0.565 - 0.440
		10000	20500	462 (5)	0.488	0.520 - 0.459
	3.4	1000	66.0	5.96 (4)	15.2	21.3 - 11.8
		5000	1510	55.1 (3)	3.31	3.93 - 2.86
		10000	3250	48.3 (5)	3.08	3.21 - 2.95

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Dimethylsulfide	5.7	1000	822	33.5 (4)	1.22	1.40 - 1.08
		5000	1010	52.4 (4)	4.95	5.93 - 4.25
		10000	1180	95.4 (3)	8.47	13.0 - 6.29
	6.35	1000	2480	90.7 (4)	0.403	0.456 - 0.361
		5000	4590	112 (4)	1.09	1.18 - 1.01
		10000	6540	190 (4)	1.53	1.68 - 1.40
	9.5	1000	15.3	2.90 (4)	65.4	165 - 40.8
		5000	120	3.51 (3)	41.7	47.7 - 37.0
		10000	270	27.4 (4)	37.0	54.7 - 28.0
Ethanol	3.3	1000	3830	181 (5)	0.261	0.301 - 0.231
		5000	18500	432 (5)	0.270	0.289 - 0.254
		10000	34300	217 (5)	0.292	0.297 - 0.287
	3.4	1000	430	16.8 (4)	2.33	2.66 - 2.07
		5000	3420	47.2 (5)	1.46	1.52 - 1.41
		10000	7530	72.1 (5)	1.33	1.36 - 1.29

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)	Response Factor	95% Confidence Interval
Ethanol	3.6	5000	386	4.24	(4)	13.0	13.4 - 12.6
		10000	941	10.7	(5)	10.6	11.0 - 10.3
	8.8	10000	668	20.8	(5)	15.0	16.4 - 13.8
	9.5	1000	2210	53.2	(4)	0.452	0.490 - 0.420
		5000	8440	290	(4)	0.592	0.665 - 0.534
		10000	16800	255	(5)	0.595	0.621 - 0.571
Ethanolamine	9.5	100	25.9	3.67	(4)	3.86	7.03 - 2.66
		500	135	8.38	(4)	3.70	4.61 - 3.09
	13.5	500	5620	1050	(4)	0.089	0.219 - 0.0750
Ethylene Dichloride (trans)	5.7	1000	684	14.5	(3)	1.46	1.61 - 1.34
		5000	815	8.02	(4)	6.13	6.33 - 5.95
		10000	940	19.1	(4)	10.6	11.4 - 9.99

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Ethylene Dichloride (trans)	6.35	1000	1160	34.1 (4)	0.862	0.951 - 0.788
		5000	1760	30.0 (3)	2.84	3.07 - 2.65
		10000	2270	136 (5)	4.41	5.29 - 3.78
	8.8	5000	658	23.1 (3)	7.60	8.95 - 6.60
		10000	1540	41.2 (4)	6.49	7.10 - 5.98
Ethyleneglycoldimethyl	3.3	1000	5110	86.2 (5)	0.196	0.205 - 0.187
Ether		5000	21100	460 (5)	0.237	0.252 - 0.223
		10000	33800	351 (6)	0.296	0.304 - 0.288
	3.4	1000	2310	42.8 (5)	0.433	0.456 - 0.412
		5000	11700	358 (5)	0.427	0.431 - 0.394
		10000	20600	501 (6)	0.485	0.518 - 0.457
	3.6	1000	284	7.09 (5)	3.52	3.78 - 3.29
		5000	1870	74.6 (5)	2.67	3.01 - 2.41
		10000	3920	93.5 (6)	2.55	2.72 - 2.40

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Ethyleneglycoldimethyl	6.35	1000	1040	150 (5)	0.962	1.61 - 0.686
Ether		5000	2280	169 (5)	2.19	2.76 - 1.82
		10000	4110	324 (6)	2.43	3.05 - 2.02
	8.8	1000	1570	82.0 (5)	0.637	0.745 - 0.556
		5000	9160	342 (5)	0.546	0.609 - 0.495
		10000	16000	268 (6)	0.625	0.653 - 0.599
	9.5	1000	1230	72.8 (5)	0.813	0.973 - 0.698
		5000	5130	202 (5)	0.975	1.09 - 0.878
		10000	9620	195 (5)	1.04	1.10 - 0.984
Ethyleneglycolmonoethyl	3.3	200	410	51.2 (4)	0.488	0.809 - 0.349
Ether Acetate		1000	3570	122 (4)	0.280	0.314 - 0.253
		2000	4890	50.3 (3)	0.409	0.428 - 0.392
	3.4	1000	457	67.0 (5)	2.19	3.69 - 1.55
		2000	817	80.0 (3)	2.45	4.23 - 1.72

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Ethyleneglycolmonoethyl	3.6	1000	50.8	5.79 (3)	19.7	38.6 - 13.2
Ether Acetate		2000	158	6.93 (3)	12.7	15.6 - 10.6
	5.7	200	2590	75.5 (3)	0.0772	0.0883 - 0.0686
		1000	5110	177 (4)	0.196	0.220 - 0.176
		2000	6960	230 (4)	0.287	0.321 - 0.260
	8.8	1000	261	32.7 (3)	3.83	8.31 - 2.49
		2000	808	58.3 (3)	2.48	3.59 - 1.89
	9.5	200	472	9.63 (4)	0.424	0.453 - 0.398
		1000	2190	165 (4)	0.457	0.600 - 0.368
		2000	3470	129 (3)	0.576	0.686 - 0.497
Formaldehyde	3.3	500	266	36.4 (6)	1.88	2.90 - 0.991
		1000	916	27.7 (6)	1.09	1.18 - 1.01
	3.4	1000	72.4	11.2 (6)	13.8	22.9 - 9.88

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Formaldehyde	3.6	500	234	47.1 (7)	2.14	4.22 - 1.43
		1000	626	34.2 (6)	1.60	1.86 - 1.40
	5.7	500	2490	147 (8)	0.201	0.233 - 0.176
		1000	3290	99.4 (7)	0.304	0.328 - 0.283
	9.5	500	180	19.8 (6)	2.78	3.87 - 2.17
		1000	347	44.0 (6)	2.88	4.27 - 2.17
Formic Acid	3.3	5000	6930	79.7 (5)	0.722	0.745 - 0.699
		10000	18900	335 (5)	0.529	0.557 - 0.504
	3.4	5000	906	11.5 (5)	5.52	5.72 - 5.33
		10000	2860	51.3 (5)	3.50	3.61 - 3.38
	3.6	5000	1410	22.8 (5)	3.55	3.95 - 3.22
		10000	4510	101 (5)	2.22	2.36 - 2.09

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN IA/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Formic Acid	5.7	500	4990	136 (5)	0.100	0.108 - 0.0931
		5000	23600	89.4 (5)	0.212	0.214 - 0.210
		10000	31300	182 (5)	0.319	0.325 - 0.314
	8.8	5000	1000	26.0 (5)	5.00	5.39 - 4.66
		10000	2920	60.6 (5)	3.42	3.63 - 3.24
	9.5	500	1190	66.7 (5)	0.420	0.498 - 0.364
		5000	9120	111 (5)	0.548	0.567 - 0.530
		10000	14100	130 (5)	0.709	0.728 - 0.691
Freon 12	6.35	1212.5	5940	270 (5)	0.204	0.234 - 0.181
		2425	6470	140 (5)	0.375	0.399 - 0.354
		4850	7490	92.6 (5)	0.648	0.671 - 0.626
	8.8	1212.5	1714	263 (5)	0.707	1.23 - 0.496
		2425	3130	74.3 (5)	0.775	0.830 - 0.727
		4850	4680	49.3 (5)	1.04	1.07 - 1.01

TABLE 12 (Cont.)

