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**PORTABLE DIRECT READING INSTRUMENTS**

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**September 1991**

**Final Report for Period July 1990 - July 1991**

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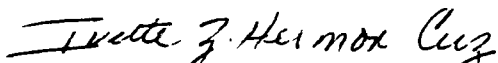
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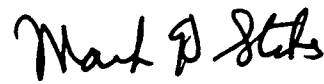
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# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE September 1991	3. REPORT TYPE AND DATES COVERED Final July 1990 - July 1991	
4. TITLE AND SUBTITLE Portable Direct Reading Instruments			5. FUNDING NUMBERS	
6. AUTHOR(S) Ivette Z. Hermon-Cruz				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Armstrong Laboratory Occupational and Environmental Health Directorate Brooks AFB TX 78235-5000			8. PERFORMING ORGANIZATION REPORT NUMBER AL-TR-1991-0087	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Direct reading instruments are those instruments in which the analysis of the contaminant is carried out within the instrument itself. When selecting equipment, the industrial hygienist must consider the physical characteristics of the instruments as well as their performance characteristics and price. Some of the methods of detection that are used in instruments with multi-gas detection capabilities are: photoionization, flame ionization, infrared, gas chromatography, infrared photoacoustic, and electrochemical.				
14. SUBJECT TERMS Direct-reading Instruments Photoionization		Infrared Electrochemical Gas chromatography	HQ TAC Flame ionization Infrared photo-acoustic	15. NUMBER OF PAGES 24
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

CONTENTS

	Page
INTRODUCTION.....	1
DISCUSSION.....	1
CONCLUSIONS.....	14
RECOMMENDATIONS.....	15
REFERENCES.....	16

List of Tables

Table  
No.

1	Principles of Detection.....	3
2	Ionization Potentials.....	5
3	Molar Response of the Photoionization Detector to Various Classes of Organic Compounds Relative to Benzene.....	6
4	Examples of Portable Photoionization Detectors.....	7
5	Examples of Portable Flame Ionization Detectors.....	8
6	Examples of Portable Infrared Detectors.....	10
7	Example of a Portable Infrared Photoacoustic Analyzer.....	12
8	Example of a Portable Electrochemical Detector.....	13

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## PORTABLE DIRECT READING INSTRUMENTS

### INTRODUCTION

#### Background

Tactical Air Command (TAC) is working on a central buy of direct reading industrial hygiene equipment for the TAC Bioenvironmental Engineering (BEE) offices. TAC requested the technical assistance of the Armstrong Laboratory, Occupational and Environmental Health Directorate (AL/OE) in determining what instrumentation best meets their needs.

#### Purpose

The purpose of this document is to provide information about direct reading instruments used in industrial hygiene applications. This report is based on equipment capable of measuring carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), hydrogen sulfide (H<sub>2</sub>S), and organic vapors. Only methods of detection applicable to multi-gas instruments are discussed.

#### Scope

The scope of the study is to provide Bioenvironmental Engineers with information about industrial hygiene equipment currently available in the market. Information provided is based on both a literature search and our experience with these instruments.

### DISCUSSION

#### Definitions of Terms

1. Accuracy - relates to the concentration of the gas measured by the instrument compared with the concentration actually present.
2. Bias - a constant error which causes results to be shifted in one direction from the true value. It is a measure of the relative closeness of a given measurement to the true value.
3. Lower limit of detection (or sensitivity) - the lowest concentration of contaminant that an instrument is capable of accurately detecting.
4. Portability - described as an instrument that can be carried or moved by one person. Normally less than 9 kg (20 lb) and battery operated.
5. Precision - the degree of agreement among measurements.
6. Response time - the time lapse between the introduction of the sample gas to the instrument and attainment of 90% of the final instrument reading. Lag time + rise time.
7. Recovery time - time required for the instrument reading to return to zero or some other background level, after the instrument has been removed from the contaminated atmosphere.

## 8. Stability -

(a) Zero drift - after zeroing in contaminant-free air, there may be a tendency for the electronics or sensor to change, which may affect the final reading.

(b) Span drift - relates to the calibration of the instrument with a span gas.

9. Upper limit of detection - the highest concentration the instrument is capable of indicating accurately.

## Selection

To select equipment most suitable for an industrial hygiene (IH) application, users should evaluate the functions, features, and performance specifications. Before selecting any instrument for IH sampling, several basic factors should be considered. The first factor is the physical characteristics of the instrument, such as:

- a. Portability
- b. Location of the instrument read-out
- c. Instruction manual
- d. Maintenance procedures
- e. Alarm
- f. Power source and life
- g. Sensor life

Sensor life is determined by the type of sensor, frequency and duration of instrument use, the presence of compounds which contaminate the sensor, and storage conditions like temperature, pressure, and humidity (6).

