# Evaluation of Portable Gas Chromatographs

Richard E. Berkley
US Environmental Protection Agency
Research Triangle Park, NC 27711

Michael Miller
IIT Research Institute
Chicago, IL 60616

Joseph C. Chang
Battelle Columbus Laboratories
Columbus, OH 43201

Karen Oliver, Christopher Fortune, and Jeffrey Adams
ManTech Environmental Services
Research Triangle Park, NC 27709

## ABSTRACT

Limits of detection, linearity of responses, and stability of response factors and retention times for five commercially-available portable gas chromatographs (PGC) were determined during laboratory evaluation. The PGCs were also operated at the French Limited Superfund site near Houston, TX during startup of bioremediation. Concentrations of volatile organic compounds (VOC) at the site were slightly above ambient background levels. Concurrent collocated grab samples were collected periodically in canisters and analyzed by Method TO-14 using a mass-selective detector. Canister data were taken to indicate correct concentrations and were used to assess the accuracy of PGC data. Durability, reliability, and complexity of operation of PGCs were also evaluated. The principal goal of the study was to determine the best way to use each instrument as a monitor for airborne VOCs.

## INTRODUCTION

Analysis of volatile organic compounds (VOC) in ambient air is usually done by collecting samples at field sites and returning them to a laboratory [1]. Laboratory analysis can be done with state-of-the-art procedures, but data are delayed and sample integrity could become compromised during collection or storage. A portable gas chromatograph (PGC) can produce data immediately and can deliver more information at less cost than laboratory-based methods [2]. We have evaluated five commercially-available PGCs as monitors for VOC in air. During the evaluation a field test was conducted at the French Limited Superfund Site near Crosby, TX in January 1992.

## EXPERIMENTAL

PGCs were borrowed from manufacturers.  They were evaluated in a laboratory and then tested at the field site.  The laboratory evaluation was repeated for some instruments because they were modified at the field site by factory personnel.

## Portable Gas Chromatographs

All PGCs were microprocessor-controlled instruments capable of unattended autosampling.  Specific features and capabilities of each PGC are summarized in Table 1.  Information specific to individual instruments, which was not included in Table 1 is given below.

The MSI 301 is an organic vapor monitor which operates on the principle of a gas chromatograph.  It can be adjusted to detect any three compounds from a large group of potential analytes.

The SRI 8610 is a field-deployable _laboratory_ chromatograph.  It can accommodate up to three detectors operating simultaneously.  Other available detectors are thermal conductivity, flame ionization, nitrogen-phosphorus, thermionic ionization, electron capture, and flame photometric.  Carrier gas flow is regulated by a digital flow controller, with which preselected flow rates can be set.

## Standards

Calibration standards were prepared by dynamic dilution of commercially-prepared 10 ppm mixtures of analytes in nitrogen (Alfagaz, Scott) using humid zero air.

## Laboratory Evaluation

Laboratory evaluation consisted of 1) learning how to operate each unit as a monitor for VOCs in air, 2) calibrating it with standard mixtures of VOCs in zero air, 3) evaluating the calibration plots, and 4) calculating detection limits from calibration data.  Each unit was first set up and operated according to manufacturer's specifications.  After operating procedures had been learned and proper function of the instrument had been verified, calibration was performed by analyzing standard mixtures at five levels.  Reliability, durability, convenience of operation, and clarity and relevance of the operator's manual were also considered.

## Field Evaluation

The instruments were shipped to the hazardous waste site and operated there.  Data from the PGCs were compared with data obtained from concurrent collocated whole-air grab samples collected in evacuated passivated canisters.  Accuracy, precision, ease of operation, and reliability were determined.

## Field Site

The French Limited Superfund site was an abandoned flooded sand pit into which refinery waste had been dumped.  Before remediation, twenty-five feet of water overlay ten feet of sludge covering an area of seven acres.  The water above the sludge was clean enough to support aquatic life, but volatile solvents were leaching from the sludge into the surface aquifer.  Bioremediation at the site was performed using selectively-nurtured indigenous microorganisms.  Pond fluid was pumped out of the pond, injected with oxygen gas and nutrients, then pumped back into the pond.  Dredges loosened sludge from the bottom and high-speed stirrers mixed it with the water.  The

bacteria fed on the sludge, converting it into biomass which eventually decayed into carbon dioxide and water. Agitation of the pond resulted in a slight increase in atmospheric concentrations of organic vapors due to release of solvents dissolved in the sludge. Concentrations were lower than anticipated from a pilot study in which air had been used to provide oxygen. Diesel exhaust from dredges and agitators contributed significantly to airborne VOC levels. The evaluation was conducted at a power-control shed which was located 20 feet south and 15 feet above the edge of the pond. Initial attempts to conduct the study on an outdoor deck were defeated by inclement weather, and all units were moved inside the shed where temperature was maintained at 20°C. All units were connected to 110 volt AC power. Each unit used its own sample pump to import outside air through 1/8 inch OD stainless steel tubing. Calibrations were performed periodically. Grab sampling was done by opening the valve of an evacuated passivated canister while holding it within three feet of the ends of the intake tubes as the PGCs sampled simultaneously. Grab samples were returned to the EPA laboratory in Research Triangle Park where they were analyzed by GC/MSD according to Method TO-14. Canister data were assumed to accurately reflect concentrations of compounds in the air sampled by the PGCs.