RESPONSE FACTORS ON Miran 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Freon 12	9.5	1212.5	6280	730 (5)	0.193	0.285 - 0.146
		2425	55000	2130 (5)	0.0441	0.0494 - 0.0398
		4850	72600	1290 (5)	0.0668	0.0703 - 0.0637
Furfural	3.6	1200	53.4	6.74 (5)	22.5	34.8 - 16.6
	5.7	100	1230	9.57 (4)	0.0813	0.0837 - 0.0793
		500	1310	12.6 (4)	0.382	0.394 - 0.370
		1200	1420	26.3 (4)	0.845	0.898 - 0.798
	6.35	100	4240	113 (4)	0.0236	0.0258 - 0.0217
		500	8040	120 (4)	0.0622	0.0652 - 0.0594
		1200	13400	420 (4)	0.0896	0.0995 - 0.0814
	9.5	100	32.3	3.50 (4)	3.10	4.72 - 2.30
		500	138	8.66 (4)	3.26	4.53 - 3.02
		1200	321	15.2 (4)	3.74	4.40 - 3.25

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Furfural	13.5	100	656	24.9 (3)	0.152	0.182 - 0.131
		500	5470	260 (4)	0.0914	0.108 - 0.0794
		1200	12200	532 (4)	0.0984	0.114 - 0.864
Glycidol	3.3	100	262	24.6 (3)	0.382	0.640 - 0.272
	3.6	100	572	27.0 (4)	0.175	0.206 - 0.152
	5.7	100	3100	52.6 (4)	0.0323	0.0341 - 0.0306
	6.35	100	6540	99.3 (4)	0.0153	0.0161 - 0.0146
	9.5	100	132	10.4 (4)	0.758	1.01 - 0.606
Hydroxyacetone	5.7	100	1950	24.3 (8)	0.0513	0.0528 - 0.0498
	6.35	100	6870	72.8 (7)	0.0146	0.0149 - 0.0142
	9.5	100	24.6	3.58 (8)	4.07	6.21 - 3.02

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)	Response Factor	95% Confidence Interval
Methanol	3.3	1000	2520	102	(5)	0.397	0.447 - 0.357
		5000	17000	7800	(5)	0.294	0.458 - 0.129
		10000	24400	340	(4)	0.410	0.429 - 0.392
	3.4	1000	101	9.56	(5)	9.90	13.4 - 7.84
		5000	1810	20.5	(5)	2.76	2.85 - 2.68
		10000	3840	45.1	(4)	2.60	2.71 - 2.51
	3.6	5000	10.3	1.63	(5)	485	867 - 337
		10000	181	3.40	(4)	55.2	58.8 - 52.1
	6.35	1000	2920	226	(5)	0.342	0.436 - 0.282
		5000	4230	785	(4)	1.18	1.26 - 1.12
		10000	5540	90.9	(4)	1.81	1.90 - 1.72
	9.5	1000	438	303	(4)	2.28	2.93 - 1.87
		5000	1940	57.4	(4)	2.58	2.81 - 2.38
		10000	2870	116	(4)	3.48	4.00 - 3.09

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Methyl Styrene, α-	3.3	1030	976	38.6 (4)	1.06	1.21 - 0.937
		5000	2830	229 (5)	1.77	2.28 - 1.44
	5.7	103	330	9.20 (4)	0.312	0.342 - 0.287
		1030	1230	10.0 (5)	0.837	0.858 - 0.819
		5000	1570	48.3 (5)	3.18	3.48 - 2.93
	6.35	1030	4490	128 (5)	0.229	0.249 - 0.213
		5000	6960	322 (5)	0.718	0.824 - 0.637
	9.5	1030	73.6	3.67 (4)	14.0	16.6 - 12.1
		5000	178	5.57 (3)	28.1	32.5 - 24.8
	13.5	1030	167	49.2 (5)	6.17	34.1 - 3.39
		5000	948	92.2 (4)	5.27	7.64 - 4.03
Methylene Chloride	3.3	5000	1740	62.7 (5)	2.87	3.19 - 2.61
		10000	3740	144 (5)	2.67	2.99 - 2.42

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Methylene Chloride	13.5	1000	30050	933 (4)	0.0333	0.0369 - 0.0303
		5000	98400	4760 (5)	0.0508	0.0587 - 0.0448
		10000	119000	2880 (5)	0.0840	0.0901 - 0.0787
Pentanethiol,1-	3.3	1000	3180	15.3 (3)	0.314	0.321 - 0.308
		5000	11300	370 (5)	0.442	0.487 - 0.406
		10000	15800	265 (3)	0.633	0.682 - 0.590
	3.4	1000	648	14.8 (4)	1.54	1.66 - 1.44
		5000	4590	115 (4)	1.09	1.18 - 1.01
		10000	8650	97.1 (3)	1.16	1.21 - 1.10
	3.6	5000	267	23.4 (5)	18.7	24.8 - 15.1
		10000	634	18.5 (4)	15.8	17.4 - 14.4
	9.5	1000	89.4	18.6 (3)	11.2	106 - 5.90
		5000	483	51.6 (4)	10.4	15.7 - 7.73
		10000	886	50.7 (3)	11.3	12.7 - 10.1

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Pentanethiol,1-	13.5	5000	5300	217 (4)	0.943	1.08 - 0.835
		10000	10500	289 (3)	0.952	1.08 - 0.852
Perchloromethylmercaptan	3.3	5000	612	28.2 (5)	8.17	9.37 - 7.24
	3.6	5000	64.0	4.99 (5)	78.1	99.7 - 64.2
	5.7	500	1730	570 (3)	0.289	0.458 - 0.120
		1000	3410	112 (4)	0.293	0.327 - 0.266
		5000	7660	306 (5)	0.653	0.734 - 0.587
	8.8	5000	426	31.2 (4)	11.7	15.3 - 9.52
	9.5	500	36.7	2.65 (3)	13.6	19.8 - 10.4
		1000	132	13.3 (4)	7.58	11.1 - 5.74
		5000	303	20.7 (4)	16.5	21.1 - 13.6

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)	Response Factor	95% Confidence Interval
Propylene Chlorohydrin	3.3	500	1240	31.1	(4)	0.403	0.438 - 0.373
		1000	2990	92.0	(5)	0.334	0.366 - 0.308
		5000	14200	81.6	(4)	0.352	0.359 - 0.346
	3.4	1000	36.6	3.39	(4)	27.3	38.7 - 21.1
		5000	1490	39.6	(5)	3.36	3.62 - 3.12
	3.6	5000	51.6	2.30	(3)	96.9	120 - 81.3
	6.35	500	3040	151	(4)	0.164	0.195 - 0.142
		1000	3630	69.4	(5)	0.275	0.291 - 0.262
		5000	3960	37.7	(5)	1.26	1.30 - 1.23
	8.8	5000	795	53.3	(5)	6.29	7.73 - 5.30
	9.5	500	462	11.4	(4)	1.08	1.17 - 1.00
		1000	966	45.4	(5)	1.04	1.19 - 0.916
		5000	4470	157	(5)	1.12	1.24 - 1.02

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)	Response Factor	95% Confidence Interval
Propylene Chlorohydrin	13.5	500	3800	128	(4)	0.132	0.147 - 0.119
		1000	8510	194	(4)	0.118	0.127 - 0.110
		5000	38600	904	(5)	0.130	0.139 - 0.122
Tetrachloroethane,1,1,2,2-	3.3	5000	582	26.1	(4)	8.59	10.0 - 7.52
		10000	1010	21.6	(4)	9.90	10.6 - 9.27
	8.8	10000	404	25.1	(4)	24.8	30.8 - 20.7
	13.5	1000	20000	616	(4)	0.0500	0.0554 - 0.0455
		5000	73000	2750	(4)	0.0685	0.0778 - 0.0612
		10000	101000	1670	(4)	0.0990	0.105 - 0.0941
Trichloroethane,1,1,1-	3.3	1000	266	17.5	(4)	3.76	4.75 - 3.11
		5000	2910	8.16	(4)	1.72	1.73 - 1.70
		10000	5920	28.9	(4)	1.69	1.72 - 1.66
	3.4	5000	38.8	3.25	(4)	129	175 - 102
		10000	421	2.59	(5)	23.8	24.2 - 23.4

