



Project Summary

Evaluation of Potential VOC Screening Instruments

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This 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 (HNU PI-101, AID 580, and Foxboro Miran 80) were modified and evaluated for 32 such compounds at concentrations of 100-10,000 ppmv. Results indicate 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 analysis of some classes of organic compounds.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The U.S. EPA has issued performance standards and guidelines to limit emis-

sions of volatile organic compounds (VOCs) from several stationary source categories; e.g., surface coating operations. It is apparent that sources other than classical point sources may also emit large amounts of VOCs into the workplace and surrounding atmosphere. As described in EPA Method 21, *Determination of Volatile Organic Compound Leaks*, technically and economically feasible devices suitable for monitoring such fugitive sources as valves include only a few that are portable. These devices can be placed near possible points of emissions and will respond to releases of the organic compounds. 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 sources 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 for two commercially available detectors using flame ionization and catalytic combustion. Among 168 compounds tested, 23 showed sufficiently poor response that the actual and measured concentrations differed by a factor of greater than five.

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.

The first step in this task was to procure one or more units of detectors that 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. Few detectors are now "approved" for such an environment.

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 (RFs) were determined at several concentrations from 100 to 10,000 ppmv:

$$RF = \frac{\text{Actual Concentration}}{\text{Concentration Calculated from Instrument Response}}$$

Measurements were limited to concentrations approaching about 90% of the saturation concentration of 75% of the lower explosive limit (LEL). 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.

Results and Discussion

Photoionization Detection

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 to permit direct comparison with response factors previously reported. The response factors observed for the 16 compounds tested on the PI-101

range from 0.50 to 48. Those for the 13 compounds evaluated at 1000 ppmv, summarized in Table 1, range from 0.5 to 8.0. Of the compounds tested, 75% (12) have response factors of less than 5.0 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. It is interesting to note that, for both alcohols tested (methanol and ethanol), the response factors are inversely proportional to carbon number. This is consistent with the large ionization potential and fewer ionizable electrons in methanol, as compared to ethanol. It also appears that non-bonding 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.

Although the 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 (toluene), an ether (acetal), an alcohol (ethanol) and chlorinated alkanes (trichloroethane and chloroform), the response factor at concentrations of 500 - 10,000 ppmv may be within a factor of five. This result is consistent with an expectation of more similar photoionization yield from sigma and pi electrons when the compound is influenced by UV radiation of approximately 12eV rather than 10eV. The expectation that photoionization yield for aliphatic and aromatic compounds may be similar indicates the potential usefulness of photoionization in VOC screening.

In terms of suitability 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 the difficulty observed in operating the prototype dilution system. Both dilution probes were designed and

Table 1. Response Factors with 95% Confidence Intervals^a

OCPDB ^b ID No.	Compound Name	Response Factor	Confidence Interval
--	Acetal	1.1	1.0 - 1.1
790	Carbon Disulfide	0.50	0.45 - 0.57
810	Carbon Tetrachloride	0.94	0.77 - 1.20
930	Chloroform	1.3	1.3 - 1.4
--	Diketene	6.8	5.9 - 7.9
--	Dimethylsulfide	0.85	0.80 - 0.90
1660	Ethanol	2.8	2.4 - 3.4
1236	Ethylene Dichloride, trans 1,2	0.96	0.84 - 1.1
2500	Methanol	8.0	6.3 - 11.0
--	Pentanethiol, 1-	0.79	0.68 - 0.96
3349	Toluene	0.85	0.67 - 1.2
3291	Tetrachloroethane, 1,1,2,2-	1.4	1.3 - 1.4
3395	Trichloroethane, 1,1,1-	0.98	0.74 - 1.4

^a Concentration = 1000 ppmv; all are of the light liquid (LL) volatility class.

^b Organic Chemical Producers Data Base.

fabricated by the respective manufacturers under severe time limitations. Neither probe was designed to permit 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 nonexistent.

Infrared Detection

A total of 32 compounds were analyzed on the Miran 80. 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-C1; C-OH. 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 indicates that the response factors for most compounds with a particular functional group, determined at an analytical wavelength which corresponds to that functional group, are generally less than 20. 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 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 - 0.394
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=C stretch wavelength as compared to less alkylated aromatics.

For 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 C-H stretch wavelength probably occurs due to nearby oxygen or halogens. A list of aliphatic compounds and corresponding response factor ranges at this wavelength is shown in Table 2. If four alkylated aromatic compounds are included in the list of compounds with response factors less than 5 at 3.3 - 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 at 13.5 μm ; 70% yielded response factors less than 5 at this wavelength.

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 indicates that 32 test compounds yield response factors of 5.0 - 0.2 at each analytical wavelength:

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. However, in any case, fewer than 50% of the compounds are reliably detected. 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. 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 5.0) 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.

Table 2. Substituted Aliphatic Compounds with Response Factors Less than 20 at 3.3 μm

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

Conclusions

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

1. Infrared (IR) spectrophotometry is not suitable for general VOC screening, except for 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-C1) may be suitable for as many as 80% of compounds in the class.
3. IR screening at a wavelength corresponding to both aliphatic and aromatic stretches may be suitable for as many as 50% of organic compounds.
4. A portable photoionization device is not available for VOC screening at concentrations of 100 - 10,000 ppmv.
5. Development of a reliable dilution probe for use on a photoionization device is readily achievable.
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.

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Merrill D. Jackson is the EPA Project Officer (see below).

The complete report, entitled "Evaluation of Potential VOC Screening Instruments," (Order No. PB 83-139 733; Cost: \$11.50, subject to change) will be available only from:

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