## RESULTS AND DISCUSSION

The ability of an instrument to reliably analyze VOCs in ambient air depends upon stability of retention times, adequate chromatographic resolution, and the sensitivity, selectivity, and stability of the detector. Stable performance is a significant problem for any sensitive instrument which travels, and it was one of two principal subjects of investigation in this study. The other subject of investigation was accuracy, which was determined by comparing PGC data with data from simultaneous canister grab samples.

### Retention Time Stability

Retention time stability is crucial to accurate identification of compounds. It was assessed in terms of the standard deviations of retention times. Retention times from each calibrated compound were averaged, and the standard deviation was calculated. Average retention times are shown as horizontal bars in Figure 1, and standard deviations are indicated at the end of each bar. They were usually small but discernible. During the Scentograph field calibration, the carrier flow rate was changed, producing two distinct groups of retention times and a large standard deviation. This was probably the result of human error and not due to a fault in the instrument. Standard deviations in all other cases were small, but they needed to be even smaller. The importance of retention time stability to compound identification cannot be over-emphasized. It is vital to be able to set carrier flow quickly and accurately. Column temperature stability is even more important, because a shift in temperature changes relative retention times and invalidates the entire calibration table. Ideally, the standard deviations in Fig 1 should have been almost invisible at the scale of the drawing.

### Detector Stability

Stable detector response is crucial to accurate quantitation. It was evaluated by observing the scatter in the calibration plots (Figures 2-4) and by noting how closely the correlation coefficients of the plots approached unity (Table 2). Significant scatter was

taken to indicate an unstable response or possibly random sample loss. The calibration plots showed some scatter, but all of the instruments were able to report approximately correct data within the range calibrated. In several cases precision was mediocre.

Sensitivity.
Sensitivity is indicated by the detection limit (Table 3), which was taken to be the concentration corresponding to a response equal to four times the baseline noise adjacent to the peak. Baseline noise was difficult to evaluate in some cases. Neither the Scentograph nor the Photovac sent a real baseline signal to external devices, and the baseline of the MSI 301 was difficult to locate. Estimates of baseline noise were made by visual inspection in those cases. The lower the correlation coefficient, the less credible are calculated detection limits. Detection limits were usually higher for the field calibrations, reflecting the stress of field operation.

Resolution and Selectivity
Resolution of PGCs is generally lower than for laboratory instruments because 1) shorter columns are used to get quicker results, 2) autosampling schemes tend to introduce dead volume into the system and thus broaden injection bandwidths, 3) field operation tends to degrade performance because instruments are vulnerable to vibration, rough handling, dust, and fluctuating ambient temperatures. Even the best resolution achievable cannot separate all of the compounds present at background levels in ambient air. Typical chromatograms obtained in laboratory analyses display as many as 200 peaks with up to four compounds coeluting in each peak. Detector selectivity must be considered together with resolution when assessing the ability of an instrument to distinguish target compounds from other compounds in authentic field samples. To some extent, selectivity substitutes for resolution in a PGC. The resolution of toluene from benzene was calculated for each PGC in the study to be twice the difference in retention times divided by the sum of the peak widths at base height. These figures are listed in Table 4 with a summary of the compounds to which each detector responds.

Field Performance
Ambient levels of analytes found during the field study were scarcely above calculated detection limits, but PGC results generally resembled data from the corresponding grab sample. Some discrepancies were probably caused by poor mixing of air close downwind of the source. Agreement between methods was not exact, but it was close enough to show that all of the PGCs provided reasonable estimates of the concentrations of compounds for which they were calibrated. In Table 5 these data are summarized by the average of the averages for the individual compounds and the average of the standard deviations for the individual compounds. The ranges shown in Table 5 are the difference between the best and worst agreement between paired canister and PGC results among all of the compounds. These data are a further condensation of data which were tabulated previously [3]. A small average difference with a smaller standard deviation and a narrow range would indicate close agreement between the two methods. A large average difference with a small standard deviation would indicate good precision but substantial disagreement due to systematic error. A small average difference with a standard deviation of about the same magnitude as the average difference would indicate data of reasonable accuracy but mediocre precision, which would be expected

when analyzing concentrations near detection limits. That is
generally what is seen in Table 5. A somewhat larger average
difference and a standard deviation larger than the average difference
with a broad range indicates some outliers among the data. A very
large average difference with a standard deviation as large as the
range would indicate little or no agreement between methods, and that
is not seen in Table 5.