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation	(n)	Response Factor	95% Confidence Interval
Trichloroethane, 1,1,1-	6.35	1000	3010	87.2	(3)	0.332	0.380 - 0.295
		5000	14500	114	(5)	0.345	0.353 - 0.337
		10000	27400	95.7	(4)	0.365	0.369 - 0.361
	9.5	1000	4330	238	(5)	0.231	0.273 - 0.200
		5000	13900	283	(5)	0.360	0.381 - 0.340
		10000	19900	1520	(4)	0.503	0.664 - 0.404
	13.5	1000	4120	431	(4)	0.243	0.364 - 0.182
		5000	16400	171	(4)	0.305	0.315 - 0.295
		10000	29100	340	(4)	0.344	0.357 - 0.331
Trichlorotrifluoro-	5.7	1000	640	46.5	(4)	1.56	2.03 - 0.127
ethane, 1,1,2-		5000	856	26.7	(5)	5.84	6.40 - 5.38
		10000	1060	55.1	(3)	9.43	12.1 - 7.71
	6.35	1000	1390	181	(3)	0.719	1.69 - 0.544
		5000	2390	97.8	(5)	2.09	2.36 - 1.88
		10000	3520	189	(4)	2.84	3.43 - 2.43

TABLE 12 (Cont.)

RESPONSE FACTORS ON MIRAN 1A/80

Compound	Wavelength (μm)	Actual Concentration (ppmv)	Instrument Concentration (ppmv)	Standard Deviation (n)	Response Factor	95% Confidence Interval
Trichlorotrifluoro-	8.8	1000	5840	76.4 (5)	0.171	0.178 - 0.165
ethane,1,1,2-		5000	16100	50.0 (4)	0.311	0.314 - 0.308
		10000	18500	134 (5)	0.541	0.552 - 0.530
	9.5	1000	977	55.0 (5)	1.02	1.21 - 0.885
		5000	3690	6.93 (3)	1.36	1.37 - 1.34
		10000	6280	58.0 (4)	1.59	1.64 - 1.55
	13.5	5000	1100	28.9 (4)	4.55	4.96 - 4.19
		10000	2270	132 (4)	4.41	5.40 - 3.72

6. DISCUSSIONS AND CONCLUSIONS

A. Photoionization Detection

As noted previously, the photoionization technique was evaluated for a limited number of compounds due to both chemical and, more significantly, equipment problems. The PI-101 was calibrated with dichloromethane so as to permit direct comparison with response factors reported in Reference 3. The response factors observed for the 16 compounds tested on the photoionization detector, PI-101, range from 0.50 to 48. Seventy-five percent (12) of the compounds have response factors of less than five and greater than 0.2. There appears to be no obvious trend of response factor with molecular weight (carbon number) or functionality within this group. On the other hand, it is interesting to note that for both alcohols tested, i.e., methanol and ethanol, the response factors are inversely proportional to carbon number. Thus, it appears that non-binding electrons on the oxygen atom of the alcohols do not provide a much greater photoionization yield than other sigma-bonded electrons in compounds with similar carbon numbers. The high response factor for trichlorotrifluorethane is consistent with its high ionization potential (11.78 eV). In fact, this ionization potential is slightly higher than the quoted energy of the UV lamp used in the study. This may indicate that thermal energy provides sufficient additional energy to permit some ionization when coupled to the energy provided by the UV light.

Although the specific response factors for the limited number of compounds tested do not unequivocally confirm the suitability of photoionization as a general VOC screening technique, an important but cautious observation can be made. That is, based on this small sample of compounds tested, which includes an aromatic compound (i.e., toluene), an ether (i.e., acetal), an alcohol (i.e., ethanol) and chlorinated alkanes (i.e., trichloroethane and chloroform), the response factor over a concentration range of 500 ppmv to 10,000 ppmv may be within a factor of five. This result is consistent with an expectation (Figure 1) of more similar photoionization yield from sigma and pi electrons when the compound is influenced by UV radiation of approximately 12 eV rather than 10 eV. The expectation that photoionization yield for aliphatic and aromatic compounds may be similar indicates the potential usefulness of photionization as a VOC screening tool.

In terms of current availability as a potential VOC detector, the most significant result with respect to the photoionization detector (HNU Systems, Inc. PI-101 and AID, Inc. 580) is probably the difficulty observed in operating the prototype dilution system. Both dilution probes were designed and fabricated by the respective manufacturers under severe time limitations. Neither probe was designed in a manner which permitted reliable independent measurement of dilution ratio or reproducible adjustment. Thus, the absolute dilution ratio is in some doubt. The ability to adjust the dilution ratios was practically non-existent. As noted previously, the fixed dilution ratios were inappropriate

for analysis of vapor concentrations which yielded instrument responses much above 10,000 ppmv or much below 1000 ppmv. Detector saturation was observed somewhat above an instrument response of 10,000 ppmv. At the span settings required for adequate operation, the background instrument response to zero air was quite high.

Whenever the intensity of the UV lamps began to decrease (note that the AID, Inc. lamp failed early in the program), the instrument span had to be increased regularly. Some alteration to the span potentiometer setting could be made to correct for this decrease in response. However, for some tests the correction was not sufficient to yield an identical calibration. Under these conditions, response factors were calculated at a different absolute instrument response. The data included in Table 11 reflects this variation in span point. However, since the calibration curve is linear over the range of 0-10,000 ppmv (with dilution, that is about 0-1000 ppmv) (Figure 5), no systematic error should occur due to the change in absolute response.

Due to declining instrument response and low vapor pressure of many compounds, one-half of the compounds tested did not yield reliable response factors. The problems noted above and limited data obtained indicate that, at the present time, a reliable photoionization system does not exist to operate over a VOC concentration range of 100 ppmv to 10,000 ppmv. More accurately, a reliable dilution/photoionization system is not available.

B. Infrared Detection

The results of the evaluation of the Miran 80 are much more complete. A total of 32 compounds were analyzed. As noted previously, other compounds were not tested for several reasons, including (1) low vapor pressure; (2) reactivity; (3) lack of availability; and (4) close chemical similarity to compounds previously tested. Prior to testing, the instrument was calibrated with individual span gases at eight analytical wavelengths which correspond to individual functional groups, e.g., C-H; C-Cl; C-OH. The calibration curve data (Table 13) indicate that the absorbance values observed over the concentration range of 100 to 10,000 ppmv are linear. Test compounds were then run and the instrument response calculated on the basis of the response indicated by the specific span gas used at individual analytical wavelengths.

An analysis of the data in Table 12 indicates that the response factors for most compounds with a particular functional group, determined at an analytical wavelength which corresponds to that functional group (Table 10), are generally less than a value of twenty. This is consistent with the general observation that the functional group is more important than the remainder of the molecule in determining the IR extinction coefficient of the compound at the wavelength of interest.