The second factor to consider when selecting an instrument is the performance characteristics of the instruments, such as:

- a. Accuracy of the manufacturer's calibration
- b. Warm-up time
- c. Response time
- d. Zero drift
- e. Span drift
- f. Calibration stability
- g. Minimum detectable change
- h. Linearity
- i. Humidity vs. temperature effects
- j. Interferences

Finally, the sampling device collecting efficiency should meet sensitivity requirements for the desired constituent analysis. Results of any device should have a high degree of reproducibility. The instrument should be simple to use and should require minimum manipulation in the field (9).

### Methods of Detection

Direct reading instruments for gases and vapors are divided into categories based on their principle of detection as shown in Table 1.

TABLE 1. PRINCIPLES OF DETECTION

Principle of Detection	Categories
Electrical Methods	Conductivity, Potentiometry, Coulometry, Ionization, Selective Sampling
Radioactive Techniques	Use of scintillation and Geiger counters
Thermal Methods	Conductivity, Combustion
Spectroscopic and Photometric Techniques	Infrared photometry, Ultraviolet photometers, Other Photometric techniques
Chemi-Electromagnetic Methods	Colorimetry, Photometric (Chemiluminescent) Methods
Magnetic Methods	Paramagnetic Analyzers Mass Spectroscopy
Special Case- Compound Separation	Gas chromatography

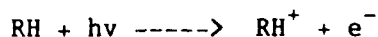
Information adapted from Nader J.S., Lauderdale J.F., and McCammon C.S.(8): Direct Reading Instruments for Analyzing Airborne Gases and Vapors. Air Sampling Instruments for Evaluation of Atmospheric Contaminants, 7th Edition (1989).

Some of these methods of detection are excellent for the analysis of CO<sub>2</sub>, CO, H<sub>2</sub>S, SO<sub>2</sub>, and organic vapors. Unfortunately, most of these methods are applicable to instruments that can measure only one chemical. The following is a summary of those methods of detection that are used in instruments with multi-gas detection capabilities.

Photoionization. Ionization is a special case of the electrical methods category. Detection by ionization is based fundamentally upon making a gas conductive by the creation of electrically charged atoms, molecules, or free electrons and the collection of these charged particles under the influence of an applied electric field. This method is in general nonspecific, but the nature of the ionization reaction may make the method more or less specific (8).

This method is particularly good for the detection of organic vapors. Small portable, total organic vapor analyzers are commercially available for the detection of volatile organic compounds (VOCs) using ionization.

Photoionization detectors (PID) use an ultraviolet (UV) light source to ionize the sample:



where  $hv$ =ionization potential of the molecule(s) of interest. As mentioned before, this method is nonspecific but has a fast response and high sensitivity. Photoionization detection can theoretically detect all inorganic and organic compounds if the lamp voltage is high enough. The lamps used in these instruments ( $hv=9.5-11.7$  eV) do not ionize major components of air, such as  $O_2$ ,  $N_2$ ,  $CO$ ,  $CO_2$ , and  $H_2O$ , but are energetic enough to ionize most VOCs. Interferences from more abundant hydrocarbons, such as methane and ethane, are minimized by selecting a lamp which does not emit photons of a high enough energy to ionize these compounds (4) (Table 2).

Some selectivity can be reached by using lamps with different photon energies. For example, the use of a less energetic 9.5 electron volt (eV) lamp allows the selective detection of aromatics in the presence of alkane or oxygenated hydrocarbons. The 10.9 eV lamp can detect formaldehyde, formic acid, and other compounds that are difficult to measure by other instruments. The 11.7 eV lamp provides a nearly universal response to hydrocarbons with the exception of methane and chlorinated hydrocarbons, such as  $CCl_4$ ,  $CHCl_3$ , and ethylene chloride (5).

A study, made by Barsky et al., reported that 90% relative humidity appears to decrease the response of the 10.2 eV lamp PID by a factor of 2 for most compounds tested, relative to the response under dry conditions (1).

Sensitivity of a PID ranges from less than a part per billion (ppb) to part per million (ppm) (Table 3). Table 4 presents examples of many portable direct reading photoionization detectors of VOC sampling instruments. A number of portable gas chromatographs (GCs) with PIDs are also available.

Interpreting the meaning of the response of a PID is the major difficulty when complex mixtures of chemicals are detected. Knowledge of the chemicals present and determination of the influences governing detector signals are critical in the interpretation of the readings.

PID instruments' prices are between \$4,000 and \$7,000 (without the GC option). If you choose to have the GC option, prices can go up to \$25,000.



TABLE 2. IONIZATION POTENTIALS

	eV
Simple Molecules	
Nitrogen	15.58
Oxygen	12.08
Water	12.59
Carbon monoxide	14.01
Carbon dioxide	13.79
Nitric oxide	9.25
Nitrogen dioxide	9.78
Chlorine	11.48
Iodine	9.28
Paraffins and Unsaturated Hydrocarbons	
Methane	12.96
Ethylene	10.52
Acetylene	11.41
1-butane	9.56
hexane	10.17
Chlorinated Hydrocarbons	
Methyl chloride	11.28
Carbon tetrachloride	11.47
Chloroform	11.42
1,2 dichloroethane	11.12
Vinylidene chloride	9.83
Vinyl chloride	10.00
Trichloroethylene	9.45
Heterocyclics and Aromatics	
Phenol	8.50
Pyridine	9.32
Benzene	9.25
Toluene	8.82
Xylene	8.45
Styrene	8.47
Aniline	7.70
Nitrogen Compounds	
Ammonia	10.15
Methyl Amine	8.27
Acetonitrile	10.22
Acrylonitrile	10.91
Sulfur Compounds	
Sulfur dioxide	12.34
Hydrogen sulfide	10.46
Carbonyl sulfide	11.18
Carbon disulfide	10.08
Methyl mercaptan	9.44
Dimethyl sulfide	8.69
Dimethyl disulfide	8.46
Aldehydes, Ketones, Alcohols, Acids, Esters	
Formaldehyde	10.87
Acetaldehyde	10.21
Acrolein	10.10
Acetone	9.69
Methanol	10.85
Ethanol	10.48
Formic acid	11.05
Acetic acid	10.37

Adapted from Daisey J.M.(4): Real-Time Portable Organic Vapor Sampling Systems: Status and Needs. Advances in Air Sampling (1988).

TABLE 3. MOLAR RESPONSE OF THE PHOTOIONIZATION DETECTOR TO VARIOUS CLASSES OF ORGANIC COMPOUNDS RELATIVE TO BENZENE<sup>a</sup>

Organic Compound Class (n) <sup>b</sup>	Relative Molar Sensitivity
C <sub>6</sub> -C <sub>22</sub> Alkanes (straight, branched and cyclic) (31)	0.011-1.13
C <sub>7</sub> -C <sub>19</sub> Alkenes (16)	0.51-1.17
C <sub>4</sub> -C <sub>9</sub> Aldehydes (6)	0.30-0.53
C <sub>3</sub> -C <sub>9</sub> Ketones (28)	0.35-0.82
C <sub>4</sub> -C <sub>12</sub> Alcohols (10)	0.023-0.36
C <sub>4</sub> -C <sub>14</sub> Esters (20)	0.01-0.82
C <sub>7</sub> -C <sub>16</sub> Aromatic hydrocarbons (13)	1.09-1.69
Chlorobenzenes (Cl <sub>2</sub> -Cl <sub>6</sub> ) (10)	1.20-1.44
Chlorophenols (Cl-Cl <sub>5</sub> ) <sup>6</sup> (19)	1.14-1.47
Polychlorinated biphenyls (10)	2.18-2.96
Phthalates (5)	0.56-1.78
Polycyclic aromatic hydrocarbons (2-4 rings) (12)	1.88-3.08

<sup>a</sup>From Langhorst (1981)(7), using HNU PID (10.2 eV lamp) as presented by Daisey J.M. (1988).

<sup>b</sup>Number of compounds tested.

Flame ionization. In a flame ionization detector (FID), a VOC in air is mixed with hydrogen and combusted to produce ions. This type of instrument will not work in oxygen deficient atmosphere unless it has a separate oxygen supply. Response of a FID is depressed by electronegative atoms such as oxygen, sulfur, and chlorine. FID is insensitive to the presence of water vapor, carbon monoxide, and NO<sub>x</sub>; however, it responds to most organic compounds. This detector has a linear response, but changes in geometry, flow, and composition of the gases supplied to the flame can alter the response of the detector (4,8).

Studies using the OVA-128, Foxboro Analytical, showed that the response to high relative humidity does not exert much practical effect on the response of the FID (1).

Prices for this type of instruments are in the range of \$4,000 to \$7,000. Table 5 has some examples of instruments that use FIDs.

Summit Interest is upgrading the Summit SP-1000 which includes a PID, FID, and thermal conductivity detector within the same instrument. This instrument will be portable and battery operated. Summit is expecting to have this instrument back on the market by the beginning of next year.

Infrared. Many pollutant gases have characteristic absorption lines in the infrared (IR) spectrum. An IR detector detects gases which absorb radiation in the spectral range of 2.5 to 15 μm (4,8).

There are two methods of IR photometry. Nondispersive infrared (NDIR) photometry does not use dispersive optics. Selectivity is achieved by using selective light sources (lasers), selective detectors, or selective filtering of light sources. A typical NDIR analyzer passes IR radiation from

TABLE 4. EXAMPLES OF PORTABLE PHOTOIONIZATION DETECTORS

Instrument	Analytes	Range (ppm)	Detection Limit (ppm)	Precision			Dimension (cm)			Weight (kg)	Power	Alarm
				(+, -)	H	W	L	H	W			
HNU Systems Photoionization Analyzer Model PI-101	most organics	0.2-2000	0.2 C <sub>6</sub> H <sub>6</sub>	-	24	28	13	4.1	110V AC 12V DC	yes		
AID Portable Organic Vapor Analyzer	most organics	Model #580 0.1-2000 Model #585 0.1-10000	-	0.1 ppm	7.6	22.8	25.4	3.5	-	yes		
AID Organic Vapor Meter Model 910	most organics	0.1-2000	-	0.1 ppm	23	43	46	11.8	110V AC	yes		
HNU Systems Model 301P (include compact GC)	most organics	-	0.1 ppb	-	27	34	28	9.8	12V DC	yes		
Photovac 10S Portable Air Analyzer (with GC)	most organics	-	0.1 ppb C <sub>6</sub> H <sub>6</sub>	-	16	46	34	13.3	12V DC 115V AC 230V AC	yes		
Sentex (with GC)	most organics	-	0.1 ppb	-	14	46	46	13.6	-	-		
Photovac Model TIP	most organics	0-2000	0.05 C <sub>6</sub> H <sub>6</sub>	1%	46	long x 6.3	dia	1.4	Ni-Cd	yes		

Information provided on this table is limited by availability. This table does not necessarily include all the portable photoionization detectors on the market. This table is provided for information purposes only.

- = information not available

TABLE 5. EXAMPLES OF PORTABLE FLAME IONIZATION DETECTORS

Instrument	Analytes	Range (ppm)	Detection Limit (ppm)	Precision (+,-)	Dimension (cm)			Weight (kg)	Power	Alarm
					H	W	L			
Century Model OVA-88	Hydrocarbons	1-100000	1 ppm	20% FS	23	30	13	5.5	12V DC/ 115V AC	yes
Model OVA-108 (with GC)		1-10000	0.2 CH <sub>4</sub>							
Model OVA-128 (with GC)		1-1000	0.2 CH <sub>4</sub>							
AID Model 710	total	0-20000	0.1	1 ppm	25	37	35	6.4	Ni-Cd	yes
Model 712	hydrocarbons		1.0							

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FS = full scale

2 filament sources through parallel tubes. One source contains clean air. The other source contains the contaminated air. Some of the radiation is absorbed by the pollutant gas in the sample cell at its absorbing wavelengths. The remainder of the radiation passes on to the detector which generates an electrical signal output (8).

Dispersive methods are used in spectrophotometers having optical elements such as prisms or gratings. These elements spatially disperse the light from a broadband source so that wavelength selection may be achieved by means of proper physical placement of mechanical slit openings. This technique permits continuous scanning of the spectrum within the wavelength region of the dispersive element (8).

Foxboro is the major manufacturer of portable IR instruments. The MIRAN Gas Analyzers uses NDIR absorption. The MIRAN IA and IB provide variable pathlengths and variable wavelengths. The MIRAN IA is manually calibrated and can be a very useful instrument when used by a person that clearly understands IR as a method of detection. However, this instrument is not completely portable, and it does not have a battery pack. The MIRAN IB is precalibrated for more than 100 compounds: the wavelength and pathlength are automatically selected. Our experience with the MIRAN IB is that it reads somewhere between 10% and 40% of the true concentration when we use the fixed library. Because of this problem a calibration with known concentrations of the sample gas is always accomplished by our staff. This calibration takes approximately 1 to 2 hours. The cost of these instruments is \$11,000-\$17,000 (Table 6).

IR absorption coefficients are typically several orders of magnitude lower than those for visible or ultraviolet absorption. The MIRAN and other portable IR instruments compensate for this low absorption with long pathlengths (up to 20 m for the MIRAN). This compensation is achieved by multiple reflections between two mirrors (4).

IR detectors give excellent results for single contaminants, for example, industrial hygiene research and toxic waste site monitoring. Their applicability for monitoring complex mixtures, such as the one found in a typical industrial shop, is very limited. In complex mixtures, interferences will be overwhelming.

Gas Chromatographs: In gas absorption chromatography, the components of a mixture migrate differentially in a porous sorptive medium. Chromatography is primarily a method of separating the components of a mixture. This method does not serve directly for the detection of substances. A detector such as an FID or PID responds to each component as it exits the GC medium. Results in the ppb range can be reached with this system.

Portable gas chromatographs are very useful for direct readings. Several manufacturers include a GC option which can be fitted with their detectors. The main disadvantages of these instruments are their weight (about 12.6 kg (28 lb)) and a price of up to \$30,000. These disadvantages make this type of instrument almost inaccessible at base level.

TABLE 6. EXAMPLES OF PORTABLE INFRARED DETECTORS

Instrument	Analytes	Range (ppm)	Detection Limit (ppm)	Precision (+,-)	Dimension (cm)			Weight (kg)	Power	Alarm
					H	W	L			
MIRAN										
Model 1A	various	-	1 ppm	2%	19	28	72	14	12V DC/	no
Model 1B	toxic gases	0-99000	-	-	28	23	71	13.6	120V AC	yes
CEA										
Model RI-550A	CO, CO <sub>2</sub> , CH <sub>4</sub> , ethane, propane, butane, ethylene	-	1% FS	2% FS	3.1	3.4	5.0	9.5	110V AC 220V AC	-

Information provided on this table is limited by availability. This table does not necessarily include all the portable photoionization detectors on the market. This table is provided for information purposes only.

FS= full scale  
- = information not available

Infrared Photoacoustic Analyzers: Photoacoustic effect is the emission of sound by an enclosed sample when light is absorbed. When a gas is irradiated with light, it absorbs some of the incident light proportional to the concentration of the gas. When the incident light is modulated at a given frequency, the pressure increase is periodic at the modulation frequency. Sound pressure is then measured with a microphone. The intensity of the sound depends on 3 main factors: the nature of the gas, the concentration of the gas, and the intensity of light (2).

One of the main advantages of this type of instrument is that it does not need to be calibrated very often, approximately once every 6 months. Response of a photoacoustic cell is linear in a wide dynamic range.

Table 7 presents an example of an instrument using photoacoustics as a method of detection. The approximate cost of this instrument is \$25,000.

Electrochemical: Electrochemical detectors are based on the electrochemical cell which, at its simplest, consists of 2 electrodes immersed in an electrolyte. This type of detector includes cells of a wide variety and subtypes. Some of these cells are (3):

- a. Conductivity cells
- b. Coulometric cells
- c. Galvanic cells
- d. Polarographic cells

Conductivity cells measure changes in the electrical conductivity when gases that form electrolytes are dissolved in an aqueous solution (8). Conductivity cells are seldom used for personal monitors as they require bubblers. These cells are mainly used for general acid gas determination.

Coulometric is the measurement of the number of electrons transferred across an electrode solution interface to carry to completion the reaction of a particular substance in a sample. Their most common application is for monitoring of inorganic gases such as CO, SO<sub>2</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, Cl<sub>2</sub>, COCl<sub>2</sub>, O<sub>3</sub>, and HCN. Two of the technique advantages are rapid response and selectivity. The main disadvantage is low accuracy when measuring very low concentrations. Selectivity can be achieved in several ways: first, by selecting a specific cell reaction; second, by setting the electrode so that other gases with higher electrode potential do not react; and third, by using a selective membrane, permeable only to a particular substance (3,8).

Galvanic and polarographic cells are mainly used for oxygen determination.

An example of an instrument which uses electrochemical sensors is the Exotox 75, manufactured by Neotronics. This instrument incorporates up to 5 detection sensors, plus temperature and humidity into one hand-held unit. The Exotox can monitor for O<sub>2</sub>, flammable gases, CO, H<sub>2</sub>S, SO<sub>2</sub>, and Cl<sub>2</sub>. The Exotox 75 also includes data logging capacity. The price of this type of instrument ranges between \$1,000 and \$3,000 (Table 8).

TABLE 7. EXAMPLE OF A PORTABLE INFRARED PHOTOACOUSTIC ANALYZER

Instrument	Analytes	Range (ppm)	Detection Limit (ppm)	Precision (+, -)	Dimension (cm)			Weight (kg)	Power	Alarm
					H	W	L			
Bruel & Kjaer Model 1302	various toxic gases	5 orders of magnitude	0.001-1	-	17.5	39.5	30	9	110V AC 220V AC	yes

Information provided on this table is limited by availability. This table does not necessarily include all the portable photoionization detectors on the market. This table is provided for information purposes only.

- = information not available



TABLE 8. EXAMPLE OF A PORTABLE ELECTROCHEMICAL DETECTOR

Instrument	Analytes	Range (ppm)	Detection Limit (ppm)	Precision (+,-)	Dimension (cm)			Weight (kg)	Power	Alarm
					H	W	L			
Neotronics Exotox	O <sub>2</sub>	0-32%	0.5%							
	SO <sub>2</sub> , Cl, NO <sub>2</sub>	0-999	0.1 SO <sub>2</sub>	2.5%	variable		variable	Ni-Cd	yes	
	H <sub>2</sub> S	0-499	1							
	CO	0-999	1							
	CO <sub>2</sub>	0-5% V	0.1% V							

Information provided on this table is limited by availability. This table does not necessarily include all the portable photoionization detectors on the market. This table is provided for information purposes only.

## CONCLUSIONS

Direct reading instruments are those instruments in which the analysis of the contaminant is carried out within the instrument itself. When selecting equipment, the industrial hygienist must consider the physical characteristics of the instruments as well as their performance characteristics and price.

TAC is looking for a multi-chemical direct-reading, simple to use, rugged, and reliable direct reading instrument with +/- 20% accuracy. An instrument with all of these characteristics does not yet exist. But, manufacturers offer a wide variety of instruments which will provide valuable information to the BEE when the advantages and disadvantages of the particular method of detection are known.

Photoionization detectors use an UV light source to ionize the sample. Specificity in photoionization analysis depends on the sensitivity of the detector to the species being measured, the number of interfering species, and the concentration of the species being measured relative to interferences. Choosing the light source (9.5 eV, 10.2 eV, 10.9 eV, 11.7 eV) to suit the application will maximize sensitivity. Photoionization detectors are particularly good for aromatics. Potential attenuation of the reading is possible when used in high humidity atmospheres.

In an FID, a VOC in air is mixed with hydrogen and combusted to produce ions. These instruments will respond to most organic compounds but are insensitive to the presence of H<sub>2</sub>O, CO and NO<sub>x</sub>. This type of detector is more sensitive to hydrocarbons than any other organic vapor. PIDs and FIDs are now available with a GC option.

Infrared can be a very useful method of detection for single contaminants. However, when complex mixtures are present, the IR spectra will be the sum of the substances present. This may give false positives in the readings. The MIRAN 1B faces the problem of dealing with a "black box." The MIRAN 1A seems to be a better instrument if used by a person with a clear understanding of IR as a method of detection.

Photoacoustic spectrometry also uses IR absorption for the analysis of gases. More studies are needed to analyze the actual performance of this instrument in a typical IH situation.

Electrochemical sensors provide the industrial hygienist with an inexpensive and very portable instrument to measure inorganic vapors in air. These types of sensors are usually very accurate and reproducible. They operate better in low relative humidity and low oxygen atmospheres. Electrochemical cells seem to be sensitive to temperature changes. The main disadvantage of this type of instrument is the relatively short life of the sensor.

## RECOMMENDATIONS

Of all the methods of detection discussed in this report, we believe that photoionization is the best method for the measurement of organic vapors in air. Instruments that use photoionization are relatively inexpensive, very portable, and extremely sensitive. A lower limit of detection in the part per billion range can be achieved with this type of instrument.

As mentioned before, some instruments include more than one type of sensor, such as PID and FID, within the same instrument. This option should also be considered.

For the measurement of inorganic vapors, electrochemical cells are an inexpensive and very portable alternative. Advanced surface mount technology, new and improved electrochemical sensors, a rugged case, and innovative engineering design provide the industrial hygienist with an easy to use and very affordable instrument.

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