## CONCLUSIONS

All of the PGCs performed substantially as expected. It would be
futile to try to rank them on the basis of performance, since they are
not uniformly applicable to the same compounds. All instruments
evaluated in this study performed substantially as claimed. Each was
able to detect compounds at the levels encountered, generally with
reasonable accuracy. A variety of instruments and detectors may be
required to match capability with need. Choice of an instrument for a
particular application should be based upon consideration of its
particular features and capabilities. All of the instruments in this
study were seriously handicapped by exposure to cold wind, and they
all required shelter in order to function properly.

## REFERENCES

1. Compendium of Methods for the Determination of Toxic Organic
Compounds in Ambient Air. Environmental Protection Agency,
Atmospheric Research and Exposure Assessment Laboratory, Research
Triangle Park, NC 27711. EPA-600/4-84-017. June 1988.

2. R. E. Berkley, J. L. Varns, and J. Pleil. Comparison of Portable
Gas Chromatographs and Passivated Canisters for Field Sampling
Airborne Toxic Organic Vapors in the United States and the USSR.
Environ. Sci. Technol., 25(8): 1439 (1991).

3. R. E. Berkley, M. Miller, J. C. Chang, K. Oliver, C. Fortune,
Evaluation of Commercially-Available Portable Gas Chromatographs, in
Proc. 1992 EPA/AWMA International Symposium on Measurement of Toxic
and Related Air Pollutants, Air and Waste Management Association,
Pittsburgh, PA, 1992, pp 413-418.

4. R. E. Berkley, K. Kronmiller, and K. Oliver, Performance
Optimization of Photovac 10S70 Portable Gas Chromatograph.
Proceedings of the 1990 EPA/AWMA International Symposium: Measurement
of Toxic and Related Air Pollutants, 1990 pp 849-854.

## TABLE 1. SUMMARY OF INSTRUMENT FEATURES AND CAPABILITIES

| | HNU 311 | MSI 301 | Photovac 10S+ | Scento-graph | SRI 8610 |
|---|---|---|---|---|---|
| Power | 110 V AC | 110 V AC 12 V DC | 110 V AC 12 V DC | 110 V AC 12 V DC | 110 V AC 12 V DC |
| Column °C | isothermal to 200 | isothermal 65 | isothermal 40, 50 | isothermal to 180 | program to 250 |
| Detector | PID | SAW | PID | AID | PID + ELCD |
| Injector | injection loop or syringe port | precon-centrate & desorb | injection loop or syringe port | precon-centrate & desorb or syringe port | precon-centrate & desorb or syringe port |
| Back-flush | yes | no | yes | no | no |
| Carrier | helium, & others | scrubbed ambient air | ultra-zero air | argon helium | helium, nitrogen, scrubbed ambient air |
| Data report | printer or computer | internal processor, external computer, or printer | magnetic card, external printer, or computer | computer disk | external printer or computer |

| | | | | |
|---|---|---|---|---|
| PID | photoionization detector | | ECD | electron capture detector |
| SAW | surface acoustic wave detector | | AID | argon ionization detector |
| TCD | thermal conductivity detector | | ELCD | electrolytic conductivity detector |

TABLE 2. CORRELATION COEFFICIENTS OF CALIBRATION PLOTS

| | | Benzene | Toluene | Tetra-chloro-ethylene | Chloro-benzene | o-Xylene |
|---|---|---|---|---|---|---|
| HNU 311 | Lab | 0.958 | 0.958 | 0.976 | 0.977 | 0.996 |
| | Field | 0.995 | 0.993 | 0.996 | 0.976 | 0.966 |
| MSI 301 | Lab | 0.985 | 0.964 | NA | NA | 0.922 |
| | Field | 0.971 | 0.971 | NA | NA | 0.979 |
| Photovac 10S+ | Lab | 0.997 | 0.998 | 0.999 | 0.997 | 0.996 |
| | Field | 0.994 | 0.996 | 0.999 | 0.990 | 0.988 |
| Scentograph | Lab | 0.939 | 0.836 | 0.955 | 0.817 | ND |
| | Field | 0.964 | 0.954 | 0.992 | 0.870 | 0.919 |
| SRI 8610 PID | Lab | 0.990 | 0.991 | 0.993 | 0.981 | 0.977 |
| | Field | 0.963 | 0.955 | 0.977 | 0.959 | 0.972 |
| SRI 8610 ELCD | Lab | NA | NA | 0.965 | 0.903 | NA |
| | Field | NA | NA | 0.845 | 0.850 | NA |