For example, three of the four aromatic compounds tested have reasonable response factors (<5) at 6.35 μm as shown below. This

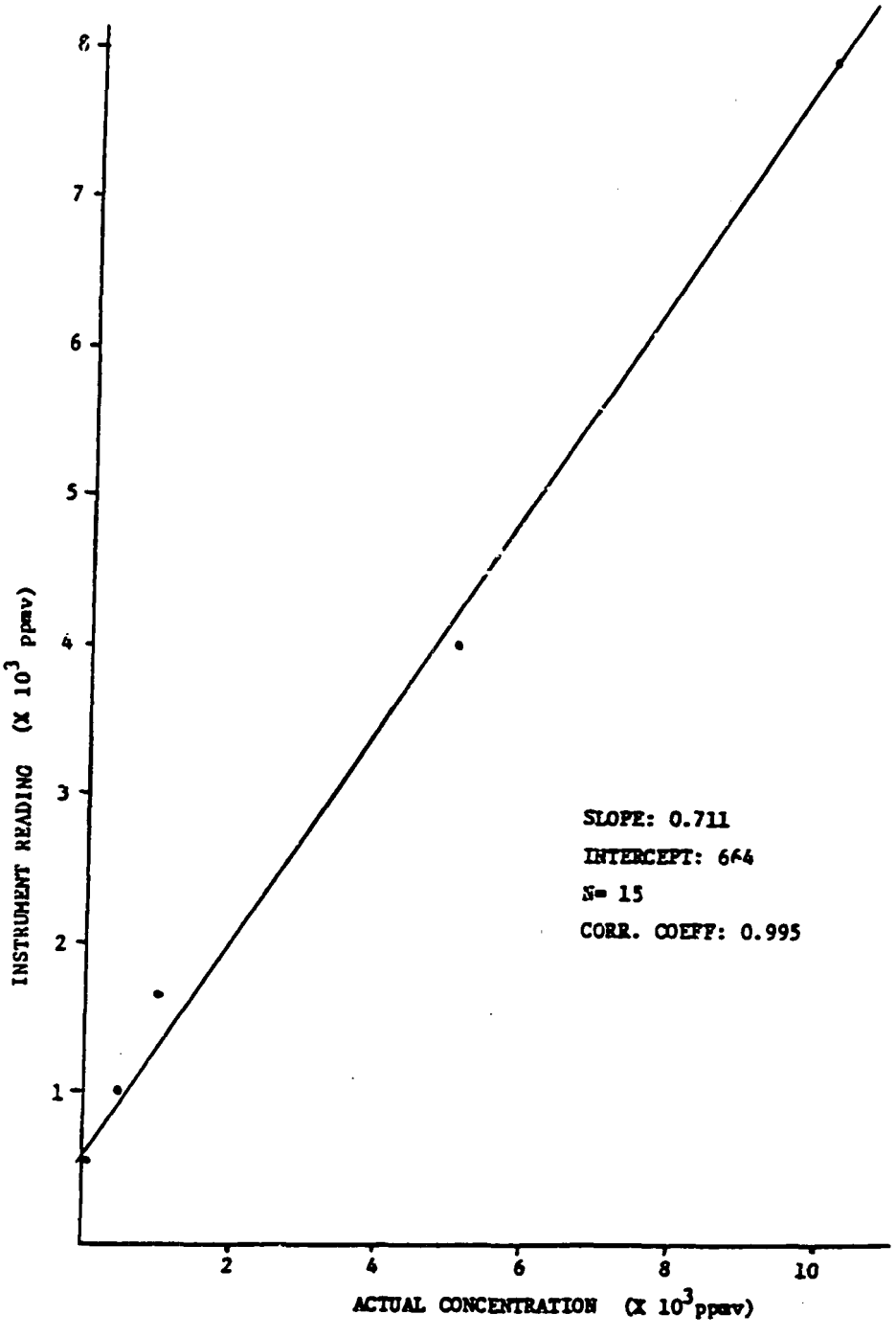

Figure 5. Calibration curve for 1,2-dichloroethane for the HNU instrument.

TABLE 13

CALIBRATION DATA FOR MIRAN 80

Wavelength (μm)	Functional Group(s)	Calibration Compound	Slope ($\times 10^{-4}$ ΔU/ppm)	Y-Intercept (ΔU)	Correlation Coefficient
3.3	Aromatic and Unsaturated C-H	Toluene	.255	.0114	.999
3.4	Saturated C-H	Pentane	1.35	.0495	.994
3.6	Aldehyde C-H	Butyraldehyde	.436	.00675	.999
5.7	Carbonyl C=O	Acetone	.307	.00449	.999
6.35	Aromatic C-C, conj C=C, N-H, C-S	Toluene	.059	.0153	.999
8.8	Ether C-O-C	Diisopropyl ether	.640	.0552	.992
9.5	Alcohol C-O-H	Isopropanol	.587	.00227	.999
13.5	C-Cl	1,2-dichloro-ethane	.105	.00670	.992

AU = Absorbance Units

wavelength is within a broad aromatic ring stretch area.

Compound	Response Factor Range
Diisopropyl Benzene	2.42 - 3.75
Dimethyl Styrene,2,4-	0.185 - 0.934
Methyl Styrene	0.229 - 0.718

Within this group, the addition of the large aliphatic group (isopropyl) on the benzene ring appears to reduce the sensitivity (larger response factor) at the aromatic C $\overset{\cdot\cdot}{-}$ C stretch wavelength as compared to less alkylated aromatics.

In the case of aliphatic and substituted aliphatic compounds, the C-H stretch wavelength of 3.3 μm yields suitable response factors (<5) for about 52% of those tested. The classical aliphatic C-H stretch is observed at 3.4 μm, but some overlap of 3.3 and 3.4 μm IR bands may occur in the Miran due to incomplete resolution. Also, some shift of the CH stretch wavelength probably occurs due to nearby oxygen or halogens. A list of aliphatic compounds and corresponding response factor ranges at this wavelength are shown in Table 14. If one includes alkylated aromatic compounds (4) in the list of compounds with response factors less than five at 3.3 μm - 3.4 μm, the percentage of compounds tested with suitable response factors increases to 62%.

Ten chlorinated hydrocarbons tested in this program yielded measurable response factors of 13.5 μm. Seventy percent were observed to yield response factors less than five at this wavelength. The compounds and respective response factors are given in Table 15.

Since the ultimate goal of this instrument evaluation is to assess the suitability of IR as a general VOC screening technique, an assessment of the usefulness of a single wavelength for measurement of organic compounds of varied molecular weight and functionality is in order. A review of the data in Table 12 indicates that the number of test compounds (total of 32) which yield response factors of less than 20 or greater than 0.05 at each analytical wavelength are as follows:

Wavelength (μm)	Number of Compounds
3.3	23
3.4	12
3.6	13
5.7	17
6.35	17
8.8	11
9.5	25
13.5	14

TABLE 14

SUBSTITUTED ALIPHATIC COMPOUNDS WITH RESPONSE FACTORS LESS THAN TWENTY AT 3.3 μm (Miran 80)

Compound	Response Factor Range
Acetyl-1-propanol,3-	1.23 - 2.02
Chloro-acetaldehyde	2.73 - 8.62
Dichloro-1-propanol,2,3-	18.5
Dichloro-2-propanol,1,3-	5.29
Diketene	8.06 - 14.1
Dimethylsulfide	0.488 - 0.495
Ethanol	0.261 - 0.292
Ethyleneglycoldimethyl Ether	0.196 - 0.296
Ethyleneglycolmonoethyl Ether Acetate	0.280 - 0.488
Formaldehyde	1.09 - 1.88
Formic Acid	0.529 - 0.722
Glycidol	0.382
Methanol	0.294 - 0.410
Methylene Chloride	2.67 - 2.87
Pentanethiol,1-	0.314 - 0.633
Propylene Chlorohydrin	0.334 - 0.403
Tetrachloroethane,1,1,2,2-	8.59 - 9.90
Trichloroethane,1,1,1-	1.69 - 3.76

TABLE 15

CHLORINATED COMPOUNDS AND RESPONSE FACTORS AT 13.5 μm
(Miran 80)

Compound	Response Factor Range
Carbon Tetrachloride	0.233 - 0.302
Chloro-acetaldehyde	0.435 - 0.705
Chloroform	0.150 - 0.292
Dichloro-1-propanol,2,3-	0.431 - 0.538
Dichloro-1-propanol,1,3-	0.467 - 0.522
Methylene Chloride	0.0333 - 0.0840
Propylene Chlorohydrin	0.118 - 0.132
Tetrachloroethane,1,1,2,2-	0.0500 - 0.0990
Trichloroethane,1,1,1-	0.243 - 0.344
Trichlorotrifluoroethane,1,1,2-	4.41 - 4.55

In some cases, the response factors at a particular wavelength (e.g., 5.7 μm) are strongly a function of concentration. It appears that this may be due to a concentration broadening phenomenon which is frequently observed in gas phase infrared spectrometry. If only those compounds which show a response factor between 5 and 0.2, and those which show no strong variation in response factor with concentration (i.e., < a factor of two from 1000 to 10,000 ppmv) are summarized as above, fewer compounds yield suitable response factors:

Wavelength (μm)	Number of Compounds
3.3	12
3.4	4
3.6	3
5.7	1
6.35	3
8.8	4
9.5	15
13.5	7

The results indicate that only 3.3, 9.5 and 13.5 μm analytical wavelengths respond acceptably for a large number of compounds (i.e., greater than 10% of the total number of compounds). However, in any case, fewer than 50% of the compounds are reliably detected. The aliphatic and aromatic compounds do not overlap at 6.35 μm but do overlap at 3.3 μm. However, note that only alkylated aromatics have good response at 3.3 μm. Thus, there is apparently no useful agreement in response factors between, for example, a large number of aromatic compounds and aliphatic compounds (e.g., 50% of those tested) at analytical wavelengths specific to each compound class. It is apparent that the overlap of IR absorbance bands of different functional groups is not sufficient to yield one analytical wavelength which might be used to quantify both compound classes with the expectation of agreement within a factor of five. This observation indicates that infrared spectrophotometry is not particularly suitable for general VOC screening.