TABLE 3. DETECTION LIMITS CALCULATED FROM CALIBRATION PLOTS

(parts per billion by volume)

| | Benzene | Toluene | Tetra-chloro-ethylene | Chloro-benzene | o-Xylene |
|---|---|---|---|---|---|
| HNU 311 | | | | | |
| Lab | 1.9 | 2.4 | 3.1 | 2.0 | 5.3 |
| Field | 2.5 | 3.2 | 4.6 | 4.1 | 9.3 |
| MSI 301 | | | | | |
| Lab | 2.4 | 9.1 | NA | NA | 4.5 |
| Field | 9.0 | 10.3 | NA | NA | 10.1 |
| Photovac 10S+ | | | | | |
| Lab | 1.1 | 2.6 | 2.1 | 3.6 | 14.4 |
| Field | 0.9 | 2.0 | 1.3 | 3.3 | 20.6 |
| Scentograph | | | | | |
| Lab | 5.1 | 4.4 | 5.9 | 5.5 | 27.9 |
| Field | 6.7 | 7.5 | 3.4 | 6.6 | 46.6 |
| SRI 8610 PID | | | | | |
| Lab | 3.4 | 2.7 | 2.9 | 2.0 | 1.1 |
| Field | 4.9 | 3.4 | 3.4 | 2.2 | 3.0 |
| SRI 8610 ELCD | | | | | |
| Lab | NA | NA | 1.9 | 3.5 | NA |
| Field | NA | NA | 2.2 | 8.8 | NA |

ND  Not detected.  NA  Detector does not respond.

TABLE 4. CHROMATOGRAPHIC RESOLUTION AND DETECTOR SELECTIVITY

=================================================================

Resolution of benzene from toluene was taken to be twice the
difference in retention times divided by the sum of the peak widths
at base height.

---------------------------------------------------------------------

|              | Resolution | Detector | Compounds Detected         |
|--------------|------------|----------|----------------------------|
| HNU 311      | 2.58       | PID      | Aromatics, halocarbons     |
| MSI 301      | 1.09       | SAW      | Benzene, toluene, xylene   |
| Photovac 10+ | 7.77       | PID      | Aromatics, halocarbons     |
| Scentograph  | 7.23       | AID      | Universal                  |
| SRI 8610     | 5.32       | PID      | Aromatics, halocarbons     |
| SRI 8610     | 5.32       | ELCD     | Halocarbons                |

=================================================================


TABLE 5. AVERAGE ABSOLUTE DIFFERENCES BETWEEN
TO-14 REFERENCE METHOD AND PORTABLE GAS CHROMATOGRAPH DATA

=================================================================

Average differences between paired canister and PGC results for the
five compounds were averaged to summarize performance of the
instrument.  Standard deviations for individual compounds were also
averaged.  Ranges are the differences between the largest and smallest
discrepancies among all five compounds.

---------------------------------------------------------------------

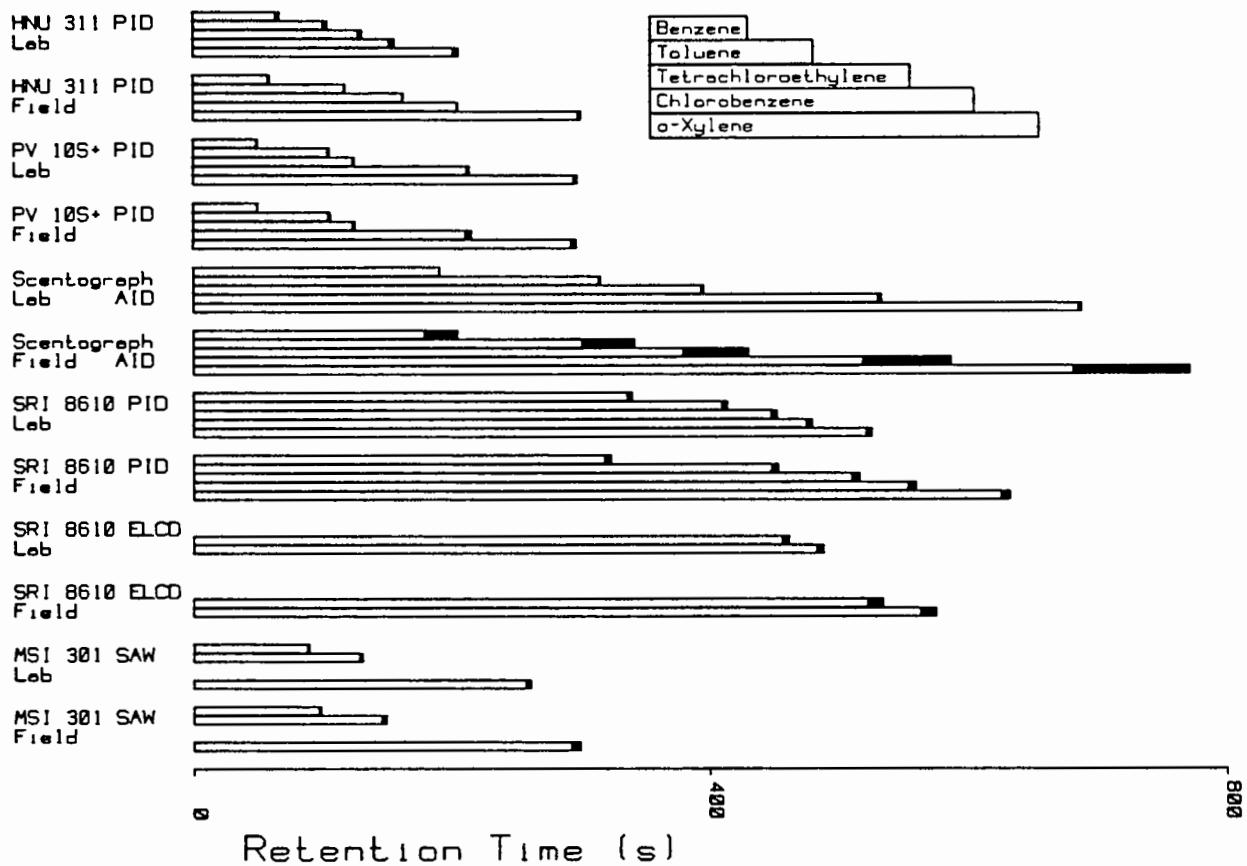|                                       | Average of per Compound Average Differences | Average of per Compound Standard Deviations | Maximum Range of All Differences |
|---------------------------------------|---------------------------------------------|---------------------------------------------|----------------------------------|
| HNU 311 15 Runs, 5 Compounds          | 4.80                                        | 15.13                                       | 61.15                            |
| MSI 301 13 Runs, 2 Compounds          | 1.75                                        | -                                           | 7.20                             |
| Photovac 10+ 14 Runs, 5 Compounds     | 0.63                                        | 0.60                                        | 2.20                             |
| Scentograph 13 Runs, 5 Compounds      | 1.08                                        | 0.73                                        | 2.58                             |
| SRI 8610 PID 13 Runs, 5 Compounds     | 1.18                                        | 1.00                                        | 3.98                             |
| SRI 8610 ELCD 13 Runs, 2 Compounds    | 1.30                                        | -                                           | 5.30                             |

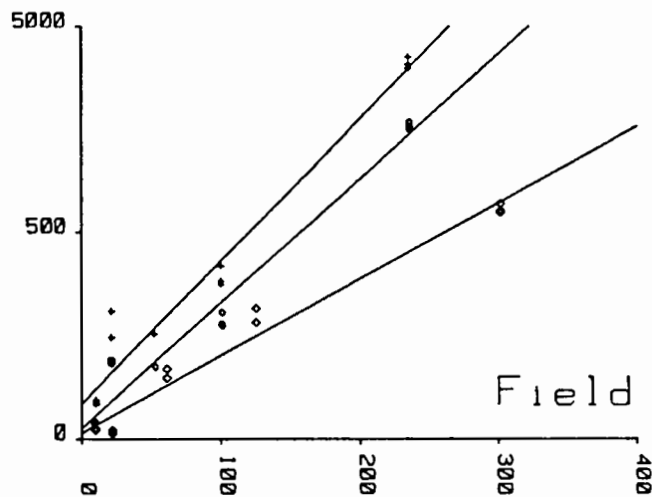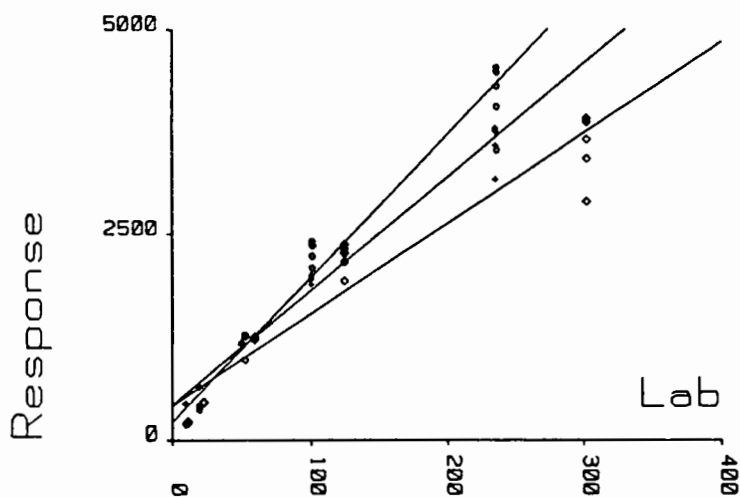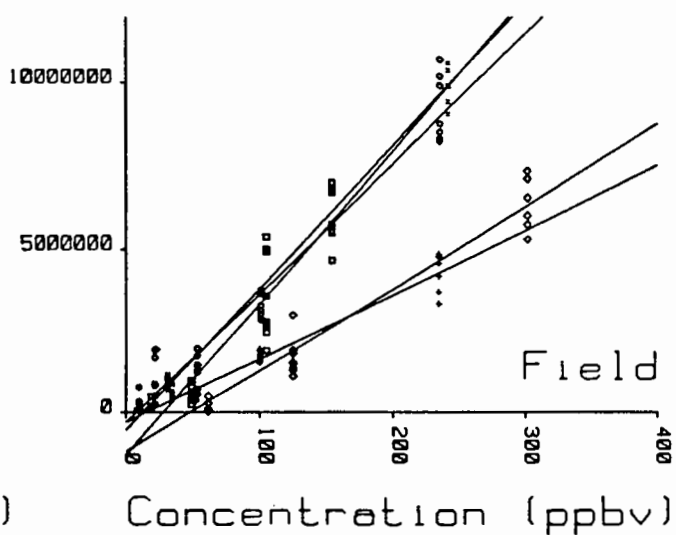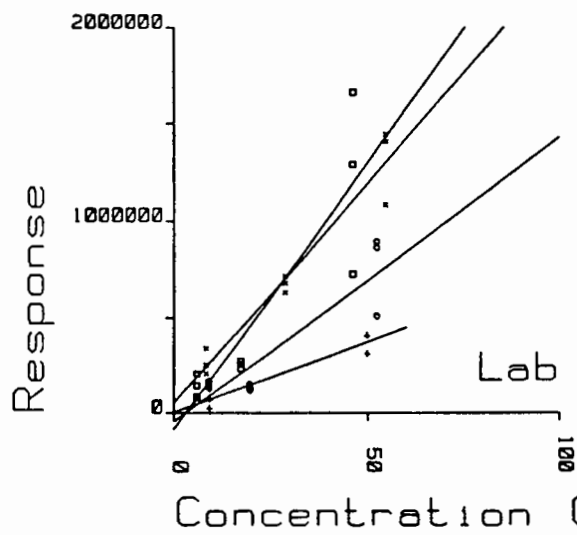=================================================================