On the other hand, the fact that the response factors do not vary by large values (i.e., greater than five) for some classes of compounds, e.g., halogenated aliphatics at 13.5 μm and aliphatic and alkylated aromatics at 3.3 - 3.4 μm, corroborates the suitability of infrared spectrophotometry for VOC screening of compounds belonging to one functional group. Even in this case, only 30 to 80% of the compounds in a given class may yield response factors less than five at a single specific IR wavelength.

C. Conclusions

In summary, based on the results of this evaluation, it appears that:

1. Infrared (IR) spectrophotometry may not be suitable for general VOC screening, with the exception of analysis of VOC emissions of a single organic functional group character.

2. IR screening of organic compounds of a single functional class, e.g., C-Cl, may be suitable for as much as 80% of compounds in the class.

3. IR screening at a wavelength corresponding to both aliphatic and aromatic CH stretches may be suitable for as much as 30-50% of organic compounds.

4. A portable photoionization device is not currently available for VOC screening in the concentration range of 100 ppmv to 10,000 ppmv.

5. The development of a reliable dilution probe for use on a photoionization device is close at hand.

6. With such a dilution probe, it appears that a photoionization device with an 11.7 or 11.8 eV UV lamp may be used for reliable analysis of VOC fugitive emissions.

7. LITERATURE CITED

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8. APPENDICES

The attached appendices include instrument operating procedures which were abstracted from instruction manuals provided by the manufacturers.

A. HNU Systems, Inc. - Model PI-101

(1) Introduction

The Model PI-101 has been designed to measure the concentration of trace gases in many industrial or plant atmospheres. The analyzer employs the principle of photoionization for detection. This process is termed photoionization since the absorption of ultraviolet light (a photon) by a molecule leads to ionization via:

$$RH + h\nu \rightarrow RH^{+} + e^{-}$$

where RH = trace gas, and
$h\nu$ = a photon with an energy $\geq$ ionization potential of RH.

The sensor consists of a sealed ultraviolet light source that emits photons which are energetic enough to ionize many trace species (particularly organics) but do not ionize the major components of air such as O_2, N_2, CO, CO_2 or H_2O. A chamber adjacent to the ultraviolet source ocntains a pair of electrodes. When a positive potential is applied to one electrode, the field created drives any ions, formed by absorption of UV light, to the collector electrode where the current (proportional to concentration) is measured.

To minimize absorption of various sample gases, the ion chamber is made of an inert fluorocarbon material, is located at the sampling point, and a rapid flow of sample gas is maintained through the small ion chamber volume.

The analyzer will operate either from a rechargeable battery for more than ten hours or continuously from the AC battery charger. A solid state amplifier board in the probe and a removable power supply board in the readout module enable rapid servicing of the unit in the field.

The useful range of the instrument is from a fraction of a ppm to about 2,000 ppm. For measurement at levels above 2,000 ppm, dilution of the sample stream with clean air is recommended. Some typical specifications for the Model PI-101 Photoionization Analyzer are given in Table A1.

(2) Operation

Turn the function switch to the battery check position. The needle on the meter should read within or above the green battery arc on the scale-plate. If the needle is in the lower portion of the battery arc, the instrument should be recharged prior to making any measurements. If red LED comes on, the battery should be recharged.

Next, turn the function switch to the on position. In this position, the UV light source should be on. Look into the end of the probe to see the purple glow of the lamp.

A brief description, Table A2, of the instrument controls and functions is shown in Figure A1.

TABLE A1

SPECIFICATIONS FOR MODEL PI 101 PHOTOIONIZATION ANALYZER

Performance (benzene referred)

Range:	0.1 to 2000 ppm
Detection limit:	0.1 ppm
Sensitivity (max):	0-2 ppm FSD over 100 division meter scale
Repeatability:	±1% of FSD
Linear Range:	0.1 to 600 ppm
Useful Range:	0.1 to 2000 ppm
Response Time:	<3 sec to 90% full scale

Ambient humidity to 95% RH
Operating temperature ambient to 40°C*

Physical

Size:	Probe 6.3 DIA x 28.5 L (cm)	(2-1/2 x 11-1/4")
	Readout 21W x 13D x 16.5H (cm)	(8-1/4 x 5-3/16 x 6-1/2")
	Stowed 21W x 13D x 24H (cm)	(8-1/4 x 5-3/16 x 9-1/2")
	Cable 80 cm long (32")	
Weight:	Probe .55 kg (20 ounces)	
	Readout 3.2 kg (7 pounds)	
	Total (shipping) 5.4 kg (12 pounds)	

Controls and functions

Mode switch OFF, Battery Check, Standby (zero), 0-2000, 0-200, 0-20 ppm
Low battery indicator light
Zero (10 turn ± 300% FSD max)
Span (10 turn counting dial 1.0 to 10 times nominal sensitivity)
Readout 4-1/2" (11.3 cm) meter Taut Band movement graduated 0-5-10-15-20 divisions
Signal output for recorder 0-(-5V) FSD
Power output for recorder 12 VDC - jack on side of instrument

*Instrument is temperature compensated so that a 20°C change in temperature corresponds to a change in reading of < ±2% full-scale at maximum sensitivity.

TABLE A1 (Continued)

Power requirements of operating times

Continuous use, battery > 10 hours
Continuous use with HNU recorder reduces instrument battery operating time to 1/2 normal time
Recharge time, max < 14 hours, 3 hours to 90% of full charge
Recharge current, max .4 amps @ 15 VDC

Construction

Designed to withstand the shock and abuse to which portable instruments are often subjected. The readout is housed in a two-piece aluminum case, and finished with a solvent resistant baked acrylic textured paint.

The probe is fabricated from extruded aluminum sections and machined plastic.

Serviceability

The probe and readout are of a modular design allowing rapid servicing and/or replacement of mechanical and electrical components. All module interwiring includes quick disconnects.

Maintenance

The instrument contains only one moving part, and consumes no gases or reagents. The only routine maintenance procedure is cleaning the light source window every several weeks.

Calibration check

Check instrument calibration at least once per week with HNU calibration standard to ensure that the high sensitivity of the instrument is maintained.

TABLE A2

BRIEF DESCRIPTION OF INSTRUMENT CONTROLS AND FUNCTIONS*

Control	Function
Six Position Switch	OFF - Shuts off all power and removes DC voltages. ON - In any other function position or measuring mode, the electronics are on. BATTERY CHECK - Indicates the condition of the battery. If needle position is in lower portion of green battery arc, the instrument should be recharged. STANDBY - UV lamp is off but electronics are on. This position will conserve power and extend the useful operating time between recharges of the battery. This position is also utilized to adjust the electronic zero. RANGES - 0-20, 0-200, 0-2000 direct reading ranges available at minimum gain for benzene. More sensitivity is available by adjusting the span potentiometer.
Zero Potentiometer	A ten-turn potentiometer is employed to adjust the zero electronically when the instrument is placed in the standby position with the probe attached. This eliminates the need for a hydrocarbon-free gas.
Span Potentiometer	A ten-turn counting potentiometer is utilized for upscale setting of the meter on calibration gas. Counter-clockwise rotation increases the sensitivity (~10 times). This pot can increase the sensitivity to make the instrument direct reading for nearly any gas which the instrument responds to.