Figure 1. Retention time stabilities. Standard deviation of retention time for each compound is represented by a shaded bar centered on the end of an unshaded bar which represents average retention time.
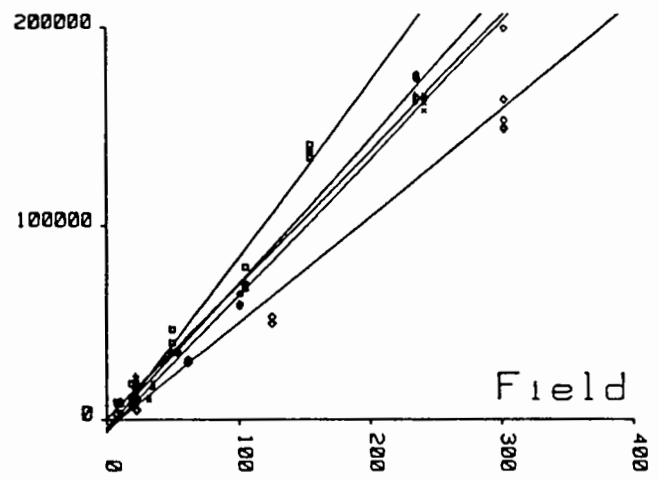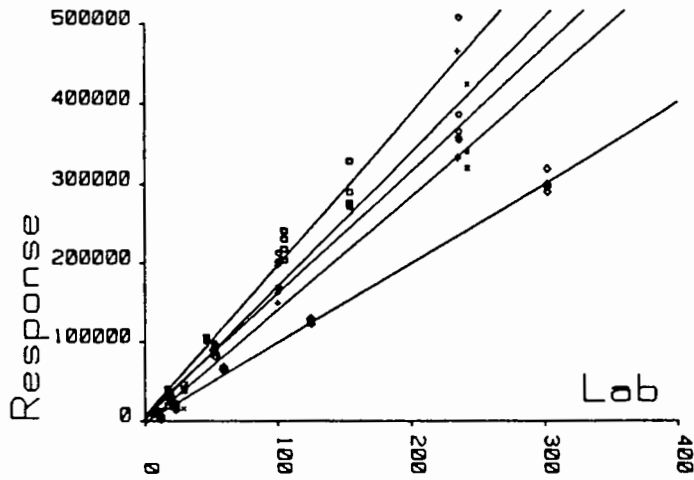
MSI 301 Calibrations
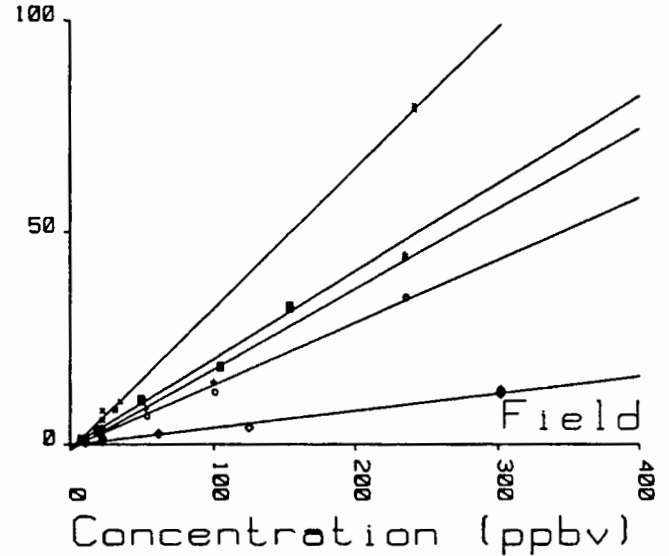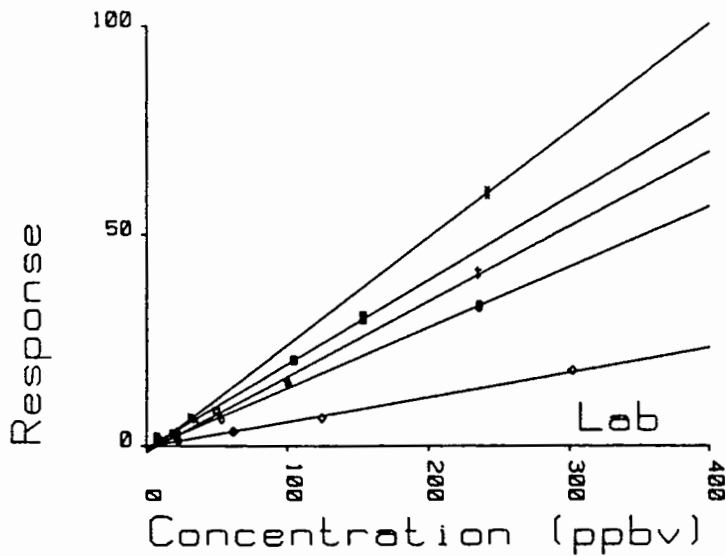


Scentograph Calibrations



+ Benzene    × Tetrachloroethylene    ◇ o-Xylene
∘ Toluene    □ Chlorobenzene

Figure 2. Calibration plots from laboratory and field studies for MSI 301 and Sentex Scentograph.
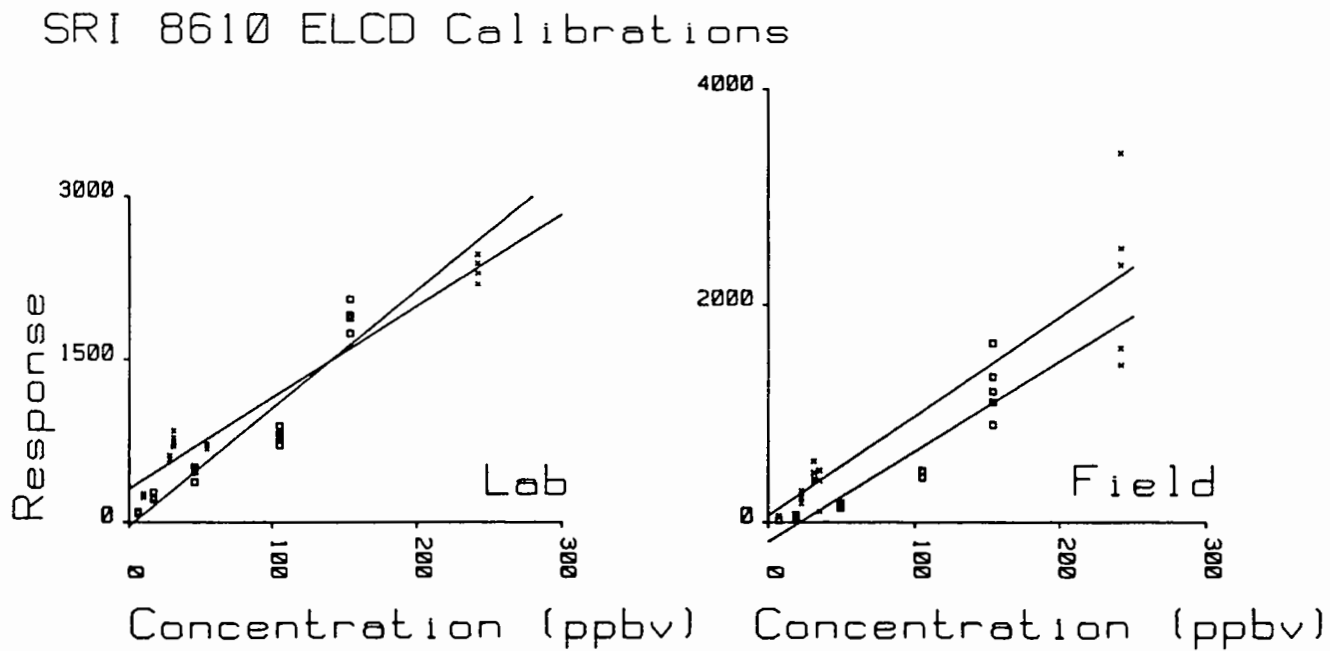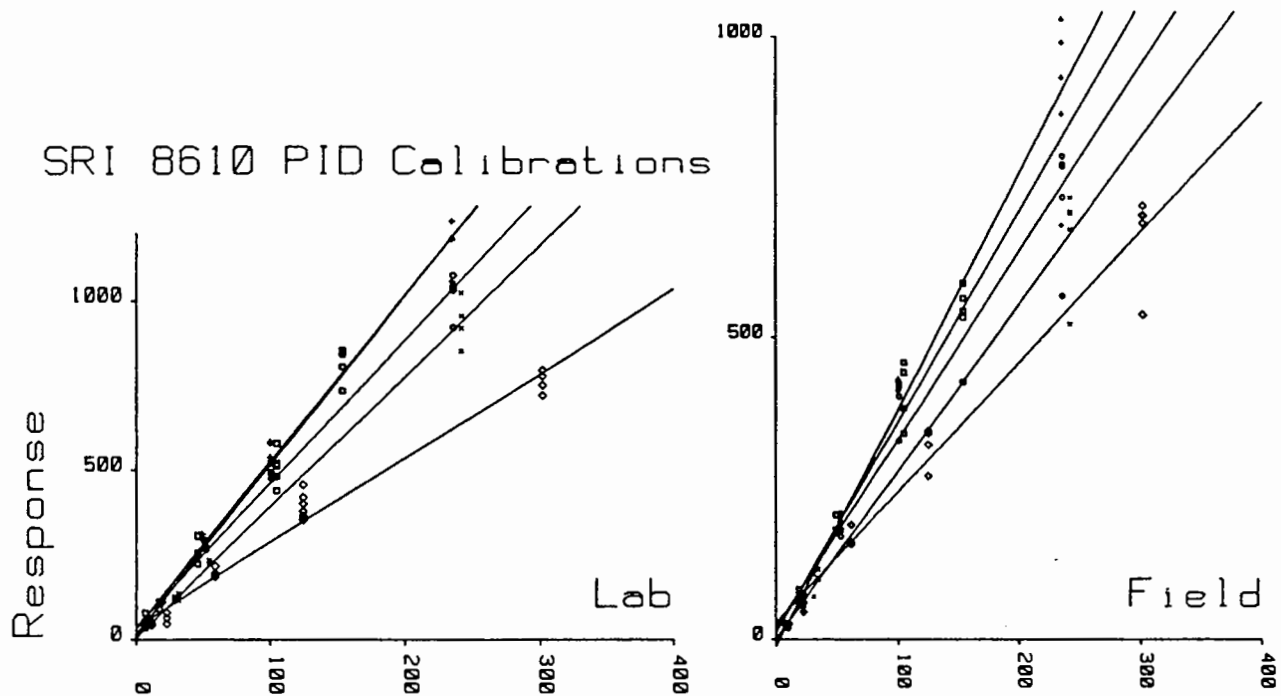
# HNU 311 Calibrations