*For position of layout controls see Figure A1.

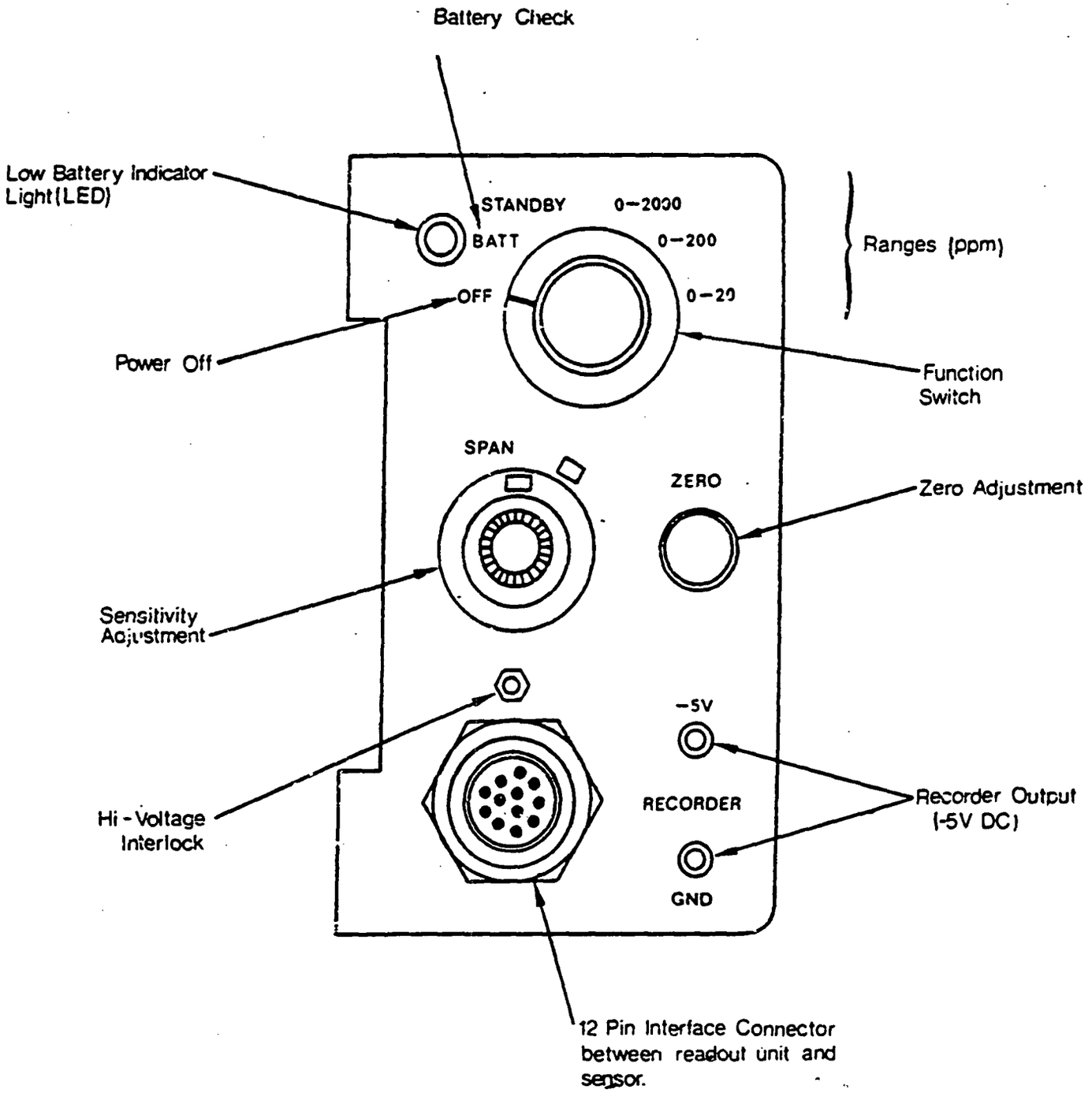

Figure A1. Control panel functions.

To zero the instrument, turn the function switch to the standby position and rotate the zero potentiometer until the meter reads zero. Clockwise rotation of the zero potentiometer produces an upscale deflection while counterclockwise rotation yields a downscale deflection. Note: No zero gas is needed, since this is an electronic zero adjustment (see below). If the span adjustment setting is changed after the zero is set, the zero should be rechecked and adjusted, if necessary. Wait 15 or 20 seconds to ensure that the zero reading is stable. If necessary, readjust the zero.

The instrument is now ready for calibration or measurement by switching the function switch to the proper measurement range. The instrument is supplied calibrated to read directly in ppm (v/v) 0-20, 0-200, 0-2000 of benzene with the span position set at 9.8. For additional sensitivity, the span potentiometer is turned counterclockwise (smaller numbers) to increase the gain. By changing the span setting from 10.0 to 1.0 the sensitivity is increased approximately tenfold. Then, the 0-20, 0-200, and 0-2000 ppm scales become 0-2, 0-20, and 0-200 ppm full scale, respectively. This span control is also utilized to make the instrument scale read directly in ppm of the compound being measured, e.g., it is adjusted to match the value of a calibration gas to that same reading on the instrument scale. The span control can be utilized to calibrate nearly any compound, measured by photoionization, to be direct reading on the 0-20 ppm range.

A small DC-operated fan is used to pull air through the photoionization sensor at a flow rate of three to seven hundred centimeters per minute (ca. 0.5 lpm). The fan provides nearly instantaneous response times while consuming little power. The characteristics of a fan are such that it cannot tolerate a significant pressure drop without affecting the flow rate and, therefore, either the instrument reading or response time. Since photoionization is essentially a nondestructive technique, changes in flow rate do not affect the signal but if a large pressure drop is imposed at the inlet of the probe, the sample may not reach the sensor.

The instrument was designed to measure trace gases over a concentration range from less than 1 ppm to 2000 ppm. Higher levels of various gases (to percentage range) can be measured but the recommended procedure is to dilute the sample with clean air to a concentration of less than 500 ppm. This is generally within the linear range of the instrument and if the measured concentration is multiplied by the dilution ratio the correct concentration in the stream can be determined. A calibration curve for diluted dichloroethane was included in the basic report.

If the probe is held close to AC power lines or power transformers, an error may be observed. For measurements made in close proximity to such items, their effect on measurements can be determined by the following procedure. Zero the instrument in an electrically quiet area, in the standby position, then move the instrument to the

questionable area involved. If AC pickup is going to be a problem, the meter (in the standby position) will indicate the magnitude of the error.

The instrument is equipped with an automatic solid state battery protection circuit. When the battery voltage drops below ∿ 11 volts, this circuit will automatically turn off the power to the instrument. This prevents deep discharging of the battery and considerably extends the battery life. If the instrument is unintentionally left on overnight, the battery will be unharmed because of the battery protection circuit. If the instrument battery check reads low and the lamp doesn't fire, plug the charger into the instrument. The power to the analyzer should then be returned.

To charge the battery, place the mini-phone plug into the jack on left side of the bezel prior to plugging charger into 120 VAC. When disconnecting charger, remove from 102 VAC before removing mini-phone plug. The battery is completely recharged overnight (ca. 14 hours). To ensure that the charger is functioning, turn the function switch to the battery check position, place phone plug into jack and plug charger into AC outlet. The meter should go upscale if the charger is working and is correctly inserted into the jack.

The instrument can be operated during the recharge cycle. This will lengthen the time required to completely recharge the instrument battery.

B. AID, Inc. Model 580

The Model 580 Organic Vapor meter has been designed for measurement of low levels of most organic vapors in an air sample. The sample is continously pulled into the Model 580 by its own internal sampling pump at a rate of approximately 600 mL/min. The sample is pulled directly into the Photionization Detector where high energy from a UV source causes ionization of organic materials in the sample. The amount of ionization that occurs is determined by measuring the ion current in an electrical field. This current is amplified through an electrometer-type amplifier and presented on a digital display on the front panel as well as being made available on the rear of the unit for attachement to a 100 millivolt recorder. The Model 580 used in this study was equipped with a lamp providing an ionizing energy of 11.8 eV. In general, anything with an ionization potential below 11.8 will be sensed by the Model 580. The ionization potentials do not necessarily give an indication of the sensitivity of the ionization detector for that particular material. Some materials that have an ionization potential as high as 12.2 will also be ionized using the 11.8 lamp.

The Model 580 is a completely portable instrument, meaning that it can operate independent of any power requirements on its own internal battery system for a period of at least 8 hours. It is also capable of being operated from a line voltage using the plug-in charger circuit that accompanies the instrument. With the charger plugged into the system, by means of the 3-position selector switch, the line voltage can be used to either recharge the batteries in the Model 850 or to operate the Model 580 from line voltage. The third position on the selector switch is the operation of the instrument from its own internal batteries.

The instrument may be set up on a bench with the charging circuit plugged to a wall outlet and into the rear of the Model 580. The power switch on the rear of the instrument should be set for AC operation. The switch on the front panel should then be turned to the ON position. When this occurs, the LCD display should be activated allowing digits to appear, the pump should be activated, and the lamp in the detector should come on. The lamp can be observed by the small hole in the end of the detector housing. The lamp gives off a pale blue light when it is in operation.

Initial calibration of the 580 requires a supply of zero air. This means simply it has to have zero concentration of the components to which the 580 will respond. Thus, it is not necessary to clean methane from ambient air for this zeroing. In many cases, ambient air itself will be sufficient for zeroing of the instrument. When basically zero air is supplied to the instrument, the zero can be set through the ZERO adjust hole in the rear panel. There is a small pot immediately inside this hole that will allow adjustment of this zero. The Model 580 is then presented with a sample of known concentration of a span gas to be

measured. The SPAN Pot, again located on the rear panel, is then adjusted via a screwdriver for proper reading of the concentration of this particular span gas.

The Model 580, as it leaves the plant, has been calibrated on a mixture of butadiene in air. The Model 580 has two ranges of operation, 0 to 200 and 0 to 2000 ppm. In general, the span gas used should be relatively close in concentration to the expected levels to be determined on the actual air being sampled. This would also imply that the particular range of the unit should be on the same range for calibration as well as for measuring.

The standard Model 580 is designed to obtain organic vapor concentrations in the ppm region with an upper limit of approximately 2000 ppm. There are two basic reasons for this upper limit. The first reason is that of the electronics in the system. If the concentration or, literally, the electrical signal arriving at the detector amplifier gets much greater than that required to provide a readout of 2000 ppm, the amplifier will begin moving into a nonlinear response region; thus, not provide adequate output for the organics present in the sample.

The second reason is the detector design itself. This particular detector was designed for industrial hygiene-type analysis in which the concentration ranges of interest are certainly covered by the 2000 ppm upper limit. As one exceeds the 2000 ppm, the detector response itself becomes nonlinear; such that doubling the amount of organic concentration in the sample does not double the output signal from the system. When it becomes necessary, such as in the area of fugitive emissions, to measure concentrations at the 10,000 ppm level using the Photoionization Detector, it is necessary to dilute the sample such that the concentration actually presented to the detector is below 2000 ppm. Dilution of the sample will lower the reading by a known factor, e.g., 1:10, on the instrument and raise the minimum discernible amount of organic vapor from, for example, .1 ppm on a standard 580 to 1 ppm on the modified version for high concentrations.

In the standard Model 580, the sample is pulled in through the probe to the probe fitting and from there into the detector. The detector exit then connects directly to the pump inlet. The pump exit exhausts through the rear panel of the instrument. In order to provide a 1:10 dilution of the incoming sample, it is necessary to add, to that stream prior to the detector, clean air at the flow ratio of 9-to-1. Thus, directly behind the sample probe fitting on the front panel, a Teflon T arrangement was installed whereby diluent air is placed into the sample line. This diluted sample then continues in the normal fashion through the detector out of the detector into the pump inlet and exits at the pump exit. Just prior to exiting the instrument, another T was placed in the sample line. The pump exit connects to one part of the T. The second part of the T goes to a restrictor valve and then to the exit connection on the rarea panel. The third part of this T passes through

tubing in the back panel to a charcoal filter. The exit from the charcoal filter passes back into the 580 and connects to an inlet of the Teflon T placed upstream of the detector. It is desired to maintain 500 mL/min through the detector. Thus, the incoming sample should be 50 mL/min and the makeup air coming from the charcoal filter to the inlet T should be 450 mL/min. This ratio is adjusted by using the restrictor between the exit T and the exit port on the rear panel of the 580. This restrictor is closed until the inlet sample sampling rate is 50 mL/min. The integrity of the system is checked by measuring the exit flow at 50 mL/min.

Under this type of system, there is 450 mL/min of air circulating from the pump outlet through the charcoal filter into the inlet line to dilute the sample. The charcoal in the filter removes interfering materials that would give a response on the Photoionization Detector. Normally, the charcoal will remove organic material, other than methane and possibly ethane, from the sample. These materials will not be ionized in the Photoionization Detector. The charcoal filter is a disposable cartridge and is held on the outside rear panel of the Model 580. This provides easy replacement of this charcoal filter.

With the 1:10 dilution introduced into the Model 580 by the modification system described above, the inlet sample flow is of necessity reduced to 50 mL/min. With the standard probe assemblies in the Model 580, this would introduce a serious time constant before the sample is actually presented to the detector for analysis. For this reason, the probe has been altered to a 1/16" ID tube to provide approximately the same time constant on the sampling tube, as one would obtain with a larger probe.

C. Foxboro/Wilks, Inc. - Miran 80

(1) General Description

The Miran 1A Portable Gas Analyzer is a single-beam, variable filter spectrometer, scanning the infrared spectral range between 2.5 and 14.5 μm. The instrument is equipped with a gas cell having pathlength variable between 0.75 and 20.25 meters. Other basic equipment are a pump and 3 m (10 ft) air sampling hose with a particulate filter, a zero gas filter, and a carrying case.

The Gas Analyzer System consists of two components, the gas cell and the analyzer (Table C1). The variable pathlength gas cell has a 5.6 liter capacity body, vacuum-tight to 10^{-5} torr and pressurizable to 1000 kPa (10 atmospheres), an internal optical path variable in 1.50 meter increments between 0.75 and 20.25 meters, a pair of windows transparent to infrared energy between 2.5 and 14.5 μm, inlet and outlet ports and a safety valve. The internal optics are gold plated and the inside of the cell is ptfe coated to resist sample absorption and corrosion.

The analyzer consists of a radiation source, mirror system, mechanical chopper, circular filter (variable in three segments between 2.5 and 14.5 μm), a scanning motor, pyroelectric detector, a signal preamplifier, logarithmic range compensating circuitry, regulated power supplies, a meter providing absorbance and percent-transmission scales and a 0-1 volt output for a strip chart recorder.

The Miran 1A System operates from either 110 or 220 V ac, 50-60 Hz power supply. By means of an inverter, portable operation from a 12 volt battery is readily accomplished. This expands the instrument's use to monitoring beyond the confines of the laboratory and greatly facilitates the determination of environmental pollutants and meeting OSHA (Occupational Safety and Health Administration) industrial requirements.

The Wilks Model 80 is a quantitative analysis system combining a high performance single beam infrared spectrometer (Model 1A) with a programmable microcomputer system (Table C2). This results in an instrument of speed and versatility. The Model 80 accepts multicomponent liquids, solids and/or gaseous samples directly without the necessity of vaporizing or dissolving them, separating them into their individual components.

The Model 80 has the following features:

- The measurement of up to 18 separate wavelengths in less than two minutes. The interval between sets of measurements is variable from 7 seconds to 30 minutes.

TABLE C1

SPECIFICATIONS

SPECTROMETER

Type:	Single-beam infrared spectrometer.
Wavelength Range:	2.5 to 14.5 μm in three steps: 2.5 to 4.5; 4.5 to 8; 8 to 14.5 with small overlaps.
Wavelength Range Control:	Manual or motor driven.
Resolution (Approximate):	0.05 μm at 3 μm wavelength 0.12 μm at 6 μm wavelength 0.25 μm at 11 μm wavelength
Noise Level:	Maximum of 0.003 absorbance units/8 hours under the following conditions: 20.25 meter pathlength, 1 mm slit, 1 second time constant, 12.0 μm wavelength, 23°C operating temperature.
Drift:	Maximum of 0.006 absorbance units/8 hours using instrument conditions as specified above for noise level.
Slit Settings:	Closed, 0.5, 1.0, 2.0 millimeters.
Response Time Settings:	1, 4, 10 and 40 seconds.
Absorbance Ranges:	0 to 0.025, 0 to 0.1, 0 to 0.25, 0 to 1 absorbance units and 0 to 100% transmission.
Wavelength Drive Speed:	2.5 minutes per segment.
Infrared Source:	Regulated nichrome wire heating element.
Infrared Detector:	Pyroelectric type, lithium tantalate element.
Power Requirements:	25 watts at either 115 or 230 VAC, 50-60 Hz.
Weight:	5.8 Kg (12.5 lb) without cell. 11.6 Kg (30.0 lb) with gas cell.

TABLE C1 (Continued)

Dimensions:	245 x 155 x 155 mm without cell. 190 x 280 x 720 mm with cell.
Temperature Range:	0° to +40"C (32° to 104°F) Operating. -20° to +60°C (-4° to 140°F) Storage.

VARIABLE PATH TWENTY METER GAS CELL

Pathlength:	0.75 to 20.25 meters in steps of 1.5 meter, externally set.
Volume:	5.6 liter.
Pressure Range, Operating:	10^{-5} torr vacuum to 1000 kPa (10 atmospheres).
Valves:	Inlet and exhaust valves designed for both vacuum and pressure, ptfe sealed.
Internal Finish:	ptfe lined, with mirrors and other components gold plated.
Windows:	NaCl or AgBr normally furnished. Others on special order.

TABLE C2

SYSTEM SPECIFICATIONS

Type:	Single-beam spectrometer.
Wavelength Range:	2.5 to 14.5 μm.
Resolution of CVF: (full width at half height)	0.05 μ at 3.5 μm, 0.08 μ at 6 μm, 0.25 μ at 12 μm.
Minimum (Wavelength Step Size):	0.0005 μm at 3.5 μm, 0.0008 μm at 6 μm. 0.0016 μm at 12 μm.
Wavelength Repeatability:	0.0007 μm at 3.5 μm, 0.0003 μm at 12 μm, 48 hrs at 23°C.
Noise Level:	Max. of 1×10^{-4} absorbance units, without cell, 1 mm slit; 3.5 microns, 1×10^{-3} absorbance units at 12 microns; 23°C.
Drift:	Maximum of 0.002 absorbance units at 23°C, 3.5 microns, 24 hours.
Photometric Accuracy:	Better than 0.1%.
Slit Settings:	0.5, 1, 2 mm, and closed.
Time Constant:	0.25 seconds for recorder output.
Full Scale Range:	1.6 absorbance units (useful range).
Wavelength Drive Speed:	Selectable from 40 seconds to 1 hour.
Power Requirements:	100, 120, 220, 240 VAC + 15%, -12%, 50-60 Hz, 75 watts.
Ambient Temperature Range:	0° to +40°C (32° to +104°F).
Dimensions:	35 x 26 x 18 cm.

- Signal averaging. 256 measurements are made at each wavelength over a 1-180 second interval, enhancing the signal to noise and improving precision.

- Quantitates up to 11 components with one reference wavelength. Compensates for interferences. Absorbance repeatability within the noise level.

- Keyboard entry of instrument settings and factors for data manipulation. Changing instrumental conditions for a new analysis is rapid, i.e., less than 10 minutes to set up a 5-component liquid analysis.

- Printout of memory parameters such as wavelengths, standard factors in data matrix, gain settings, etc.

- Scans a short section of the spectrum (automatically) and prints out absorbance as a function of wavelength.

- Data printout presentation includes absorbance for each wavelength and concentration for each component.

- Digital display shows keyboard entry, and displays wavelength during the analysis routine.

- Compatible with all Wilks standard liquid, gas and solid sampling accessories.

(2) Operation

(a) Precautions and Preliminary Steps

Precautions

Using the particulate filter whenever sampling to prevent dust and dirt from damaging optical components.

Avoid water condensation in the cell when the instrument is cold. Before use, purge the cell with dry air or inert gas, such as nitrogen or helium. Allow sufficient warm-up time to prevent water condensation on cold internal surfaces.

Before storage or transporting the instrument in a cold environment, purge the cell and close cell ports.

Preliminary Steps

The operator should first perform Initial Checkout. The following quick tests verify proper instrument operation and detect long-term changes in performance.

1. Switch on POWER and allow 5 to 15 minutes warm up. Adequate warm-up is indicated by no detectable down scale drift on the 0.1A scale. Some random fluctuation due to noise is normal and should not be confused with drift. Drift is indicated by uniform meter deflection in one direction over a period of a minute or two.

2. Set the following conditions:

RANGE	ZT
PATH	0.75 meters
SLIT	1 mm
WAVELENGTH	3.5 μm
ZERO CONTROLS	X1, minimum (0.0)
RESPONSE TIME	1.0 second

Record the reading. This record will show long-term changes in instrument performance. Some degradation in infrared optical components should be expected. After several years of normal service, cell windows, for example, may have to be replaced. A continous record of this test is useful in deciding whether instrument service is required. It will also show sudden performance changes as occur with exposure of NaCl windows to very wet samples or exposure of AgBr windows to ammonia or pyridine.

(b) Atmospheric Sampling Techniques

Atmospheric sampling requires only that samples be flushed directly through the instrument via the sampling hose and particulate filter. The analyzer's built-in pump is used. To minitor a single material or contaminant, the analyzer is set to the appropriate wavelength for the substance and changes in concentration are recorded. Periodic flushings of the cell with zero gas or clean air is necessary to recheck the zero absorbance setting. Where there is high level local contamination of certain organic compounds, bottled air may be necessary for cell flushing purposes. Such situations may arise during analysis within closed environments such as solvent tanks or storage areas or when checking for leaks in pipes or duct work.

(c) Monitoring Concentration of a Test Gas

Where several substances are of interest, such as in VOC screening, select wavelengths to be used based on likely compounds (functional groups) and proceed as follows:

1. The instrument should have first passed the Initial Checkout.

2. Set up instrument for wavelengths to be monitored.

3. Select a RESPONSE TIME setting that will give a smooth meter response without being unduly sluggish.

4. With clean air or "zero gas" in the cell, adjust for zero absorbance reading with the ZERO CONTROL.

5. With the FUNCTION SWITCH on the 0-1 absorbance scale, the meter should read zero.

6. Select the desired absorbance RANGE for monitoring.

7. Connect the sampling hose and particulate filter to the sample inlet port.

8. Open VALVES and switch on the ambient air pump.

9. Read or record absorbance values.

(d) Calibration for Quantitative Analysis

For optimum accuracy, it is necessary to calibrate the analyzer at the wavelengths used for each sample. This is a one-time procedure unless the wavelength filter is replaced or a new cell is installed. Absorbance is recorded at one-to-five concentrations and a calibration curve prepared. An inversion matrix may be used with the Model 80 microprocessor to convert directly to ppmv.