# Photovac 10S+ Calibrations



+ Benzene   × Tetrachloroethylene   ◇ o-Xylene
∘ Toluene   □ Chlorobenzene

Figure 3. Calibration plots from laboratory and field studies for HNU 311 and Photovac 10S+.

Figure 4. Calibration plots from laboratory and field studies for SRI 8610 photoionization and electrolytic conductivity detectors.

# TECHNICAL REPORT DATA
*(Please read Instructions on the reverse before completin,*

| 1. REPORT NO. *EPA/600/A-93/267* | 2. | 3. RI |
|---|---|---|

**4. TITLE AND SUBTITLE**
Evaluation of Portable Gas Chromatographs

**5. REPORT DATE**

**6. PERFORMING ORGANIZATION CODE**

**7. AUTHOR(S)**
R. E. Berkley, M. Miller, J. Chang, K. Oliver,
C. Fortune, J. Adams

**8. PERFORMING ORGANIZATION REPORT NO.**

**9. PERFORMING ORGANIZATION NAME AND ADDRESS**
IIT Research Institute    ManTech Environmental Serv.
10 West 35 Street         2 Triangle Drive
Chicago, IL 60616         RTP, NC  27709

**10. PROGRAM ELEMENT NO.**
Y105C/A04/F01

**11. CONTRACT/GRANT NO.**
68-D8-0002
68-D0-0106

**12. SPONSORING AGENCY NAME AND ADDRESS**

AREAL/MRDD/AMRB
MD-44
RTP, NC  27711

**13. TYPE OF REPORT AND PERIOD COVERED**
Conference Proceeding

**14. SPONSORING AGENCY CODE**

**15. SUPPLEMENTARY NOTES**

**16. ABSTRACT**

Limits of detection, linearity of responses, and stability of response factors and retention times for five commercially-available portable gas chromatographs (PGC) were determined during laboratory evaluation.  The PGCs were also operated at the French Limited Superfund site near Houston, TX during startup of bioremediation. Concentrations of volatile organic compounds (VOC) at the site were slightly above ambient background levels.  Concurrent collocated grab samples were collected periodically in canisters and analyzed by Method TO-14 using a mass-selective detector.  Canister data were taken to indicate correct concentrations and were used to assess the accuracy of PGC data.  Durability, reliability, and complexity of operation of PGCs were also evaluated.  The principal goal of the study was to determine the best way to use each instrument as a monitor for airborne VOCs.

**17.  KEY WORDS AND DOCUMENT ANALYSIS**

| a.  DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c.  COSATI Field/Group |
|---|---|---|
| | | |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES 12 |
|---|---|---|
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |