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Compendium of ERT Field Analytical Procedures

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COMPENDIUM OF ERT FIELD ANALYTICAL PROCEDURES

Sentex Scentograph Gas Chromatograph

Portable XRF Analyzer

Photoionization Detector -- HNU

Photovac 10A10 Portable Gas Chromatograph Operation

Photovac 10S50, 10S55, and 10S70 Gas Chromatograph Operation

Photovac GC Analysis for Air, Soil Gas, Water, and Soil

Micromonitor M200

Interim Final

Environmental Response Team
Emergency Response Division

Office of Emergency and Remedial Response
U.S. Environmental Protection Agency
Washington, DC 20460

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Questions, comments, and recommendations are welcomed regarding the Compendium of ERT Field Analytical Procedures. Send remarks to:

Mr. William A. Coakley
Removal Program QA Coordinator
U.S. EPA - ERT
Raritan Depot - Building 18, MS-101
2890 Woodbridge Avenue
Edison, NJ 08837-3679

For additional copies of the Compendium of ERT Field Analytical Procedures, please contact:

National Technical Information Service (NTIS)
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
(703) 487-4600

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1.0 SENTEX SCENTOGRAPH GAS CHROMATOGRAPH: SOP #1702

1.1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) primarily deals with the assessment of gaseous matrix samples. The Sentex Scentograph Gas Chromatograph (GC) can work in two detector configurations: the Electron Capture Detector (ECD) or the Argon Ionization Detector (AID). The ECD analyzes volatile chlorinated compounds, as it is very sensitive to electrophilic compounds such as chlorinated organics. The AID is a more universal detector, responding to most compounds with ionization potentials at or below 11.7 eV. It will respond to most aromatic compounds and many chlorinated compounds of environmental interest.

At present, only vapor-phase samples (e.g., soil gas samples, Tedlar bag gas samples, and ambient air samples) are analyzed through the activation of the instrument's internal sampling pump. The Sentex GC unit does have a syringe injection port, but this is not being used for any ERT applications at present. An optional purge and trap unit is available to determine purgeable organics in soil or water matrices. However, this SOP does not cover that capability.

1.2 METHOD SUMMARY

The initial step in Sentex Scentograph Gas Chromatograph sampling is to turn on and boot the Toshiba T1100 computer. The computer runs the data acquisition program and stores all parameters and data. Begin by inserting the program disk "A" and the data "B" disk into the appropriate upper and lower disk drives of the computer. Next, turn on the Sentex GC and, following the menu prompts, enter the GC operational parameters into the computer. Calibration analysis is then performed and stored. Calibration standards can be run either in the field, or in the laboratory prior to field sampling. In the latter case, a field calibration run must still be conducted to ensure that the lab calibrations are valid. A Tedlar bag of a standards mixture can be attached to the Sentex GC upper inlet port at this point, or the internal calibration gas cylinder can be used. Once calibration analysis is validated and stored, a Tedlar bag containing an unknown sample is attached to the Sentex GC's lower sampling inlet port, and the bag valve is opened. By selecting *Function #3* from the computer menu, a manual analysis can be run.

Once the sampling pump stops, the valve of the sample bag is closed, and the entire bag is removed from the inlet port and stored for future laboratory analysis.

While this procedure is standard for all Sentex GC sampling, actual operating conditions (e.g., detector used, column packing material, oven temperature) will vary as required by the sample matrix encountered, and by the physical and chemical nature of the samples analyzed. New operating parameters are determined as new target compounds are selected for analysis.

1.3 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The vast majority of Sentex applications are for soil gas analysis. These soil gas samples are collected and stored as outlined in ERT SOP #2149, Soil Gas Sampling.

1.4 INTERFERENCES AND POTENTIAL PROBLEMS

Since the Sentex units use gas chromatography, target compounds are identified by retention time indices (RTI). If the RTI of the sample peak(s) matches the RTI of the standard peak(s), it is assumed to be identical. If any non-target compound has the same RTI, it can be misidentified as a target compound. This problem occurs more frequently with the AID, since it will respond to any compound at or below 11.7 eV. Often, soil gas samples will have very high (ppm) levels of C_1 to C_6 hydrocarbons, as well as low (ppb) levels of target compounds. The AID will respond to these hydrocarbons, whose signal often can "swamp" or obscure the signal of the lower level target compounds. In this case, it is better to use the ECD. If this is not possible, a different GC column (one able to separate the target compounds from

the interference of the sample matrix) must be utilized. Moisture within the Tedlar bags will yield interference peaks that can obscure the resolution of the target compounds. It has not been determined whether the moisture itself, or contaminants in the moisture, yields these contamination peaks, but the effect is seen on both the AID and the ECD. Typically, when water is found in the Tedlar bags, the results of that bag's analysis are considered questionable. Typical ambient air relative humidity has no appreciable effect on the signal response.

1.5 EQUIPMENT/APPARATUS

A Sentex model Scentograph GC can be configured for AID or ECD. Interfaced with the unit is a Toshiba model T1100 lap top computer which runs the data acquisition program and stores all parameters and data. The Sentex unit has an internal battery pack which is charged from a Power Sonic Corporation model PSC-12400 (115 VAC to 12 VDC) charger. Attached to the T1100 is a Hewlett-Packard Model 2225P Think Jet printer which produces hard copies of chromatograms and peak data information. No other equipment is required to operate the Sentex Scentograph unit.

1.6 REAGENTS

The Sentex AID requires ultrahigh purity (99.99% or above) Argon as carrier gas. The ECD can use either ultrahigh purity Argon or Helium (these can be ordered from Scott Gas, Matheson or any other reliable vendor). Gas standards are purchased as certified mixtures from Scott Gas or Matheson, at fairly high concentrations (i.e., 1-50 ppm). These concentrations subsequently dilute to various concentrations that enable construction of a standard calibration curve. If the internal calibration cylinder is used, a low-level standard, such as 0.5-1.0 ppm, should be used.

If liquid phase standards are required, they must also be of the highest purity, such as Aldrich Gold Label or Supelco Environmental standards kits. If air is to be used for sample/standards dilutions, it must also be ultrahigh purity gas.

1.7 PROCEDURES

All operational parameters are entered from the T1100 computer and accessed from the operations menu, *Function #1*, which appears when the Sentex unit is turned on. Once the parameters are entered, run for calibration, *Function #4*. This is not a true calibration, since the Sentex calculates a pseudo-concentration against only one concentration. The calibration function is used only when operating parameters under *Function #1* are changed. In all other cases, it is ignored. After the first "junk" or noise peak is identified in the calibration run, the run is typically aborted. Occasionally, a Tedlar bag or the internal calibration gas cylinder can be sampled in the calibration mode, but this would be only for peak identification and semi-quantification purposes, since it is a single point calibration.

1.7.1 Calibration

The generation of calibration standards to be run in the field can be performed either in the field or in the laboratory prior to entering the field. If the latter is done, field standards must still be run to ensure calibration runs stored on the data disks are valid and close to standards run in the lab. Dilutions are typically made from the certified gas standards' cylinders using Hamilton 500, 1000 and 1500 cm^3 model "Super syringes", and from Tedlar sampling bags. Simple volumetric dilutions are made and the set of standards analyzed as if they were typical samples.

At least three concentrations of each standard must be run; however, more standards are run to establish the minimum ranges for the linear response of the Sentex detectors for each individual target compound. In the laboratory, a Multi-Channel Mass Flow Control can be used to meter selected flow rates from two to four separate compressed gas cylinders. Establish a continuous flow of a selected concentration of mixtures to either fill Tedlar bags for analysis or to create a flow-through-cell from which the Sentex GC can sample. This method has been used extensively to establish minimum and maximum detection levels in an efficient and timely manner.

1.7.2 Sampling

Follow this procedure for analyzing Tedlar bags with the Scentograph.

1. Insert Disks "A" and "B" into upper and lower T1100 disk drives respectively, and turn on Sentex GC.

2. Follow menu prompts and input GC parameters according to Table 1, Scentograph Operating Parameter Menu.

3. Select *Function #4* to run and store calibration analysis.

4. Attach Tedlar bag with unknown sample to lower sample inlet port and slide bag valve down to open.

5. Select *Function #3* to run a manual analysis. Type the sample name; press <ENTER> a second time to inject.

6. Immediately after the sampling pump stops, pull bag valve out to close; remove bag from inlet port.

7. To abort sample and calibration analysis, hold down the *Reset* key on the GC panel until the "Return" prompt appears.

8. Any changes in operating parameters entered in Function #1 must be followed by a calibration run prior to an analysis run.

1.8 CALCULATIONS

A calibration curve of at least three concentrations must be constructed for each target compound. A straight line equation in the form of $y = (m)(x) + b$ (where: x = concentration, y = area counts, m = slope and b = the intercept) is fit to the standards raw data. The (y), or the unknown concentration for the sample, is determined from the above straight line equation. Non-linear data is indicative of erroneous detector response. Alternatively, sample concentration can be calculated as shown below:

$$\text{Sample Conc.} = \frac{(\text{standard conc.})(\text{sample area})}{(\text{standard area})}$$

The Sentex performs a one point calibration for those compounds entered in the library. If the samples and library standard are in the linear range, this one point calibration is considered valid for screening purposes.

1.9 QUALITY ASSURANCE/ QUALITY CONTROL

The following QA/QC protocols are applicable:

- Run a complete calibration curve daily.

- Duplicates of a standard, in the mid-range of the calibration curve and preferably close to sample results, should be run every 10 samples or so, to ensure detector response is constant.

- Run two to three duplicates for each sample and standard. In terms of area count and retention time values, these duplicate responses should be within 10-20% of each other.

- Matrix spikes, or spiking samples with known levels of standards, are not typically required, as the same Tedlar bag may be analyzed by other field instrumentation (e.g., Photovac, OVA, etc.) and/or collected onto traps for GC/MS confirmation. If Tedlar bags are used to prepare standards, the time of preparation should be noted.

- During sample analysis, one of the standards should be periodically re-analyzed to test for any sample loss in the bag over time.

- A performance evaluation (PE) sample is typically sent along with the samples to test for any loss or contamination from transit or handling during sampling.

- Send a trip blank of zero air along for analysis at the end of the sampling run to determine if any contamination of the Tedlar bags occurred during transit.

Table 1: Scentograph Operating Parameter Menu

#	Operating Parameter		Example
1	Calibration Sample Name	up to 8 letters	SAMPLE
2	Sample Time	1 - 300 seconds	15
3	Delay Time	0.1 - 4.0 seconds	1
4	Desorption Time	0.1 - 4.0 seconds	4
5	Inhibit Time	10 - 999 seconds	50
6	Oven Temperature	30° C - 140° C	50
7	Chart Duration	1; 3; 5; 10; 15; 20; 30 minutes	30
8	Analysis per Calibration	1 - 99	99
9	Auto Analysis Duration	0 - 120 minutes	manual
10	Backflush Option	0 = off; 1 = on	
11	Detector	.... 1-AID, 2-ECD, 3-TCD, F-PID	AID
12	Column	up to 8 letters	6 ft. 10% CP5
13	Column Pressure	5 - 40	20
14	Number of Calibration Peaks	1 - 16	1
15	Peak Number 1 • Substance Name • Concentration Range • Calibration Concentration • Peak Alarm Values	 up to 8 letters 0 = ppm; 1 = ppb 99.9 ppm; 9999ppb 0 - 99.99 ppm; 9999ppb	 U1/AID PPM 1.00 99
16	Upload Scentograph Parameters		

1.10 DATA VALIDATION

As mentioned previously, peak identification is by retention time index (RTI). Sample spikes, using known levels of target compounds, can be prepared to identify the absence/presence of target compounds in the samples, if peaks are eluting close to the target compounds. Typically, only the RTI is needed to identify the peaks of interest. Quantification is determined from the linear calibration curve, and solving for concentration "(y)" from the straight line equation. The coefficient of variation on the straight line equation should have an R squared (R^2) of 0.95 or better. Confirming the identity of any particular target compound must be done by other analytical methods, typically GC/MS. Standards must be run along with the samples and should bracket the levels found in the field samples.

Alternatively, a statistical approach to data validation can be sought. Once the linear range is established, an appropriate standard of either low or midrange concentration will be analyzed 10 or more times throughout the day. The standard deviation of the mean ($\sigma(n-1)$) for the response of the standard selected is determined. The statistical method detection limit (MDL) will be three times the standard deviation (3σ). The method quantitation limit (MQL) will then be 10 times the standard deviation (10σ). Results below the MDL are considered "nondetects" (ND). Results above

the MDL but below the MQL are considered "detected", but below the quantitation limit, so are ascribed a "J" value. This "J" value will flag the data to let the user know the results are questionable. Results above the MQL are considered statistically reliable data.

1.11 HEALTH AND SAFETY

Analysis should be performed in a well-ventilated room. When liquid reagents are used to prepare standards, etc., disposable protective gloves and suitable eye protection should be worn. Work should be performed under a vented hood.

2.0 PORTABLE XRF ANALYZER: SOP #1707

2.1 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to describe the procedures for portable X-ray fluorescence spectroscopy (XRF), an analytical technique which allows for qualitative and quantitative analysis of a sample's chemical composition. In a source-excited XRF analysis, primary X-rays emitted from a sealed radioisotope source are utilized to irradiate a sample. These X-rays cause the sample to emit characteristic fluorescent X-rays from the elements contained in the sample. From the energy, or wavelength, of these fluorescent X-rays, a qualitative analysis can be made. From the number of X-rays at a given energy, a quantitative analysis is possible. Solid and liquid samples can be analyzed with proper X-ray source selection. Typical environmental applications are:

- heavy metals in soils, sludges, and liquids;
- light elements in liquids;
- heavy metals in industrial waste stream effluent;
- PCBs in transformer oil by Cl analysis; and
- heavy metal air particulates collected on membrane filters.

Measurements may be made in situ, or samples may be collected, homogenized, and placed into sample cups for analysis.

2.2 METHOD SUMMARY

XRF instruments use radioactive isotopes, such as Fe-55, Cm-244, Cd-109 and Am-241, for the production of primary X-rays. Each source emits a specific energy range of primary X-rays that causes a corresponding range of elements in a sample to produce fluorescent X-rays. When more than one source excites the elements of interest, the appropriate source(s) is selected according to its excitation efficiency for the elements of interest.

For measurement, the sample is positioned in front of the source-detector window and exposed to the primary (source) X-rays by pulling a trigger on the probe (or pushing back the top of the probe unit on the sample type probe), which exposes the sample to radiation from the source. The sample's fluorescent and backscattered X-rays enter through the detector beryllium (Be) window and are detected in the active volume of a high-resolution, gas-filled, proportional counter.

Elemental count rates (the number of net element pulses per second) are used in correlation with actual sample compositions to generate calibration models for qualitative and quantitative measurements.

The user selects an analysis time from 1 to 32,767 seconds. Generally, the shorter measurement times (30 s - 100 s) are used for initial screening and hot spot delineation, while longer measurement times (100 s - 500 s) are used for higher precision and accuracy requirements.

2.3 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Use appropriate sample containers (glassware) with Teflon-lined lids for sample collection. Disposable 31-mm diameter plastic cups are used for XRF measurements.

2.4 INTERFERENCES AND POTENTIAL PROBLEMS

- **Sample Placement.** The X-ray signal decreases the greater the distance from the radioactive source. Minimize decrease by maintaining the sample's distance from the source within a 1-mm range.
- **Sample Representation.** Representation is affected by the soil macro- and micro-homogeneity. This can be minimized by either homogenizing large samples prior to analyzing an aliquot, or by analyzing several samples (in

situ) at each sampling point and averaging the results.

- **Reference Analysis.** XRF soil chemical and physical matrix effects may be corrected by using inductively coupled plasma (ICP), or atomic absorption (AA) spectrometer-analyzed, site-specific soil samples as calibration samples. A major source of error can result if the samples analyzed are not representative of the site and/or the analytical error is large. With XRF calibrations based on reference analysis results, the XRF analytical results may be in the same units used for the calibration samples reference analysis. For example, total metals can be used for comparison using the toxicity characteristic leachate extraction procedure (TCLP).

- **Chemical Matrix Effects.** Chemical matrix effects result from differences in concentrations of interfering elements. These effects appear as either spectral interferences (peak overlaps) or as X-ray absorption/enhancement phenomena. Both effects are common in soils contaminated with heavy metals. It is critical to establish all chemical matrix relationships during the time of instrument calibration. This is done by using ICP or AA analyzed soil samples as the XRF calibration standard (as discussed in Step 3).

- **Physical Matrix Effects.** Physical matrix effects result from variations in the physical character of the sample. They include such parameters as particle size, uniformity, homogeneity and surface condition. Physical matrix effects can be minimized by sieving and thoroughly homogenizing a soil sample prior to analysis.

- **Ambient Temperature.** Changes in ambient temperature can affect the gain of the amplifiers producing instrument drift. As long as the gain control is allowed to make periodic adjustments however, the unit will compensate for the influence of temperature on its energy scale. If increasing or decreasing ambient temperature is a concern, allow the XRF unit to gain control after every five measurements.

- **Moisture Content.** Moisture content of soil samples poses potential interference. Soil samples should have a percent moisture of no more than 20%. Dry samples, if necessary.

- **X-Ray Spectrum Overlap.** Certain X-ray lines from different elements (when present in the sample) can be very close in energy, and therefore, interfere by producing a severely overlapped spectrum. The lead/arsenic overlap is a typical example.

- **Pure Element Calibration.** When doing the pure element calibration, be sure to include all elements of interest at the site, as well as elements adjacent to the target compound. In addition to target elements, include all elements present in detectable amounts with the X-ray source being used. Use that information to determine potential spectral interferential effect on the target element.

2.5 EQUIPMENT/APPARATUS

- portable XRF-X-MET model 840, model 880 or equivalent
- pure element samples
- battery charger
- battery pack
- 31-mm diameter disposable sample cups
- polypropylene film, 0.2 mil thickness
- plastic bags
- 20-mesh sieve
- moisture balance oven
- nylon reinforced, water-repellant backpack
- metal reinforced shipping case with die-cut foam inserts

2.6 REAGENTS

- pure element spectral calibration standards
- matrix calibration standards -- ICP- or AA-analyzed site matrix calibration standards

2.7 PROCEDURES

2.7.1 Calibration

Calibration of the XRF should be based on previously collected samples which were analyzed by AA or ICP. The field-portable unit uses samples collected from the site to generate a calibration curve.

Samples used for XRF calibration, more commonly referred to as site-specific calibration standards

(SSCS), must be representative of the matrix and concentration range which will be sampled at the site. For example, if conducting an investigation for off-site contamination, then SSCS samples should not come from on site. The matrices could be different and may introduce a source of error in the calibration model.

In addition, a full concentration range of the target element(s) of interest is needed to generate a representative calibration curve. The highest and lowest SSCS samples will be used to determine the linear calibration range. Samples used to generate the calibration curve must be prepared in a fashion similar to samples analyzed by the XRF. Samples used for the calibration, especially those samples at approximately the level of concern, are used as QC check samples during field activities.

The more the sampler knows about how the matrix varies at the site, the more representative the calibration model, and the more accurate the results. A minimum of 10 samples are recommended to generate the calibration; the maximum number is 30. A general rule is to add 5 samples for each element of interest and 5 samples for each adjacent element. As the number of elements under analysis increases, more calibration samples are required to adequately characterize the concentration ranges present for each element. Be aware that there may be a need for more than one calibration model to maintain linearity over the concentration ranges in question.

2.7.2 In Situ Soil Analysis

In situ soil measurements provide a rapid means of data collection at a large number of sample points, eliminate the need for sample containers and chain of custody forms, and yield real-time measurements. Two primary scenarios exist for in situ measurements. First, perform rough, rapid, non-quantitative XRF screening with a non-site-specific or generic calibration model; this allows for decisions such as where to collect samples for use in a site-specific calibration model. This scenario takes into account previous data collected at the site, a visual inspection of the site, and historical background information. Care should be exercised when using non-site-specific or generic calibration models, as variations in sample representativeness and matrices may significantly limit the validity of the model. Second, in situ XRF screening is conducted with a site-specific calibration model providing rapid, semi-quantitative data.

In addition to these two in situ scenarios, XRF analysis may be performed on samples which have been collected and undergo some type of sample preparation. When sampling is employed, the prepared sample is analyzed by XRF measurement, and the same portion is then submitted for confirmation analysis by AA/ICP, according to QA/QC protocols. A split portion of the sample is archived.

Remove all surface debris in the sampling location. To avoid cross contamination, place a single thickness plastic sample bag or polypropylene film over the probe and firmly press the probe to the ground. Where possible, maximize instrument performance by placing it 3 mm from the ground surface. It should be noted that in situ measurements can exhibit a high degree of variability due to the natural heterogeneity of the soil. This effect may be minimized by averaging multiple readings within a predetermined area based on sampling objectives. Single in situ measurements may be used at any one sample location; however, this can reduce the precision and representativeness associated with the XRF results. Therefore, the minimum recommended measurement time or duration for in situ analysis is 30 seconds. All sample readings should be recorded.

The depth of X-ray penetration for analysis is only the first two or three millimeters of soil. Therefore, **in situ measurements represent data from the ground surface only, and in no way reflect sub-surface soil conditions.** As little as 0.5 cm of clean soil cover can completely mask a hot spot. Also, in situ analysis can have a high degree of error due to the heterogeneity and possible wide range of particle size fractions present in the sample. Data obtained from in situ analysis is best suited for site characterization activities where the user is interested in obtaining a quick overview of site conditions at the surface. It can also define extent of contamination if confirmation samples are used.

2.7.3 Soil Samples for XRF Analysis

Discrete sample collection involves physical collection of a soil sample (4 oz.) and some type of field preparation prior to XRF analysis. Two types of discrete XRF sampling are utilized in the field. One type involves collecting a sample in a plastic bag, rough sieving it to remove organic debris and rocks, and homogenizing it by mixing in the bag.

Take the XRF reading by directly measuring through the sample bag. Take three measurements from each bag, shaking the bag between measurements. A measurement time of 15-30 seconds is recommended. Be consistent with sampling time for all samples collected. Once XRF measurements are complete, prepare a minimum of 10% of the samples for confirmation analysis by AA/ICP. It is imperative that the same sample utilized for XRF analysis be sent for the confirmation analysis; this is typically accomplished by splitting the volume of the original sample prepared, one half being sent for analysis to the lab and one half being archived.

A second method of discrete XRF sampling involves a more rigorous method of sample preparation. The first step in sample preparation is drying, either by air, in a conventional oven at 105°C, or with a moisture balance. Drying is a recommended step and is necessary based on moisture content of the soil. Use care when using a microwave oven or conventional oven for drying due to their potential to vaporize lead, arsenic and mercury, if present in samples. Not only does this lead to error, but it may be a health hazard. Small, air-circulating or moisture balance ovens are recommended. Proper respiratory protection should be worn.

Once dry, remove any visible organic debris and sieve the sample through a 20-mesh sieve. Fill a sample cup with the prepared sample and retain it for confirmation analysis. Settle contents in the sample cup by tapping; this will yield a more smooth, uniform surface for analysis. Cover the sample with polypropylene film (making certain there are no wrinkles in the film) and analyze it for 240 seconds. Shake the cup and analyze again. Repeat this procedure for a total of three readings on each sample. Record the individual results and calculate an average. Save the prepared sample cup. A minimum of 10% of the prepared sample cups should be sent for confirmational analysis by AA/ICP procedures.

2.8 CALCULATIONS

Mathematically model the matrix calibration for optimum linearity, as per the XRF operating instructions.

2.9 QUALITY ASSURANCE/ QUALITY CONTROL

There are a number of QA/QC measurements which must be utilized when performing XRF analysis.

- **Precision** is determined by repeated measurements of a low matrix calibration standard at the beginning of sampling activities, and then after every tenth sample. This sample is analyzed for the same time as the field samples. The precision objective for XRF should be ±20% relative standard deviation. A mid-range matrix calibration sample is also recommended to aid in determining instrument precision. This sample should be at or near the concentration level of interest. By running low-level calibration samples, gain changes and baseline drift can be monitored.

- **Accuracy** is best determined by using site-specific, low-, mid- and high-level calibration samples that are analyzed by AA/ICP.

- **Representativeness** is best determined by developing an adequate sampling scheme which characterizes the range of contaminants and matrix variability at the site. When the calibration samples accurately characterize the range of contaminant concentrations on site, the calibration model will be representative of the site.

- The question of **comparability** arises when XRF data are compared to AA or ICP data obtained from a sample digestion procedure. XRF data may not be comparable to data obtained by AA or ICP. The portable XRF should be used as a screening tool in conjunction with these more rigorous analytical methods, especially with the acid digestion method procedures. Using AA/ICP, samples should be prepared in the same manner as those for XRF analysis.

- **Completeness** is determined on a site-specific basis and is a measure of the desired number of samples analyzed versus the actual number of samples analyzed.

- **Replicates** are recommended at a minimum rate of 5-10%. Replicate samples should be prepared independently of other samples and go through the same sample preparation procedure. Replicates are a check on homogeneity of the sample matrix, consistency of sample preparation, and precision of the analysis.

- **Confirmation samples** are recommended at a minimum rate of 10%. Ideally, the sample that was analyzed by XRF should be the same sample that is sent for AA/ICP confirmation analysis. When confirming an in situ analysis, collect a sample from a six-inch by six-inch area for both an XRF measurement and a confirmation analysis. The correlation factor between XRF and AA/ICP data should be 0.7 or greater.

- **Performance evaluation (PE) samples** are another possible QC mechanism for checking AA/ICP analysis, but are not typically applicable to XRF analysis due to a dissimilar matrix. If the site matrix does not match the PE matrix, the user should not utilize the PE samples.

1.10 DATA VALIDATION

This section is not applicable to this SOP.

1.11 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and site-specific health and safety procedures.

3.0 PHOTOIONIZATION DETECTOR (HNU): SOP #2056

3.1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedure for using a photoionization detector (PID). The PID is a portable, non-specific, vapor/gas detector employing the principle of photoionization to detect a variety of chemical compounds, both organic and inorganic, in air. This procedure is applicable to the HNU-PI 101.

3.2 METHOD SUMMARY

The PID is a useful general survey instrument at hazardous waste sites. A PID detects and measures real-time concentrations of many organic and inorganic vapors in air. A PID is similar to a flame ionization detector (FID) in application; however, the PID has somewhat broader capabilities as it can detect certain inorganic vapors. Conversely, the PID is unable to respond to certain low molecular weight hydrocarbons, such as methane and ethane, which are readily detected by FID instruments.

The PID employs the principal of photoionization. The analyzer responds to most vapors with an ionization potential less than, or equal to, that supplied by the detector, which is an ultraviolet (UV) lamp. Photoionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and form a positive ion. This action occurs when the ionization potential of the molecule in electron volts (eV) is less than the energy of the photon. The sensor is housed in a probe and consists of a sealed ultraviolet light source that emits photons with an energy level high enough to ionize many trace organics, but not enough to ionize the major components of air. A chamber exposed to the light source contains a pair of electrodes, one bias electrode and one collector electrode. When a positive potential is applied to the bias electrode, a field is created in the chamber. Ions formed by the adsorption of photons are driven to the collector electrode. The current produced is then measured and the corresponding concentration is directly displayed on a meter in units above background. Several probes are available for the PID, each having a different source and a different ionization potential. The selection of the appropriate probe is essential to obtain useful field results. Though it can be calibrated to a particular compound, the instrument cannot distinguish between detectable compounds in a mixture of gases, and therefore produces an integrated response to the mixture.

Three probes, each containing a different UV light source, can be used with the HNU. Energies are 9.5, 10.2, and 11.7 electron volts (eV). All three detect many aromatic and large molecule hydrocarbons. In addition, the 10.2 eV and 11.7 eV probes detect some smaller organic molecules and some halogenated hydrocarbons. The 10.2 eV probe is the most useful for environmental response work, as it is more durable than the 11.7 eV probe and detects more compounds than the 9.5 eV probe.

Gases with ionization potentials near to, or less than, that of the lamp will be ionized, and thus be detected and measured by the analyzer. Gases with an ionization potential higher than that of the lamp will not be detected. The ionization potentials for various atoms, molecules, and compounds are given in Appendix B. The ionization potential of the major components of air (oxygen, nitrogen, and carbon dioxide) range from about 12.0 eV to about 15.6 eV, so are not ionized by any of the three lamps.

Ionization sensitivity for a number of chemical groupings when exposed to photons from a 10.2 eV lamp is illustrated in Table 2. Applications of each probe are included in Table 3.

While the HNU is primarily used as a quantitative instrument, it can also be used to detect certain contaminants, or at least narrow the range of possibilities. Noting instrument response to a contaminant source with different probes eliminates some contaminants from consideration. For instance, a compound's ionization potential may be such that the 9.5 eV probe produces no response, but the 10.2 eV and 11.7 eV probes do elicit a response.

Table 2: Relative Photoionization Sensitivities for Various Gases

Chemical Group	Relative Sensitivity	Examples
Aromatic	10	benzene, toluene, styrene
Aliphatic Amine	10	diethylamine
Chlorinated Unsaturated	5 - 9	vinyl chloride, vinylidene chloride, trichloroethylene
Carbonyl	5 - 7	MEK, MIBK, acetone, cyclohexanone
Unsaturated	3 - 5	acrolein, propylene, cyclohexanone, allyl alcohol
Sulfide	3 - 5	hydrogen sulfide, methyl mercaptan
Paraffin (C_5-C_7)	1 - 3	pentane, hexane, heptane
Ammonia	0.3	
Paraffin (C_1-C_4)	0	methane, ethane

Note: Relative sensitivity is the actual HNU meter reading observed when measuring a 10 ppm gas concentration of the listed chemical, using the 10.2 eV probe (calibrated for 10 ppm of benzene) and a span setting of 9.8 (for direct reading of benzene).

3.3 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

This section is not applicable to this SOP.

3.4 INTERFERENCES AND POTENTIAL PROBLEMS

3.4.1 PID Instrument Limitations

- The PID is a non-specific, total vapor detector. It cannot be used to identify unknown substances; it can only quantify them.

- The PID must be calibrated to respond to benzene using isobutylene calibration gas which has been analyzed and compared to a known benzene standard.

- The PID does not respond to certain low molecular weight hydrocarbons, such as methane and ethane, and does not detect a compound if the probe has a lower energy than the compound's ionization potential. Methane absorbs ultraviolet lamp energy. One-half percent methane will result in a 30 percent reduction in detector sensitivity and 5 percent methane will yield a 90 percent decrease in detector sensitivity.

- Certain toxic gases and vapors, such as carbon tetrachloride and hydrogen cyanide, have high ionization potentials and cannot be detected with a PID.

- Certain models of PID instruments are not intrinsically safe. The HNU-PI 101 PID is not designed for continuous use in potentially flammable or combustible atmospheres. Therefore, a PID should be used in conjunction with a Combustible Gas Indicator.

Table 3: Typical Applications of Interchangeable Probes

Compound	Ionization Potential (eV)	Relative Sensitivity	
p-xylene	8.44	0.10	0.104
p-chlorotoluene	8.70	0.09	0.112
toluene	8.82	0.09	0.112
o-chlorotoluene	8.83	0.075	0.112
ethyl acetate	9.19	0.075	0.112
benzene	9.24	0.10	0.10
methyl mercaptan	9.24	0.10	0.072
pyridine	9.32	0.075	0.122
allyl alcohol	9.67	0.10	0.112
crotonaldehyde	9.88	0.075	0.104
amyl alcohol	9.80	0.09	0.116
cyclohexane	9.88	0.075	0.104
vinyl chloride	9.95	0.085	0.112
butanol	10.94	0.09	0.176
ammonia	10.15	0.06	0.160
acetic acid	10.37	0.04	0.560
ethylene	10.52	0.0	0.320
ethylene oxide	10.56	0.0	0.298

Note: Relative sensitivity equals the response with the 9.5 eV probe or the 11.7 eV probe divided by the response with the 10.2 eV probe.

- Electrical power lines, radiotransmissions or power transformers may cause interference with the instrument and thus cause measurement errors.

- Winds and high humidity will affect measurement readings. The HNU may become unusable under foggy or humid conditions, when condensation occurs on the lamp. This is indicated by the needle dropping below zero, or a slow constant climb on the read-out dial.

- The lamp window must be periodically cleaned to ensure the maximum transmission of the ionizing protons into the detector chamber.

- The 11.7 eV lamp window is a type of fluoride crystal which is hygroscopic and

will absorb water vapor from the sample stream. In high humidity applications, the lamp should be cleaned with an oil-free, chlorinated hydrocarbon, or freon on a daily basis.

- The HNU measures concentrations from about 1-2000 ppm, although the response is not linear over this entire range. For example, the response to benzene is linear from about 0-600 units above background. This means the HNU reads a true concentration of benzene only between 0 and 600. Greater concentrations are detected at a lower level than the true value.

- Do not use this instrument for head space analysis where liquids can inadvertently be drawn into the probe.

3.4.2 Regulatory Limitations

- Transport of calibration gas cylinders by passenger and cargo aircraft must comply with the U.S. Code of Federal Regulations, 49 CFR Parts 100-177. A typical calibration gas included with a PID is isobutylene. It is classified as a non-flammable gas, UN #1556 and the proper shipping name is Compressed Gas. It must be shipped by cargo aircraft only.

3.5 EQUIPMENT/APPARATUS

- PID (HNU)
- operating manual
- probes: 9.5 eV, 10.2 eV, or 11.7 eV
- battery charger for PID
- spare batteries
- jeweler's screwdriver for adjustments
- Tygon tubing
- NBS traceable calibration gas (type)
- "T" valve for calibration
- field data forms
- intake assembly extension
- strap for carrying PID
- Teflon tubing for downhole measurements
- plastic bags for protecting the PID from moisture and dirt

Note: This instrument may be kept on continuous charge without battery damage.

3.6 REAGENTS

- isobutylene standards for calibration
- methanol for cleaning ionization chamber (GC grade)
- mild soap solution for cleaning unit surfaces
- specific gas standards when calibrating to a specific compound
- light source cleaning compound Cat No. PA101534-A1 (for 9.5 and 10.2 eV lamps only)
- oil-free, chlorinated solvent, or freon for cleaning the 11.7 eV lamp

The HNU is calibrated according to the operations manual, using isobutylene as the calibration standard. Also, refer to the operations manual for alternate calibration to a specific compound. Current HNU manuals contain an error with the isobutylene response factor for the 10.2 eV lamp. The manual indicates 7.0 whereas the correct value is approximately 5.5.

3.7 PROCEDURES

3.7.1 Start-up

1. Check to ensure the proper operation of the PID, as appropriate, using the equipment checklist provided in Sections 3.5 and 3.6 and the steps listed below.

2. Allow the temperature of the unit to equilibrate to its surrounding (about 5 minutes).

3. Attach the probe to the read out unit. Match the alignment key, then twist the connector clockwise until a distinct locking is felt.

4. Turn the *Function* switch to the battery check position. Check to ensure that the indicator reads within or beyond the green battery arc on the scale plate. If the indicator is below the green arc, or if the red LED comes on, the battery must be charged prior to using.

5. To zero the instrument, turn the *Function* switch to the Standby position and rotate the *Zero Potentiometer* until the meter reads zero. Wait 15-20 seconds to ensure that the zero adjustment is stable. If not, then readjust.

6. Check to see that the *Span Potentiometer* is set at the appropriate setting for the probe being used.

7. Set the *Function* switch to the desired range.

8. Listen for the fan operation to verify fan function.

9. Look for ultraviolet light source in the probe to verify function. Do not look at this light source from closer than 6 inches with unprotected eyes; observe briefly.

10. Prior to survey, check instrument with an organic point source such as a Magic Marker to verify instrument function.

11. Routinely throughout the day, verify the remaining useful battery life by turning the *Function* switch to BATT. Schedule the instrument's use accordingly.

3.7.2 Field Operation

Field Calibration

1. Follow the startup procedure in Section 3.7.1.

2. If the PID does not start up, check out, or calibrate properly, the instrument should not be used. Under no circumstances should work requiring PID air monitoring be done without a properly functioning instrument.

3. Set the *Function* switch to the range setting for the concentration of the calibration gas.

4. Attach a regulator to a disposable cylinder of calibration gas. Connect the regulator to the probe of the HNU with a piece of clean Tygon tubing. Open the valve on the regulator.

5. The latest technical information from HNU is that the external *Span Adjustment Control* should be used to calibrate the instrument. That is, if you are calibrating an HNU to a 60 ppm isobutylene as benzene standard with the unit set at 9.8, and the HNU reads 50 ppm, the external *Span Adjustment Control* should be adjusted to a lower number setting until the correct reading has been obtained. The lower the number on the Span Adjustment Control the greater the instrument sensitivity.

6. Record the following information in the site logbook: the instrument ID number (EPA decal or serial number if the instrument is a rental), the initial and final span settings, the date and time, concentration and type of calibration gas used, and the name of the person who calibrated the instrument.

7. Record the calibration data in the field.

8. In some field applications, with the exception of the probe's inlet and exhaust, the PID should be wrapped in clear plastic to prevent it from becoming contaminated and to prevent water from getting inside in the event of precipitation.

Operation

1. Record all readings in the site logbook. Readings should be recorded as "units above background," not ppm.

2. As with any field instrument, accurate results depend on the operator being completely familiar with the operator's manual. In order to obtain accurate results, follow the instructions in the operating manual explicitly.

3. Position the probe assembly close to the area to be monitored because the low sampling rate allows for only very localized readings. Under no circumstances should the probe tip assembly be immersed in fluid.

4. While taking care not to expose the PID to excessive moisture, dirt, or contamination, monitor the work activity as specified in the site health and safety plan. Conduct the PID survey at a slow to moderate rate and the intake assembly (the probe) should slowly sweep from side to side. There is a 3 to 5

second delay in read-out, depending upon the instrument's sensitivity to the contaminant.

5. During drilling activities, perform PID monitoring at regular intervals downhole, at the headspace, and in the breathing zone. In cases with elevated organic vapor levels, monitor in the breathing zone during actual drilling. When the activity being monitored is not drilling, readings should emphasize breathing zone conditions.

6. When the activity is completed, or at the end of the day, carefully clean the outside of the PID with a damp disposable towel to remove any visible dirt. Check calibration again before storing. Return the PID to a secure area and place on charge.

3.7.3 Post Operation

1. Turn *Function* switch to "off."

2. Place the instrument on the charger. When on charge, the probe must be connected to the readout unit to ensure charging.

3. Complete logbook entries, verify the accuracy of entries, and sign/initial all pages. Following completion of a series of "0" readings, verify the instrument is working.

4. Check the equipment, repair or replace damaged equipment, and charge the batteries.

3.8 CALCULATIONS

The HNU is a direct reading instrument. Readings are interpreted as units above background, rather than ppm.

3.9 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance activities which apply to the implementation of these procedures. However, the following QA procedures apply:

- All data must be documented on field data sheets or within site logbooks.

- All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and must be documented.

3.10 DATA VALIDATION

This section is not applicable to this SOP.

3.11 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and site-specific health and safety practices.

The HNU-PI 101 is certified for use in Class 1, Division 2, Groups A, B, C, and D.

4.0 PHOTOVAC 10A10 PORTABLE GAS CHROMATOGRAPH OPERATION: SOP #2107

4.1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the use, calibration, and maintenance of the Photovac 10A10 portable gas chromatograph. The Photovac 10A10 gas chromatograph is used for field and laboratory analysis of air, soil gas, and water/soil headspace samples. Chlorinated and non-chlorinated alkenes and aromatic hydrocarbons down to the 1 to 20 part per billion (ppb) range can be detected.

4.2 METHOD SUMMARY

The Photovac 10A10 is a battery/AC-operated photoionization detector (PID) portable gas chromatograph. It is a field instrument capable of monitoring for many organic vapors using an ultraviolet light source and a photoionization detector. The samples are introduced into the 10A10 via gas-tight syringes. Gaseous contaminants are ionized as they emerge from the column. The ions are then attracted to an oppositely charged electrode, which causes a current and sends an electronic signal to a strip chart recorder or, alternately, to an integrator/plotter system.

4.3 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

This section is not applicable to this SOP.

4.4 INTERFERENCES AND POTENTIAL PROBLEMS

- This instrument should not be exposed to precipitation or high humidity.
- The instrument works best in a stable, temperature-controlled environment.
- Liquids should not be injected into this instrument.
- Readings can only be reported relative to retention times of the calibration standard used.
- Combustion fumes can contaminate the columns.
- High concentrations of short chain alkanes and alkenes in samples may interfere with the resolution and detector sensitivity of early-eluting chlorinated alkenes, and aromatic compounds.
- Since the Photovac is a GC, the target compounds are identified by their retention times (RTs). If the RT of the sample peak(s) matches the RT of the standard peak(s), they are assumed to be identical. If any non-target compound has the same RT, it can be misidentified as a target compound.

4.5 EQUIPMENT/APPARATUS

- Photovac 10A10 gas chromatograph, with manual and power cord
- extra source lamp
- Photovac lamp tuning screwdriver
- extra columns/fittings
- ultrazero air carrier gas
- two-stage regulator, with quick-connect fitting
- 1 flowmeter per Photovac, either bubble-meter, rotameter, or Gilibrator
- septa, 6 mm diameter
- syringes, gas-tight, 10 μL to 1 mL
- VOA vials filled with activated charcoal, for syringe cleaning
- integrator or strip-chart recorder, with appropriate connections
- labels
- extra Photovac integrator pens
- extra Photovac integrator paper
- tools -- large adjustable wrench, wrenches (5/16 inch to 9/16 inch), screwdrivers (flat and Phillips head), needle-nose pliers, jeweler's screwdrivers, Allen wrenches
- duct tape

- Teflon tape
- power strip
- snoop
- Kimwipes (or similar lint/static free wipe)
- Pelican cases (or equivalent)

4.6 REAGENTS

- carrier gas cylinder (compressed ultrazero air, 0.1 ppm total hydrocarbons).

- headspace calibration standards (Supelco A and B or equivalent).

- certified gas calibration standards with a ± 2% level of accuracy (from Scott Speciality Gas, Matheson Gas, or other reliable source).

4.7 PROCEDURES

4.7.1 Laboratory Operation

1. Attach the carrier gas (air) cylinder to the 10A10, and, via the second stage of the dual-stage regulator, deliver a maximum of 40 psi.

2. The flow rate will vary according to the target compounds in question and the column used. Adjust the carrier gas flow using the knurled knob to the left of the 10A10, labeled Column 1 or Column 2. The flow is measured by attaching a flowmeter to the vent port at the top left of the unit. Once the flow is set, the PID will stabilize after approximately 1/2 hour of warm up time. Set the output at 10 mV using the offset knob in the center of the unit.

3. Attach an interface cable from the output lead on the 10A10 to a strip chart recorder, or preferably, a plotter-integrator such as the Hewlett Packard 3396A. The voltage input and/or attenuation is selected on the chart or integrator to keep peaks on scale. Check that the electrical controls are set as follows:

   - power switch to "off"

   - charge switch to "off"

   - attenuation switch to 100 (lowest sensitivity)

   - offset dial to zero

   - chart recorder connected to the coaxial output connector

   - chart recorder set to 100 mV (full scale) and chart speed to 1 cm/min

   - power cord plugged into the panel socket (the red AC indicator light will come on)

   The instrument is now in its power down condition and is ready for starting.

4. With the chart recorder off, switch on the power switch. The red *Source Off* indicator will light and stay on for up to 5 minutes. During this time the lamp-start sequence is being automatically initiated.

5. As soon as the *Source Off* light is extinguished, the meter shows a high reading which should fall as conditions in the photoionizing chamber stabilize.

6. Establish an acceptable base line on the chart recorder.

The instrument is now ready for calibration.

4.7.2 Calibration

Refer to Table B, Appendix B, for the calibration and maintenance schedule. Photovac Incorporated conducts an instrument calibration and includes the chromatogram as a component of that instrument's instruction manual. A check of the instrument's performance can be accomplished by duplicating the factory calibration check and comparing the results. The procedure is as follows:

1. Completely flush a clean 1-L sample bottle (or a clean 1-L Tedlar bag fitted with a septum cap) with good quality bottled air.

2. Using the factory calibration data sheet, calculate the required amounts of each calibration compound required to generate an air standard (with a total volume of 1 liter) which is identical to that run by Photovac in the factory calibration.

3. Using an appropriate volume gas-tight syringe, aspirate the required amount of each

compound from the headspace of the storage bottles at room temperature, and inject it into the purged 1-L sample bottle (or Tedlar bag). Be careful to fully flush the syringe with clean air before injecting a new compound.

4. Allow 10 minutes for the standard to equilibrate.

5. Using a clean 100 μl gas-tight syringe, aspirate the required injection volume from the 1-L standard. With a crisp and snappy action, inject the standard into the proper "injection port" of the Photovac 10A10.

6. Start and mark the strip chart recorder. The resulting chromatogram should be similar to the factory calibration chromatogram, under similar conditions.

7. A simple calibration curve can be constructed by injecting the same volume of several standards with varying concentration levels of the target compounds. Alternatively, a calibration curve can also be constructed by injecting various volumes (10 - 1000 μL) of the same standard. In this case, the response of the standards and samples should be normalized to one injection volume. Both standards and samples present in Tedlar bags can be diluted in the field.

4.7.3 Field Operation

1. Prior to any field analyses, check to ensure that the instrument is operational and clean. Remove closure fittings on the *Detector Out* port. Closure fittings may have been engaged to prevent static contamination.

2. Check that the carrier gas supply is adequate (charge supply is 1800 PSI and should last up to approximately 3 days, depending on carrier flow rates).

3. Set the pressure regulator to zero (fully counterclockwise) and turn on the main valve of the lecture bottle.

4. Slowly turn the regulator control clockwise until air begins to escape from the quick-disconnect connection. Allow the line to purge for 10 seconds.

5. Plug the quick-disconnect fitting into the free *Carrier in* port. Shut off and disconnect the laboratory air supply. Adjust the lecture bottle regulator to 40 psig. Set the required flow rate as described previously using a bubble meter, calibrated rotameter, or Gilibrator.

6. With the instrument in the "power down" mode, disconnect the AC power supply. This automatically switches the instrument to battery power. The instrument is now completely self-contained, and, with a battery powered recorder, may be taken into the field. Check the battery charge on the Photovac.

7. The instrument is now ready to be run through the start-up procedures described under Laboratory Operation, parts 4-8 of the manual.

8. If there is a significant change in ambient temperature when the instrument is moved from one place to another, the column will require time to stabilize thermally. At higher sensitivities, a non-thermally stabilized column will manifest itself as baseline drift.

9. For troubleshooting information, refer to Appendix B.

4.7.4 Shut Down

1. Turn the power switch to "off."

2. Reduce the carrier gas flow to 2-5 cm^3/min.

3. Place the instrument on low charge while on the bench and maintain it as described in Table F and Section 4.7.6 below.

4. Unplug the unit except when charging batteries.

4.8 CALCULATIONS

4.8.1 Calibration Curve

A calibration curve of at least three concentrations must be constructed for each target compound. A straight line equation in the form of $y = (m)(x)+b$ (where: x = concentration, y = area counts, m = slope and b = the intercept) is fit to the standards raw data. The (y), or the unknown concentration for the sample, is determined from the above straight line equation. Non-linear data is indicative

of detector response range limitations.

Alternatively, sample concentration can be calculated as shown below:

$$[Sample] = [Std] \frac{A_1}{A_2} \cdot \frac{V_2}{V_1}$$

where:

sample	=	concentration of sample (ppb or ppm)
A_1	=	peak area of sample (volts x seconds)
A_2	=	peak area of standard (volts x seconds)
V_1	=	injection volume of sample (μL)
V_2	=	injection volume of standard (μL)
std	=	concentration (ppb or ppm)

4.8.2 Standard Response Generation/Duplication of Factory Calibration Data

If appropriate gas standard mixtures are not available, gas standards can be made using the headspace from 40-mL VOA bottles, with Teflon-lined septa screw caps, partially filled with the desired neat volatile liquid. Factory instrument response is generally determined using the following three compounds:

Compound	P_{vap} @ 20° C
methylene chloride	347 mm Hg
n-hexane	126 mm Hg
benzene	74 mm Hg

These compounds are toxic and should be stored and worked with under a hood. The general formula for preparing a standard from the headspace above a volatile liquid is:

$$V_{HS} = \frac{760\ (C)\ (V)}{P_{vap}}$$

where:

V_{HS}	=	volume of headspace (μL)
P_{VAP}	=	vapor pressure of liquid (mm HG)*
C	=	desired concentration (ppm)
V	=	volume of standard vessel (liters)

* Use appropriate tables to determine compound vapor pressure if working environment is not 20° C.

A determined volume of neat liquid headspace may be introduced to the standard vessel through the septa if using a Tedlar bag is used with the appropriate fitting. Bags or vessels used should be labelled with content concentrations, date, and time of preparation.

4.9 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance activities which apply to the operation of the Photovac. However, all instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling or operation and they must be documented.

4.10 DATA VALIDATION

This section is not applicable to this SOP.

4.11 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and site-specific health and safety practices.

5.0 PHOTOVAC 10S50, 10S55, AND 10S70 GAS CHROMATOGRAPH OPERATION: SOP #2108

5.1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) pertains to the use, calibration, and maintenance of the Photovac 10S series portable gas chromatographs. The 10S series gas chromatographs are used for field and laboratory analysis of air, soil gas, and water and soil headspace. It tests for chlorinated and non-chlorinated, alkene and aromatic, compounds with detection limits of 1-5 ppb (parts per billion) for headspace analysis and 10-50 ppb for soil gas analysis.

5.2 METHOD SUMMARY

The Photovac 10S series are battery/AC operated, portable gas chromatographs with photoionization detectors. They are field/laboratory instruments capable of screening for many organic vapors using an ultraviolet light source and photoionization detector. Gaseous contaminants are ionized as they emerge from the column. The ions are then attracted to an oppositely charged electrode which causes a current and sends an electronic signal to the Photovac internal microprocessor or optional integration device. Refer to ERT SOP #2109, Photovac GC Analysis for Air, Soil Gas, Water, and Soil, for additional information.

5.3 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

This section is not applicable to this SOP.

5.4 INTERFERENCES AND POTENTIAL PROBLEMS

- These instruments should not be exposed to precipitation or high humidity.

- The instruments are best utilized in stable, temperature-controlled environments (even when using the internal temperature-controlled oven assembly, which may only reduce the effect of external atmospheric temperature variances). When used directly in the field, it is best to maintain constant temperatures to avoid the fluctuating retention times which may occur with changing temperatures.

- Readings can only be reported relative to retention times of the calibration standard used.

- Combustion fumes can contaminate the column.

- High concentrations of short chain alkanes and alkenes in samples may interfere with the resolution and detector sensitivity of early-eluting chlorinated alkenes and aromatic compounds.

- Since the Photovac is a GC, the target compounds are identified by their retention times (RTs). If the RT of the sample peak(s) matches the RT of the standard peak(s), they are assumed to be identical. If any non-target compound has the same RT, it can be misidentified as a target compound.

5.5 EQUIPMENT/APPARATUS

5.5.1 Equipment List

- Photovac 10S series gas chromatograph, with manual and power cord
- extra source lamp
- Photovac lamp tuning screwdriver
- extra columns/fittings
- ultrazero air carrier gas
- two-stage regulator, with quick-connect fitting
- one flowmeter per Photovac, either bubble-meter, rotameter, or Gilibrator
- septa, 6-mm diameter
- syringes, gas-tight, 10-μL to 1-mL
- VOA vials filled with activated charcoal, for syringe cleaning
- extra Photovac integrator pens

- extra Photovac integrator paper
- labels
- tools -- large adjustable wrench, wrenches (5/16 inch to 9/16 inch), screwdrivers (flat head and Phillips head), needle-nose pliers, jeweler's screwdrivers, Allen wrenches
- duct tape
- Teflon tape
- power strip
- snoop
- Kimwipes (or similar lint/static free wipes)
- Pelican cases

5.5.2 Carrier Gas Supply System Options

In most applications, the carrier gas used is ultra-zero compressed air (<0.1 ppm THC).

Use of the Internal Reservoir as Carrier Gas Supply

To recharge the internal reservoir, a special (optional) device known as the High Pressure Filling Station is needed. This device consists of the high pressure connection (normally male, left-hand thread) for cylinder attachment followed by a two-way valve. The two-way valve can be positioned to deliver gas from the cylinder to a long flexible hose and then to the *Refill* receptacle located on the rear right of the 10S50 panel. Alternatively, the valve can be turned to release high pressure gas held in the hose, after filling. A pressure relief valve is provided for safety at the upper end of the flexible hose. This is set at 1700 psi. A flow restricter is also incorporated in line with the hose, to limit the escape rate of gas. **Under no circumstances should the high pressure filling station be modified or disassembled by the user.** In the event of any problems, the unit must be returned to Photovac for repair or replacement.

Filling procedure is as follows:

1. Attach the high pressure fitting to the gas cylinder and turn the valve handle so that it points away from the cylinder.

2. Open the cylinder valve and check for leaks.

3. Now turn the filling station valve so that it points toward the cylinder. A steady flow of gas will be heard escaping from the end of the flexible hose; this purges the hose of any impurities.

4. Return the filling station valve to its previous position.

5. Place the Photovac on a sturdy, flat surface within easy reach of the flexible receptacle; press in firmly until a click is heard.

6. Turn the filling station valve until it again points toward the cylinder and carefully watch the *Contents* gauge on the Photovac as the needle climbs.

7. As the needle reaches approximately 1600 psi, the pressure relief valve on the high pressure filling station should prevent further increase. The pressure indicated on the *Contents* gauge must not exceed 1800 psi; switch the pressure relief valve before this occurs. Switching the valve allows high pressure gas trapped in the flexible hose to escape, while a check valve in the Photovac prevents the reservoir contents from escaping.

8. After relieving the pressure in the hose, it can be removed from the *Refill* receptacle by pulling upward on the knurled collar and extracting the fitting.

Use of External Tank for Carrier Gas Supply

Whenever possible, connect the Photovac to an external air cylinder to ensure a longer, more stable carrier gas supply. A high quality, two-stage regulator with output at 40 psi is required. Connection between this regulator and the Photovac is made using 1/8-inch Teflon tubing with a male quick-connect fitting attached to one end.

5.6 REAGENTS

- carrier gas, ultrazero air (<0.1 ppm total hydrocarbons)
- appropriate calibration standards (gas or liquid)

5.7 PROCEDURES

5.7.1 Shipping

The Photovac is initially shipped to the user in a cardboard box provided by Photovac International. Repeated shipping of Photovacs to field locations (in these boxes) has resulted in occasional electrical and mechanical problems. Shipping Photovacs in a more rugged container, such as the Pelican King Size Case (Orr Safety Equipment Co.), or equivalent is recommended. The Photovac can be left in this case while in use to prevent static electricity and to provide thermal stability.

5.7.2 Pre-Operational Checkout

1. Check the instrument for any obvious damage. Plug the power cord into an AC power source, if available. Remove any closure fittings which may have been affixed to the *Detector Out*, *Aux Out*, and *Cal Out* ports in order to minimize contamination.

2. Raise the computer module. Check that all compression fittings associated with the columns (the pre-column and analytical column) and all valves which are subject to carrier gas flow, are **finger** tight. **Do not overtighten.** Fittings may loosen in transit. Check which injection port is connected to the columns (only one may be used at a time). Normally, the Photovac is supplied with an SE-30, 5% packed, 6-inch pre-column and 4-feet of analytical column unless otherwise specified (see Figure 1, Appendix B). If a capillary column (usually CP Sil-5, blue, equivalent to the properties of the SE-30) with oven temperature control module is being used, make sure the oven ribbon connection is tight. Attach the external 12V battery with adapter to the BNC connector (labeled *ext DC*) on the left side of the Photovac top panel. Adjust the oven module temperature to at least 5° greater (usually $\geq$ 40°C) than internal operating temperature. Close the computer module. Allow at least 40 minutes for oven temperature stabilization.

3. Check that the septum is new. Make sure the septum retainer is tight. **Do not overtighten.**

4. Engage the carrier gas flow (ultrazero air). Carrier gas can be introduced either by connecting an external low pressure source (attached by a Quick-Connect to the *External Carrier In* receptacle) or by recharging the Photovac internal high pressure refill attachment. If operating from an external cylinder, a clean, GC grade, two-stage regulator should be used. Set delivery pressure to a maximum of 40 psi. One-eighth inch Teflon lines, brass or stainless steel swagelock fittings and a quick-connect are used to attach the external carrier gas to the Photovac GC. Lines are purged 5-10 seconds with ultrazero air carrier gas before connection to the Photovac *External Carrier* gas inlet.

5.7.3 Carrier Gas Flow Rate Adjustment

1. Set carrier gas flow rates by attaching appropriate flow rate indicators (calibrated rotameters, Gilibrators, bubble meters, etc.) to the *Detector Out* port (red dial) and adjusting the appropriate needle valves to give a flow of 40-50 cm^3/min for a packed column and 10-15 cm^3/min for a capillary column.

2. After flow rate through the detector is set, turn on the instrument to warm it up while fine tuning the desired flow rates. For at least one hour prior to use, purge the instrument (column/valving/detectors) of residual contamination encountered in transit by carrier gas flow.

5.7.4 Photovac Settings

1. Press <ON> to turn on the instrument. "Lamp not ready" appears on the LCD. It takes approximately 1-2 minutes for the lamp to light. **Do not** allow more than 3 minutes for the lamp to light, or electronic problems can occur.

2. To enter the date and time, press <USE> in the *Library* section on the top control panel (there are four libraries which may be used). Then press <ENTER>. The LCD will prompt for entry of the "date" and "time."

3. Obtain a listing of compounds contained in the library selected for use by pressing <LIST>, then <ENTER>. If any compounds are not needed, they may be deleted by pressing <EDIT>. You will be prompted by the LCD

to enter the ID of the compound in the library you wish to edit, and the ID# as stated on the printout. Press <CLEAR>, then <ENTER>. That compound is then removed from the library. Repeat the edit sequence until all undesired compounds have been removed from the library selected for use.

4. Whenever the Photovac is turned off and then on, it reverts to the default gain setting of 2. A gain setting of at least 50 is necessary for detection of most common pollutants (i.e., aromatics and chlorinated alkenes) down to a 5-20 ppb range using a 100-250 μL sample injection volume. Since this is a non-destructive detector, small sample injection volumes are desirable to minimize analyst exposure. Aside from safety factors, injection volumes greater than 1 mL are not recommended due to column and detection volume capacity. Peak resolution and quantitation may be distorted by large injection volumes. To adjust the gain setting, press <GAIN> in the *Set Up* section of the Photovac top panel. Increase the gain setting to 50 by depressing the up arrow key.

   When "50" appears on the LCD, press <ENTER>. Perform a pre-operational checkout (Section 5.7.2) to fine tune carrier flow, if necessary. Otherwise, proceed with instrument settings.

5. To set the chart recorder, press <CHART>. Using arrow keys, obtain LCD readout "Chart Recorder on with Baseline." Press <ENTER>. The baseline mode is recommended because it allows the operator to observe integration parameters and make adjustments when necessary. "Speed? cm/min" appears on the LCD. Use arrow keys to obtain 0.5 cm/min on the LCD, and press <ENTER>.

6. To enter peak integration parameters, press <SENS>. When prompted by the LCD, using the arrow keys and <ENTER> adjust settings to:

   UPSLOPE: 18
   DOWNSLOPE: 14
   PW @ 4: 6

   "Upslope" and "downslope" refer to the change in baseline slope necessary for the integrator to recognize a beginning and end of a peak. The downslope is kept lower than the upslope so the tails of peaks are fully integrated. "PW@4" refers to the peak width in seconds at 4 min. This value is proportionally adjusted by the integrator for retention times other than 4 minutes.

7. The peak window settings are pertinent only if using the internal Photovac microprocessor's library. Peak identification in gas chromatography is based on retention time (RT) matches with the standards used. When operating at "ambient" temperature, fluctuations in external temperature will affect compound retention times, making peak identification difficult and questionable. It is for this reason that the Photovac should be operated in a stable temperature environment. Press <WINDO>, using the arrow keys and <ENTER> to adjust the settings for the packed column to 10 seconds and for the capillary column to 5 seconds.

   The internal microprocessor applies an equation allowing for more extensive fluctuations in RTs of later eluting compounds relative to early eluting compounds, using the window setting selected.

8. The area of rejection setting is used to eliminate the reporting of "noise" peaks on the report printed at the end of each run. It designates the minimum peak area (volt - seconds) recognized by the integration system. A setting of 100 mVs is usually sufficient for detection of aromatics and chlorinated alkenes at the 5-20 ppb level at a gain setting of 50.

   Press <AREA>. Press the arrow keys until 100 mVs appears on the LCD. Press <ENTER>.

9. Events (Manual Injection)

   - Manual injection operation of the Photovac 10S series with serial flow only involves EVENT (valve actuators) 1 (a pump, with audible sound used only for injection timing). EVENT 1, the pump timer, is set for a recommended maximum of 2 seconds.

- Press <EVENT>. When prompted by the LCD readout, make the following entries:

EVENT #	ON (Sec)	OFF (Sec)
1	5	7
2	0	0
3	0	0
4	0	0
5	0	0
6	0	0
7	0	0
8	0	0

- Pressing <STATUS/TEST>, then <ENTER> produces a hard copy of the events just entered to check for accuracy of entries and to document analytical procedures.

10. The Photovac GC analysis run time (length of time peaks are recognized for integration by the internal microprocessor) is set using the *Cycle* key. Press <CYCLE>. The LCD will prompt you for "Timer Delay (sec)." The number of seconds entered (by the numeric keys) will be the length of time between pressing the start key and the start of the chart record (i.e., the zero reference point for all peak retention times). This value should normally coincide with the point at which the sample is injected (i.e., the EVENT-1 "off" time). Type "7," and press <ENTER>.

11. "Analysis Time" will appear on the LCD readout. Using the numeric key pad, type "3000," and press <ENTER>. This can be shortened later. The longest analysis time possible with the Photovac is 3267 seconds (54 minutes).

12. "Cycle Time" appears on the LCD. Type "0" and press <ENTER>.

13. Perform a baseline check for Photovac operational readiness. To determine run time progression, press the up arrow key. For operational readiness, runs need only be 600-700 seconds. An initial negative baseline indicates the detector is still "warming up." An elevated or irregular baseline, after proper flow adjustments, indicates possible contamination which may require additional purging time. After a suitable baseline has been obtained, the instrument is ready for calibration.

5.7.5 Calibration

Refer to Table B, Appendix B, for the calibration and maintenance schedule. Photovac Incorporated conducts an instrument calibration and includes the chromatogram as a component of the instruction manual. Check the instrument's performance by duplicating the factory calibration check and comparing the results.

1. Take a clean 1-L sample bottle or a clean 1-L Tedlar bag fitted with a septum cap, and completely flush with a good quality bottled air.

2. Using the factory calibration data sheet, calculate the required amounts of each calibration compound required to generate an air standard (with a total volume of 1 liter) identical to that run by Photovac in the factory calibration. Refer to section 7.0 in the Photovac manual (titled Calculations) if a suitable gas standard mixture is not available.

3. Using an appropriate volume gas-tight syringe, aspirate the required amount of each compound from the headspace of the storage bottles at room temperature, and inject it into the purged 1-L sample bottle or Tedlar bag. Be careful to fully flush the syringe with clean air between each compound. Fill the Tedlar bag with the factory calibration standard.

4. Allow 10 minutes for the standard to equilibrate.

5. Using a clean 100-μL, gas-tight syringe, aspirate the required injection volume from the 1-L standard. With a crisp, snappy action, inject the standard into the proper "injection port" of the Photovac.

6. Compare the chromatograph generated with the factory-supplied "specification chromatogram." If the difference is significant, review the procedures and technique used in the analysis and repeat. If results are still unsatisfactory, call Photovac technical service.

Alternate Procedures for Calibration

1. Following the start up procedure in the instruction manual, get the Photovac on line ready to accept a sample.

2. Obtain a gas standard mixture certified to ±2% accuracy, commercially available from Matheson Gas Products or equivalent.

3. Using a clean, 100-μL, gas-tight syringe, aspirate the required injection volume from the standard. With a crisp, snappy action, inject the standard into the proper "injection port" of the Photovac.

4. Compare the chromatograph generated with the factory-supplied "specification chromatogram." If the difference is significant, review the procedures and technique used in the analysis and repeat. If results are still unsatisfactory, call Photovac technical service.

5.7.6 Shut Down

1. Press <OFF>, then press <ENTER>.

2. Reset the carrier gas flow to 2-5 cm^3/min.

3. Place instrument on charge while on the bench and maintain as described in Section 5.7.7.

4. Unplug the unit except when charging batteries.

5.8 CALCULATIONS

5.8.1 Calibration Curve

A calibration curve of at least three concentrations must be constructed for each target compound. A straight line equation in the form of y = (m)(x) + b, (where: x = concentration, y = area counts, m = slope and b = the intercept) is fit to the standards' raw data. The (y), or the unknown concentration for the sample, is determined from the above straight line equation. Non-linear data is indicative of detector response range limitations.

Alternatively, sample concentration can be calculated by:

$$[Sample] = [Std]\ \frac{A_1}{A_2} \cdot \frac{V_2}{V_1}$$

where:

sample = concentration of sample in ppm or ppb
A_1 = peak area of sample (volts × seconds)
A_2 = peak area of standard (volts × seconds)
V_1 = injection volume of sample (μL)
V_2 = injection volume of standard (μL)
std = concentration in ppm or ppb

5.8.2 Standard Response Generation/Duplication of Factory Calibration Data

If appropriate gas standard mixtures are not available, gas standards can be made using the headspace from 40-mL VOA bottles with Teflon-lined septa screw caps partially filled with the desired neat volatile liquid. Generally, factory instrument response is determined using the following three compounds:

Compound	P_{vap} @ 20° C
methylene chloride	347 mm Hg
n-hexane	126 mm Hg
benzene	74 mm Hg

These compounds are toxic and should be stored and worked with under a hood. The general formula for preparing a standard from the headspace above a volatile liquid is:

$$V_{HS} = \frac{760\ (C)\ (V)}{P_{vap}}$$

where:

V_{HS} = volume of headspace (μL)
P_{VAP} = vapor pressure of liquid (mm HG)*
C = desired concentration (ppm)

V = volume of standard vessel (liters)

* Use appropriate tables to determine compound vapor pressure if working environment is not 20° C.

A determined volume of neat liquid headspace may be introduced to the standard vessel through the septum if using a Tedlar bag with the appropriate fitting. Bags or vessels used should be labelled with content concentrations, date, and time of preparation.

5.9 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance activities which apply to the operation of the Photovac. However, all instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

5.10 DATA VALIDATION

This section is not applicable to this SOP.

5.11 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and site-specific health and safety practices.

6.0 PHOTOVAC GC ANALYSIS FOR AIR, SOIL GAS, WATER, AND SOIL: SOP #2109

6.1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes a low-cost field laboratory screening tool for tentative identification and determination of concentration levels of select contaminants for site assessment and health and safety surveys.

This method describes the rapid screening of air, soil gas, water, and soil samples using a Photovac portable gas chromatograph (GC) model 10S series to determine the presence of various volatile organic compounds.

The data allows only rapid evaluation of site conditions and is applied to, but not limited to, the following activities: determining the extent and degree of contamination; defining the pollutant plume; assessing health and safety; and tentatively identifying and quantifying pollutants. The data should not be used for site ranking or for enforcement, since only limited QA/QC is required, and the reported data is qualified as "tentative."

6.2 METHOD SUMMARY

Air, soil gas, water, or soil samples can be analyzed by the Photovac. Brief method summaries are provided below. All methods use a Photovac 10S series GC equipped with a 10.6 eV photoionization detector (PID), and use external standards to tentatively identify and quantify compounds of interest. Refer to ERT SOP #2108, Photovac 10S50, 10S55 and 10S70 Gas Chromatograph Operation for additional information.

6.2.1 Air and Soil Gas Samples

Ambient air or soil gas samples are collected in 1-L Tedlar bags. An aliquot of each bag sample is withdrawn using a gas-tight syringe and directly injected into the GC. Vapor from selected samples can then be absorbed onto Tenax/CMS cartridges for confirmational GC/MS analysis.

6.2.2 Water Samples

Water samples are collected in 40-mL VOA vials with Teflon-lined, silicone septum screw caps. A 20-mL aliquot of sample is transferred by pipette into a second, clean VOA vial. The vial is capped, shaken vigorously for one minute, and allowed to stand at room temperature for at least 30 minutes for vapor phase equilibration. An aliquot of the water headspace is then injected into the GC using a gas-tight syringe.

6.2.3 Soil Samples

Soil samples are also collected in VOA vials. A 5 g aliquot of sample is weighed into a second, clean vial. Enough reagent water is added to bring the total volume of the soil/water extract to 20 mL. The vial is then capped, shaken vigorously for 1 minute, and allowed to stand at room temperature for at least 1 hour for vapor phase equilibration. An aliquot of the soil headspace is then injected into the GC using a gas-tight syringe.

6.3 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

6.3.1 Air and Soil Gas Samples

Air and soil gas samples are collected and stored in 1-L Tedlar gas sampling bags, using procedures outlined in ERT SOP #2149, Soil Gas Sampling. Samples should be kept in a cooler out of direct light and heat. Samples should be analyzed within 48 hours of collection, preferably within 12 hours.

Alternatively, samples may be collected in SUMMA canisters (see ERT SOP #1704, SUMMA Canister Sampling). In this case, sample stability may extend up to 2 months, depending upon sample matrix.

6.3.2 Water Samples

Water samples are collected, in triplicate, in 40-mL VOA vials. One sample is analyzed by the Photovac; the two remaining vials are used for

confirmation analysis by another method. They are filled completely, with no visible air bubbles. Samples are immediately stored out of direct light, in a cooler packed with ice from the time of collection until analysis. Sample vials are protected against breakage, and analyzed within seven days of collection.

6.3.3 Soil Samples

Soil samples are collected in 40-mL VOA vials, and stored out of direct light, in a cooler packed with ice (see ERT SOP #2012, Soil Sampling). Sample containers need to be protected from breakage.

6.4 INTERFERENCES AND POTENTIAL PROBLEMS

6.4.1 All Samples

- High concentrations of short chain alkanes and alkenes in samples may interfere with the resolution and detector sensitivity of early-eluting chlorinated alkenes and aromatic compounds.

- Syringes may cause carryover contamination between samples. This can be monitored by running regular syringe blanks and can be minimized by decontaminating syringes properly between samples.

- Since the Photovac is a GC, the target compounds are identified by their retention times (RTs). If the RT of the sample peak(s) matches the RT of the standard peak(s), they are assumed to be identical. If any non-target compound has the same RT, it can be misidentified as a target compound.

6.4.2 Air and Soil Gas Samples

- Samples can be contaminated by diffusion of volatile organics through the septum seals and the walls of the sampling bag during shipment and storage. A field blank (clean Tedlar bag filled with ultrazero air, carried through sampling and handling protocol) can serve as a check on such contamination.

- To prevent contamination by off-gassing, use Teflon or equivalent inert fittings and tubing in all procedures.

6.4.3 Water and Soil Samples

- Liquid samples should not be directly introduced into the GC. Direct injection of liquids, without heated injection ports, may result in damage to the GC.

- Samples can be contaminated by diffusion of volatile organics through the septum seal during shipment and storage. A field reagent blank (a clean sample container filled with reagent water, carried through sampling and handling protocol) can serve as a check on such contamination.

- Some of the sample will volatilize when the vials are opened during sample preparation. This loss is minimized by proper sample handling.

6.5 EQUIPMENT/APPARATUS

6.5.1 Photovac Operation

- Photovac 10S series gas chromatograph, with power cord and manual
- extra source lamp
- Photovac lamp tuning screwdriver
- extra columns/fittings
- ultrazero air carrier gas
- two-stage regulator, with quick-connect fitting
- one flowmeter per Photovac, either bubble-meter, rotameter, or Gilibrator
- septa, 6-mm diameter
- syringes, gas-tight, 10 μL to 1 mL
- VOA vials filled with activated charcoal, for syringe cleaning
- integrator or strip-chart recorder, with appropriate connections
- extra Photovac integrator pens
- extra Photovac integrator paper
- labels
- tools -- large adjustable wrench, wrenches (5/16 inch to 9/16 inch), screwdrivers (flat and Phillips head), needle-nose pliers, jeweler's screwdrivers, Allen wrenches
- duct tape
- Teflon tape

- power strip
- snoop
- Kimwipes (or similar lint/static free wipe) and
- Pelican cases (or equivalent)

6.5.2 Soil Gas Analysis

- Tedlar bags, 1 liter
- SUMMA canisters for holding gas standards
- extra-large syringe, 100 mL to 500 mL, for serial dilutions

6.5.3 Tenax/CMS Sampling

- Tenax/CMS cartridges in sealed glass ampules
- culture tubes (labeled) with glass wool to ship cartridges
- cotton gloves or cloths for cartridge handling
- fitting to connect syringe to cartridge
- fitting to connect cartridge to Tedlar bag
- 1/4-inch silicone o-rings for a tight seal around cartridge

6.5.4 Water Headspace Analysis

- headspace standards, purgeable A and B or equivalent
- 1.8-mL vials for holding standards (either screw-cap or crimp-top vials)
- Pasteur pipettes for transferring standards
- 40-mL VOA vials (1 per sample plus extras for standards and QA/QC requirements)
- 10-mL or 20-mL pipettes and pipette bulb
- liquid standard syringes
- surgical gloves

6.5.5 Soil Headspace Analysis

- same equipment for water headspace analysis
- portable scale, accurate to ± 0.1 g
- spatulas, or equivalent, for transferring soil

6.6 REAGENTS

6.6.1 Air Sample Analysis

- gas standards -- certified to ± 2% level of accuracy. Although there may be other sources, gas standards are available through Scott Specialty Gas. In-house laboratory preparation of calibration gas standards with confirmational GC/MS analysis is acceptable

- ultrazero air carrier gas

6.6.2 Water and Soil Sample Analysis

- reagent water -- organic-free chromatographic grade or equivalent, free of any contaminants which may interfere with the detection and resolution of target parameters

- ultrazero air carrier gas

- stock standard solutions -- stock standard solutions may be prepared from pure standard materials or purchased as certified solutions (e.g., Supelco purgeable A or B, or equivalent). Reagents used as standards may depend on site-specific suspected volatile contaminants

6.7 PROCEDURES

6.7.1 Method Detection Limits

Determine the method detection limit (MDL) just before the analysis with a serial dilution of the standard. The MDL is the lowest concentration that can be detected at the gain setting selected for the analysis. MDLs depend on the type of analysis performed and the condition of the gas chromatograph. Because of the difference in matrices, air and soil gas analyses usually have MDLs an order of magnitude above headspace analyses. Factors that can vary the sensitivity of a Photovac from site to site are the age of the source lamp, detector age, column condition, shipment of GC to the site, and location of the field lab. Typical MDLs for soil gas range from 10 ppb to 50 ppb, and headspace MDLs range from 1 ppb to 5 ppb.

If sample concentrations are high, injection volumes may be reduced to obtain on-scale response for parameters of interest, and to avoid contamination of the GC system. Calculate the method detection limit for compounds not detected at reduced injection volumes by using:

$$MDL = \frac{(V_{std})\ (C_{std})}{V}$$

where:

V_{std} = lowest volume of standard headspace injected (µL)
C_{std} = concentration of standard (ppm or ppb)
V = volume of sample headspace injected (µL)

6.7.2 Calibration

Photovac analyses are calibrated by the external standard method using the gas standards described in Section 6.6.1. At the beginning of the analysis, a three-to-five point calibration curve is run to demonstrate linear instrument response over a specified concentration range. The development of this method has shown the best linearity of the PID response to be from 10 ppb to 1 ppm for air and soil gas analysis and from 1 ppb to 100 ppb for headspace analysis. Most PIDs will be linear above that range but eventually, at high enough concentrations, the PID will become saturated. The curve is verified daily by running a calibration check standard from the middle of the curve.

If the response of any parameter varies from the curve by more than ±25%, RSD instrument response has changed and a new calibration curve should be run.

Air and Soil Gas Calibration

Prepare the concentrations needed for calibration by performing a serial dilution of the gas standard. For example, add 50 mL of a 1-ppm standard and 450 mL of ultrazero air carrier gas to a new Tedlar bag to acquire a 100-ppb calibration standard. The 100-ppb bag can then be used to make up lower concentration standards.

Alternatively, construct a calibration curve by varying injection volumes. By designating a 250-µL injection volume as the 1-ppm standard, a 100-ppb standard is created by injecting 25 µL of a 1-ppm standard. This method is more convenient and does not require the large syringes needed for serial dilution, but the calibration curve is then limited by the sizes of the available syringes.

Water and Soil Calibration

Headspace standards can be created at selected concentrations by adding the appropriate volumes of stock standard into clean 40-mL VOA vials containing 20 mL of reagent water. These volumes (V) are calculated by using:

$$V = \frac{20\ mL \cdot (stock\ conc.)}{(calibrant\ conc.)}$$

From the 200-ppm purgeable A and B standards, first prepare a 2-ppm stock solution to allow calibration standards between 1 ppb and 10 ppb to be prepared with the syringes listed in Section 6.5.1.

6.7.3 Operation

Air and Soil Gas Analysis

Typical columns used for this method include SE-30 (packed) and CP-Sil 19 (capillary). An example of compound separation using CP-Sil 19, with typical chromatographic conditions, is shown in Figure 1, Appendix A.

1. Inject standards after every 10-15 samples or every 6 hours, whichever is more frequent, to bracket possible parameter RT variations.

2. If sample concentrations are high, reduce injection volumes to obtain on-scale response. The method detection limit (MDL) for compounds not detected at reduced injection volumes is calculated according to the equation in Section 6.7.1.

3. Identify the compounds in the sample by comparing the retention time of the peaks in the sample chromatogram with those of the peaks in the standard chromatograms. The width of the RT windows used to make identifications should be based on measurements of actual RT variations of standards which bracket a series of sample injections. Three times the standard deviation of a retention time can be used to calculate a suggested window size; however, the judgment of the analyst should be a major factor in the interpretation of chromatograms.

Water Sample Analysis

1. Use a pipette to place a 20-mL aliquot of sample into a clean 40-mL VOA vial. Seal the vial with a Teflon-lined septum screw cap.

2. Shake the capped vial vigorously by hand for 1 minute. Allow it to stand, inverted and undisturbed, for at least 30 minutes at ambient temperature for vapor phase equilibration.

3. Use a gas-tight syringe to extract an aliquot of headspace by inserting the syringe needle through the vial septum to a distance approximately halfway between the liquid surface and the septum's Teflon face.

4. Purge the syringe barrel three to five times by withdrawing and expelling a volume of headspace in slight excess of the volume anticipated to be used for analysis.

5. If sample concentrations are high, injection volumes may be reduced to obtain on-scale response. If sample headspace injection volume is reduced below the volume of the aqueous calibration standard used to establish the method detection limit (MDL), the detection limit for target compounds detected at the reduced headspace volume must be determined. Do this by injecting headspace aliquots at the reduced volume into the GC, beginning with the 10-ppb calibration standard and increasing or decreasing standard concentrations, as warranted, until a response for all target compounds has been obtained. The detection limit for parameters detected at the lower headspace injection volume is then calculated using the equation in Section 6.7.1.

6. Identify the compounds in the sample by comparing the RTs of the peaks in the sample chromatogram with those in standard chromatograms. The width of the retention time windows used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of an RT can be used to calculate a suggested window size; however, the judgment of the analyst should be a major factor in the interpretation of chromatograms.

Soil Sample Analysis

1. Place a clean, empty, 40-mL glass vial on the balance. Zero the balance. Using a clean stainless steel spatula, add 5.0 g ± 0.1 g of soil sample.

2. Using a pipette, place enough reagent water in the vial to bring the total volume of the soil and water to 20 mL. Seal the vial with a Teflon-lined septum screw cap.

3. Shake the capped vial vigorously for 1 minute, to promote dispersion of the soil sample and increase surface area. Allow to stand, undisturbed, at ambient temperature for at least 1 hour for vapor phase equilibrium.

4. Use a gas-tight syringe to extract an aliquot of headspace by inserting the syringe needle through the vial septum to a distance approximately halfway between the slurry surface and the septum's Teflon face. Although 5 g is recommended for most soil matrices, other amounts ranging from 1 g to 10 g have also been used, depending on sample concentrations and the consistency of the matrix.

5. Purge the syringe barrel three to five times by withdrawing and expelling a volume of headspace in slight excess of the volume anticipated to be used for analysis. Wipe the syringe needle with a Kimwipe before injection into the GC.

6. If sample concentrations are high, either reduce the injection volumes or analyze less soil to obtain on-scale response. If sample headspace injection volume is reduced below the volume of the aqueous calibration standard used to establish the MDL, follow the procedure in Section 6.7.1 to determine the MDL for target compounds detected at the reduced headspace volume. Alternatively, weigh out as little as 1 g, keeping in mind that this means a 10% error if using a portable balance accurate to ± 0.1 g.

7. Identify the parameters in the sample by comparing the retention times (RTs) of the peaks in the sample chromatogram with those in standard chromatograms. The width of the retention time windows used to make identifications should be based on

measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of an RT can be used to calculate a suggested window size; however, the judgment of the analyst should be a major factor in the interpretation of chromatograms.

6.8 CALCULATIONS

6.8.1 Air and Soil Gas Samples

Determine the concentration of individual compounds in each sample by using:

$$[Sample] = [Std] \frac{A_1}{A_2} \cdot \frac{V_2}{V_1}$$

where:

sample	=	concentration of sample in ppb or ppm
A_1	=	peak area of sample (volts × seconds)
A_2	=	peak area of standard (volts × seconds)
V_1	=	injection volume of sample (μL)
V_2	=	injection volume of standard (μL)
std	=	concentration in ppm or ppb

6.8.2 Water Samples

Determine the concentrations of individual compounds in the sample by using:

$$*[Sample] = [Std] \frac{A_1}{A_2} \cdot \frac{V_2}{V_1}$$

where:

sample	=	concentration of sample in ppb or ppm
A_1	=	peak area sample (volts × seconds)
A_2	=	peak area standard (volts × seconds).
V_1	=	injection volume of sample (μL)
V_2	=	injection volume of standard (μL)
std	=	concentration in ppb or ppm

*This is the same as Equation 3, except the concentration of the headspace standard is used.

6.8.3 Soil Samples

Determine the concentrations of individual compounds in the sample by using:

$$[Sample] = [Std] \cdot \frac{A_1}{A_2} \cdot \frac{V_2}{V_1} \cdot \frac{V_{hdsp}}{W_{samp}}$$

where:

sample	=	concentrations in μg/kg (ppb)
A_1	=	peak of area sample (volts × seconds)
A_2	=	peak of area standard (volts × seconds)
V_2	=	injection volume of standard (μL)
V_1	=	injection volume of sample (μL)
V_{hdsp}	=	volume of headspace (always 20 mL)
W_{samp}	=	weight of sample (usually 5 g)
std	=	concentration in μg/kg (ppb)

6.9 QUALITY ASSURANCE/ QUALITY CONTROL

In order to meet the QA2 data quality objectives, at least 10% of all field samples must be confirmed by GC/MS analysis. The following QA/QC requirements must be followed and provided in the data package submitted:

- Chain of custody documentation;
- Sample log -- date/time of sample collection, date/time of analysis, and run numbers;
- Blanks (see Section 6.9.1);
- Instrument calibration data;
- Labeling of chromatograms -- identify each chromatogram clearly by analysis type (i.e., syringe blank, sample number, or calibrant concentration), injection volume, run number, date, and time;
- Replicate sample analysis -- after every ten samples to check method/analyst precision. The RSD of the area response of any of the compounds should be within 15%;

- Retention time/instrument response check -- since compound identification is based upon retention time matches, run a calibration standard after every 10-15 samples;

- Spikes -- soil and water samples only (see Section 6.9.2); and

- Confirmational analysis for air and soil gas (see Section 6.9.3).

6.9.1 Blanks

- Air and soil gas analysis -- for each day of analysis, field standards (Tedlar bags filled with gas standards) and field blanks (Tedlar bags filled with ultrazero air) accompany samples through collection, handling, and storage.

- Water analysis -- field blank; duplicate 40-mL VOA vials completely filled with reagent water accompany each cooler used for sample collection, storage, and/or shipment.

- Soil analysis -- reagent blank; 20 mL of the reagent water used in the soil analysis is placed by pipette into a clean 40-mL VOA vial, allowed to equilibrate, and analyzed before any samples.

- Syringe blanks -- syringe blanks are to be run prior to each sample analysis. In practice, there is no need to run syringe blanks if the previous sample is clean.

6.9.2 Spikes

- For every 20 (soil or water) samples, one matrix spike (MS) and one matrix spike duplicate (MSD) must be analyzed. If there are less than 20 samples in a matrix, at least one MS/MSD must be analyzed.

- The samples spiked should have moderate concentrations, if possible. The amount spiked should be equivalent to the middle of the calibration range or one to five times the sample background concentrations, whichever is higher.

- Calculate the percent recovery (%R) of each compound of interest from:

$$R = 100 \cdot \frac{(A-B)}{S}$$

where:

R = percent recovery
A = concentration of sample and spike
B = concentration of sample
S = concentration of the spike

- The percent recovery (%R), should be 50-90% for a soil matrix, and 80-120% for a water matrix. Due to the complexity of the soil/water/vapor equilibria, recoveries from soil matrices are consistently below 100%.

6.9.3 Confirmatory Analysis

Depending on work plan stipulations, at least 10% of the air and soil gas samples analyzed by this GC method must be submitted for confirmatory GC/MS analysis according to modified methods TO-1 (Tenax absorbent) and TO-2 (Carbon Molecular Sieve [CMS] absorbent). Each soil gas sample must be absorbed on replicate Tenax/CMS tubes. The volume absorbed on a Tenax/CMS tube is dependent on the total concentration of the compounds measured by the Photovac as shown below:

Total Concentration	Sample Volume (mL)
> 10	use serial dilution
10	10 - 50
5	20 - 100
1	100 - 250

A range of volumes is given to account for sample variability. The low end of the range should be used for samples whose total concentrations are primarily one large peak, since too large a volume will overload the GC/MS column when that peak is confirmed. The high end of the range should be used for multi-peak samples.

6.10 DATA VALIDATION

Data should be reviewed to ensure that the QA/QC requirements listed above have been met.

6.11 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety practices. More specifically, the samples should be stored in a cooler away from the analysis area, if possible. The analysis area should have adequate ventilation.

7.0 MICROMONITOR M200: SOP #2111

7.1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) presents an overview of the Micromonitor M200 dual-channel microchip gas chromatograph (GC), including analytical capabilities, operating methods and technical limitations. This microchip gas chromatograph, complete with high resolution capillary columns, is linked to a Macintosh personal computer, allowing for rapid field analysis of environmental samples.

The M200 is a portable, high-speed gas chromatograph that samples gases and vapors, separates any volatile components, and then identifies and calculates the concentrations of these compounds. Only vapor-phase samples can be introduced into the M200. Purgeable organics from soil and water matrices are collected via a portable sample concentrator and converted to vapor phase for analysis by the M200. No liquids should ever be introduced into the M200 GC system.

7.2 METHOD SUMMARY

A Macintosh computer system connected to the M200 processes sample data and identifies selected compounds found in vapor-phase samples. The M200 unit contains two high-resolution capillary columns. Simple front panel controls on the unit allow the operator to adjust all method parameters (Figure 2, Appendix D). After the correct parameters are set, a vapor sample is drawn into the unit via the sample port and an internal vacuum pump. The sample gas is then analyzed on one or both capillary columns and specific volatile compounds are detected, separated and identified by the attached computer system.

Calibration standards must be analyzed prior to field sampling. Once the calibration has been validated and the points plotted using the Macintosh library and software, sample analyses can proceed. The Macintosh calibration library currently contains only target compounds historically encountered in U.S. EPA/ERT field work.

7.3 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Since the M200 is involved with vapor-phase samples, all samples are collected directly or stored in Tedlar gas sampling bags, as per ERT SOP #2050, Tedlar Bag Sampling.

The actual introduction of any calibration or sample gas into the instrument is done by attaching a 2 cm^3 Beckton-Dickerson glass syringe via a Teflon Luer lock valve directly to the sampling inlet port in the front of the unit.

7.4 INTERFERENCES AND POTENTIAL PROBLEMS

Even considering the powerful analytical capabilities in the M200's design configuration, the instrument has several inherent limitations that impact its ability to be used during responses to chemical releases. These limitations are as follows:

- Commercial versions of the device can detect only preselected compounds that can be identified by parameters stored within its internal read-only memory (ROM) library.
- Large quantities of other vapors could be present and may seriously interfere with the analysis using the M200.
- The presence of common fuels containing many individual components, such as gasoline, will confuse the M200's computerized interpretation of data.
- Large quantities of a preselected vapor may overload the capillary columns, and the retention times of the preselected compounds may fall outside of expected retention time windows.
- Commercial versions of the device are programmed with detection limits which are too high (by factors of 10 to 100) for determining levels of hazardous chemicals at or

below TLV concentrations. For typical soil gas analysis, parts per billion (ppb) will be required, and the M200 cannot detect levels that low. To compensate, a sample preconcentrator is used to concentrate the compounds of interest prior to injection.

7.5 EQUIPMENT/APPARATUS

In addition to the basic Micromonitor M200 unit, several optional pieces of equipment are required for its operation. These pieces include a 12-volt power supply, a Macintosh computer system, and a RS232DB9-DB9 cable (Figure 3, Appendix D). An optional sample preconcentrator is required to analyze air samples with detection limits in the parts per billion range. If purgable organics are to be determined in soil or water matrices, the sample preconcentrator is a required piece of equipment.

7.6 REAGENTS

The M200 utilizes high purity (99.995% or above) helium as a carrier gas. Pressure at the two-stage regulator on the tank should be approximately 80 psig. The capillary column head pressure inside the M200 unit should be 15 to 40 psig. This capillary column head pressure can be adjusted via two regulators found on the back of the instrument (Figure 4, Appendix D).

Gas standards are purchased as certified mixtures at fairly high concentrations (i.e., 10 ppm or greater) from Scott Gas or Matheson. These concentrations are for subsequent dilution to various concentrations that enable construction of a standard calibration curve.

Liquid phase standards, if required, must be of the highest purity, such as Aldrich Gold Label or Supelco Environmental standards kits. If air is to be used for sample/standards dilutions, it must also be ultrahigh purity gas.

7.7 PROCEDURES

1. Plug in your M200 unit. The following message should appear on the display reading: "Self test OK."

2. An asterisk (*) should appear in the first character of the display within 3 minutes of turning on the unit, signaling that the unit is ready (i.e., the temperatures are at the setpoints, the pressures are above 5 psig and the system self test found no errors). If the asterisk does not appear, consult the troubleshooting guide in Appendix C.

3. Enter the method parameters by pressing the <METHOD> key. The first item reads "Column Temperature." If column temperature is 30°C, press <ENTER> to accept the value and go on to the next item. If it does not read 30°C, press <UP> or <DOWN> to achieve this required temperature. Once 30°C is shown, press <ENTER> to accept the value and to advance to the next parameter. The temperature can be set at any level between 30° and 180°C. Table 4 gives appropriate values for three often-used GC columns.

4. Continue through all the items in the method the same way.

5. Now read the "Column Head Pressure" on the front panel by pressing <STATUS>. Press <ENTER> once to advance to the next line where the column pressure will be indicated.

6. Adjust the pressure regulator in the rear of the instrument until the pressure reads about 20±5 psig (or the appropriate pressure required for the selected method). Press <STATUS> to monitor column pressure.

7.7.1 Macintosh Software

The procedures used when the M200 unit is being controlled from the computer system are outlined in the Macintosh M200 Chromatography Applications Manual.

Table 4: M-200 Operating Conditions for Various Sample Columns

	Column Type		
Operating Conditions	**DB-5/DB-1701**	**MOL Sieve 5A**	**HAYESEP A**
Column Head Pressure	20 ± 5 psig	12 ± 5 psig	18 ± 5 psig
Column Temperature	30° C	60° C	60° C
Run Time	40 sec	30 sec	40 sec
Sampling Time	5 sec	5 sec	5 sec
Inject Time	40 msec	40 msec	40 msec
Detector filament	on	on	on
Auto Zero	on	on	on
Detector Sensitivity	medium	medium	medium
Integrator/ Data System Conditions		Printer/Plotter chart speed	20 cm/min
		Printer/Plotter Attenuation	256X
		Input Signal	1 Volt

7.7.2 Calibration

The M2001 software used with the M200 GC uses Retention Time Indices (RTIs) based on a homologous series of compounds, in this case n-alkanes. A calibration run using three or more n-alkanes is run at the appropriate GC conditions. The RTIs are updated in the library as per M2001 manual. The RTIs for the entire library are **not** updated by correcting stored library values against the current "experimental" calibration run. It is important to bracket the entire library retention time with the three or more n-alkanes used in the calibration run.

A second calibration run using the target compounds of interest is then performed. This second calibration establishes the correct response factor which will be used to calculate the concentrations of the target compounds. This second calibration is required because the first calibration, using the n-alkanes, will establish the correct RTIs but will not yield the correct response factors for the target compounds. Therefore, two calibrations, the first to establish the correct RTI, and the second to calculate the correct response factor, are required at least once a day. Note: the results for compounds not in the calibration run are estimated from the response factor of their nearest neighbor.

The generation of calibration standards can be performed either at the site or in the laboratory prior to entering the field. In the latter case, standards must still be run in the field to ensure that the calibration runs stored on the data disks are valid and close to standards run in the lab. Dilutions are typically made from the certified gas standards cylinders using Hamilton 500, 1000 and 1500 cm^3 model "Super syringes" and Tedlar sampling bags. Simple volumetric dilutions are made and the set of standards analyzed as if they were typical samples. If the sample pre-concentrator is used, the trapping efficiency must be recorded.

At least three concentrations of each standard must be run. Preferably more standards are analyzed to establish the minimum ranges for the linear

response of the detectors for each individual target compound. Linear regression must be performed and an R^2 value of 0.90 or greater should be achieved.

7.7.3 Sample Analysis

To analyze a sample, fill a 2.0 cm^3 glass syringe with the sample, attach a Teflon Luer lock to the syringe tip and carefully place this assembly into the sample port located on the unit. Make sure the Luer lock is in the open position. The internal sampling pump will automatically draw a portion of the sample from the syringe into the instrument, once the injection command is executed (Figure 3, Appendix D).

7.8 CALCULATIONS

A calibration curve of at least three concentrations must be constructed for each target compound. A straight line equation in the form of y = (m)(x) + b; (where: x = concentration, y = area counts, m = slope and b = the intercept) is fit to the standard's raw data. The (y), or the unknown concentration for the sample, is determined from the above straight line equation. Non-linear data is indicative of erroneous detector response. Alternatively, sample concentration can be calculated as below:

$$\text{Sample Conc.} = \frac{(\text{standard conc.})\ (\text{sample area})}{(\text{standard area})}$$

The M2001 software will automatically calculate the concentration based on the response factor generated in the calibration mode of the program. Calibrations can be single point or multipoint calculations.

7.9 QUALITY ASSURANCE/ QUALITY CONTROL

The following QA/QC protocols are applicable:

- A complete calibration curve must be run daily.
- Duplicates of a standard, in the mid-range of the calibration curve and preferably close to sample results, should be run every 10 samples to ensure constant detector response.
- Two or three duplicates for each sample should also be run. These duplicate responses should be within 10-20% of each other in terms of area count and retention time values.
- Matrix spikes, or spiking samples with known levels of standards, must be run along with the samples, and should bracket the levels found in the field samples.
- The same Tedlar bag may be analyzed by other field instrumentation (e.g., Photovac, OVA, Sentex, etc.) and/or collected into tubes for GC/MS confirmation. If Tedlar bags are used to prepare standards, the time of preparation should be noted.
- During sample analysis, one of the standards should be periodically re-analyzed to ascertain if any sample loss occurs in the bag over time.
- A performance evaluation sample (PE) is typically sent along to determine if any loss or contamination occurs from transit or handling during sampling.
- A trip blank of zero air is also sent and analyzed at the end of the sampling run to determine if any contamination of the Tedlar bags occurred during transit.

7.10 DATA VALIDATION

The Retention Time Index (RTI) is used for peak identifications. If peaks are eluting close to the target compounds, sample spikes using known levels of target compounds can be prepared to identify the absence/presence of these target compounds in the samples. Typically, only the RTI is needed to identify the peaks of interest. Quantification is determined from the linear calibration curve, and by solving for concentration (y) from the straight line equation. The coefficient of variation on the straight line equation should have an R^2 of 0.90 or greater. Confirmation of the identity of any particular target compound must be done by other analytical methods, typically GC/MS.

Alternatively, a statistical approach to data validation can be sought. Once the linear range is established, analyze an appropriate standard, either a low or midrange concentration, 10 or more times throughout the day. Determine the standard deviation of the mean (σ(N-1)) for the response of the standard selected. The statistical method detection limit, or MDL, is 3 times the standard deviation (3σ). The method quantitation limit, or MQL, is then 10 times the standard deviation (10σ). Results below the MDL are considered "nondetects" (ND). Results above the MDL but below the MQL are considered "detected," but below the quantitation limit and thus are ascribed a "J" value. This "J" value flags the data as questionable. Results above the MQL are considered statistically reliable data.

7.11 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety practices. Analysis should be performed in a well-ventilated room. The sample vent port on the back of the M200 should be equipped with either a carbon scrubber or a long Tygon tube to vent sample gases outside of the work area. All carrier gas cylinders must be securely bolted to a table or piece of heavy furniture. When liquid reagents are used to prepare standards, the work should be performed under a vented hood with the analyst wearing safety glasses and disposable protective gloves.

APPENDIX A

Ionization Potentials

Ionization Potentials

Some Atoms and Simple Molecules			
Atom/Molecule	IP (eV)	Molecule	IP (eV)
H	13.595	I_2	9.28
C	11.264	HF	15.77
N	14.54	HCl	12.74
O	13.614	HBr	11.62
Si	8.149	HI	10.38
S	10.357	SO_2	12.34
F	17.42	CO_2	13.79
Cl	13.01	COS	11.18
Br	11.84	CS_2	10.08
I	10.48	N_2O	12.90
H_2	15.426	NO_2	9.78
N_2	15.580	O_3	12.80
O_2	12.075	H_2O	12.59
CO	14.01	H_2S	10.46
CN	15.13	H_2Se	9.88
NO	9.25	H_2Te	9.14
CH	11.1	HCN	13.91
OH	13.18	C_2N_2	13.8
F_2	15.7	NH_3	10.15
Cl_2	11.48	CH_3	9.840
Br_2	10.55	CH_4	12.98

Ionization Potentials (continued)

Alkyl Halides			
Molecule	IP (eV)	Molecule	IP (eV)
HCl	12.74	CH_2BrCl	10.77
Cl_2	11.48	$CHBr_2Cl$	10.59
CH_4	12.98	ethyl bromide	10.29
methyl chloride	11.28	1,1-dibromoethane	10.19
dichloromethane	11.35	1-bromo-2-chloroethane	10.63
trichloromethane	11.42	1-bromopropane	10.18
tetrachloromethane	11.47	2-bromopropane	10.075
ethyl chloride	10.98	1,3-dibromopropane	10.07
1,2-dichloroethane	11.12	1-bromobutane	10.13
1-chloropropane	10.82	2-bromobutane	9.98
2-chloropropane	10.78	1-bromo-2-methylpropane	10.09
1,2-dichloropropane	10.87	2-bromo-2-methylpropane	9.89
1,3-dichloropropane	10.85	1-bromopentane	10.10
1-chlorobutane	10.67	HI	10.38
2-chlorobutane	10.65	I_2	9.28
1-chloro-2-methylpropane	10.66	methyl iodide	9.54
2-chloro-2-methylpropane	10.61	diiodomethane	9.34
HBr	11.62	ethyl iodide	9.33
Br_2	10.55	1-iodopropane	9.26
methyl bromide	10.53	2-iodopropane	9.17
dibromomethane	10.49	1-iodobutane	9.21
tribromomethane	10.51	2-iodobutane	9.09

Ionization Potentials (continued)

Alkyl Halides (continued)		Paraffins and Cycloparaffins	
Molecule	IP (eV)	Molecule	IP (eV)
1-iodo-2-methylpropane	9.18	methane	12.98
2-iodo-2-methylpropane	9.02	ethane	11.65
1-iodopentane	9.19	propane	11.07
F_2	15.70	n-butane	10.63
HF	15.77	i-butane	10.57
$CFCl_3$ (Freon 11)	11.77	n-pentane	10.35
CF_2Cl_2 (Freon 12)	12.31	i-pentane	10.32
CF_3Cl (Freon 13)	12.91	2,2-dimethylpropane	10.35
$CHClF_2$ (Freon 22)	12.45	n-hexane	10.18
$CFBr_3$	10.67	2-methylpentane	10.12
CF_2Br_2	11.07	3-methylpentane	10.08
CH_3CF_2Cl (Genetron 101)	11.98	2,2-dimethylbutane	10.06
$CFCl_2CF_2Cl$	11.99	2,3-dimethylbutane	10.02
CF_3CCl_3 (Freon 113)	11.78	n-heptane	10.08
$CFHBrCH_2Br$	10.75	2,2,4-trimethylpentane	9.86
CF_2BrCH_2Br	10.83	cyclopropane	10.06
CF_3CH_2I	10.00	cyclopentane	10.53
n-C_3F_7I	10.36	cyclohexane	9.88
n-$C_3F_7CH_2Cl$	11.84	methylcyclohexane	9.85
n-$C_3F_7CH_2I$	9.96		

Ionization Potentials (continued)

Aliphatic Alcohol, Ether, Thiol, and Sulfides	
Molecule	IP (eV)
H_2O	12.59
methyl alcohol	10.85
ethyl alcohol	10.48
n-propyl alcohol	10.20
i-propyl alcohol	10.16
n-butyl alcohol	10.04
dimethyl ether	10.00
diethyl ether	9.53
n-propyl ether	9.27
i-propyl ether	9.20
H_2S	10.46
methanethiol	9.440
ethanethiol	9.285
1-propanethiol	9.195
1-butanethiol	9.14
dimethyl sulfide	8.685
ethyl methyl sulfide	8.55
diethyl sulfide	8.430
di-n-propyl sulfide	8.30

Aliphatic Aldehydes and Ketones	
Molecule	IP (eV)
CO_2	13.79
formaldehyde	10.87
acetaldehyde	10.21
propionaldehyde	9.98
n-butyraldehyde	9.86
isobutyraldehyde	9.74
n-valeraldehyde	9.82
isovaleraldehyde	9.71
acrolein	10.10
crotonaldehyde	9.73
benzaldehyde	9.53
acetone	9.69
methyl ethyl ketone	9.53
methyl n-propyl ketone	9.39
methyl i-propyl ketone	9.32
diethyl ketone	9.32
methyl n-butyl ketone	9.34
methyl i-butyl ketone	9.30
3,3-dimethyl butanone	9.17
2-heptanone	9.33
cyclopentanone	9.26
cyclohexanone	9.14
2,3 butanedione	9.23
2,4-pentanedione	8.87

Ionization Potentials (continued)

Aliphatic Acids and Esters		Aliphatic Amines and Amides	
Molecule	IP (eV)	Molecule	IP (eV)
CO_2	13.79	NH_3	10.15
formic acid	11.05	methyl amine	8.97
acetic acid	10.37	ethyl amine	8.86
propionic acid	10.24	n-propyl amine	8.78
n-butyric acid	10.16	i-propyl amine	8.72
isobutyric acid	10.02	n-butyl amine	8.71
n-valeric acid	10.12	i-butyl amine	8.70
methyl formate	10.815	s-butyl amine	8.70
ethyl formate	10.61	t-butyl amine	8.64
n-propyl formate	10.54	dimethyl amine	8.24
n-butyl formate	10.50	diethyl amine	8.01
isobutyl formate	10.46	di-n-propyl amine	7.84
methyl acetate	10.27	di-i-propyl amine	7.73
ethyl acetate	10.11	di-n-butyl amine	7.69
n-propyl acetate	10.04	trimethyl amine	7.82
isopropyl acetate	9.99	triethyl amine	7.50
n-butyl acetate	10.01	tri-n-propyl amine	7.23
isobutyl acetate	9.97	formamide	10.25
sec-butyl acetate	9.91	acetamide	9.77
methyl propionate	10.15	N-methyl acetamide	8.90
ethyl propionate	10.00	N,N-dimethyl formamide	9.12
methyl n-butyrate	10.07	N,N-dimethyl acetamide	8.81
methyl isobutyrate	9.98	N,N-diethyl formamide	8.89
		N,N-diethyl acetamide	8.60

Ionization Potentials (continued)

Other Aliphatic Molecules with N Atom	
Molecule	IP (eV)
nitromethane	11.08
nitroethane	10.88
1-nitropropane	10.81
2-nitropropane	10.71
HCN	13.91
acetonitrile	12.22
propionitrile	11.84
n-butyronitrile	11.67
acrylonitrile	10.91
3-butene-nitrile	10.39
ethyl nitrate	11.22
n-propyl nitrate	-----
methyl thiocyanate	10.065
ethyl thiocyanate	9.89
methyl isothiocyanate	9.25
ethyl isothiocyanate	9.14

Olefins, Cyclo-olefins, Polenes, Acetylenes	
Molecule	IP (eV)
ethylene	10.515
propylene	9.73
1-butene	9.58
2-methylpropene	9.23
trans-2-butene	9.13
cis-2-butene	9.13
1-pentene	9.50
2-methyl-1-butene	9.12
3-methyl-1-butene	9.51
3-methyl-2-butene	8.67
1-hexene	9.46
1,3-butadiene	9.07
isoprene	8.845
cyclopentene	9.01
cyclohexene	8.945
4-methylcyclohexene	8.91
4-cinylcyclohexene	8.93
cyclo-octatetraene	7.99
acetylene	11.41
propyne	10.36
1-butyne	10.18

Ionization Potentials (continued)

Some Derivatives of Olefins		Heterocyclic Molecules	
Molecule	IP (eV)	Molecule	IP (eV)
vinyl chloride	9.995	furan	8.89
cis-dichloroethylene	9.65	2-methyl furan	8.39
trans-dichloroethylene	9.66	2-furaldehyde	9.21
trichloroethylene	9.45	tetrahydrofuran	9.54
tetrachloroethylene	9.32	dihydropyran	8.34
vinyl bromide	9.80	tetrahydropyran	9.26
1,2-dibromoethylene	9.45	thiophene	8.860
tribromoethylene	9.27	2-chlorothiophene	8.68
3-chloropropene	10.04	2-bromothiophene	8.63
2,3-dichloropropene	9.82	pyrrole	8.20
1-bromopropene	9.30	pyridine	9.32
3-bromopropene	9.7	2-picoline	9.02
$CF_3CCl=CClCF_3$	10.36	3-picoline	9.04
$n\text{-}C_5F_{11}CF=CF_2$	10.48	4-picoline	9.04
acrolein	10.10	2,3-lutidine	8.85
crotonaldehyde	9.73	2,4-lutidine	8.85
mesityl oxide	9.08	2,6-lutidine	8.85
vinyl methyl ether	8.93		
allyl alcohol	9.67		
vinyl acetate	9.19		

Ionization Potentials (continued)

Aromatic Compounds			
Molecule	IP (eV)	Molecule	IP (eV)
benzene	9.245	2-methylnapthalene	7.955
toluene	8.82	biphenyl	8.27
ethyl benzene	8.76	phenol	8.50
n-propyl benzene	8.72	anisole	8.22
i-propyl benzene	8.69	phenetole	8.13
n-butyl benzene	8.69	benzaldehyde	9.53
s-butyl benzene	8.68	acetophenone	9.27
t-butyl benzene	8.68	benzenethiol	8.33
o-xylene	8.56	phenyl isocyanate	8.77
m-xylene	8.56	phenyl isothiocyanate	8.520
p-xylene	8.445	benzonitrile	9.705
mesitylene	8.40	nitrobenzene	9.92
durene	8.025	aniline	7.70
styrene	8.47	fluoro-benzene	9.195
α-methyl styrene	8.35	chloro-benzene	9.07
ethynylbenzene	8.815	bromo-benzene	8.98
napthalene	8.12	iodo-benzene	8.73
1-methylnapthalene	7.96	o-dichlorobenzene	9.07

Ionization Potentials (continued)

Aromatic Compounds (continued)		Miscellaneous Molecules	
Molecule	IP (eV)	Molecule	IP (eV)
m-dichlorobenzene	9.12	ethylene oxide	10.565
p-dichlorobenzene	8.94	propylene oxide	10.22
1-chloro-2-fluorobenzene	9.155	p-dioxane	9.13
1-chloro-3-fluorobenzene	9.21	dimethoxymethane	10.00
1-bromo-4-fluorobenzene	8.99	diethoxymethane	9.70
o-fluorotoluene	8.915	1,1-dimethoxyethane	9.65
m-fluorotoluene	8.915	propiolactone	9.70
p-fluorotoluene	8.785	methyl disulfide	8.46
o-chlorotoluene	8.83	ethyl disulfide	8.27
m-chlorotoluene	8.83	diethyl sulfite	9.68
p-chlorotoluene	8.70	thiolacetic acid	10.00
o-bromotoluene	8.79	acetyl chloride	11.02
m-bromotoluene	8.81	acetyl bromide	10.55
p-bromotoluene	8.67	cyclo-$C_6H_{11}CF_3$	10.46
o-iodotoluene	8.62	$(n\text{-}C_3F_7)(CH_3)C{=}O$	10.58
m-iodotoluene	8.61	trichlorovinylsilane	10.79
p-iodotoluene	8.50	$(C_2F_5)_3N$	11.7
benzotrifluoride	9.68	isoprene	9.08
o-fluorophenol	8.66	phosgene	11.77

APPENDIX B

Photovac Maintenance and Calibration

Photovac Maintenance and Calibration: Supplement to SOPs #2107 and #2108

PHOTOVAC 10A10

Septum Change

The Photovac 10A10 uses a Teflon-faced, silicon rubber, 6-mm diameter septum. The Hamilton "Micro Sep" F-138 is suitable. The septum can easily be replaced with the following procedure.

1. Unscrew septum retainer.
2. Remove the old septum using the needle of one of the gas tight syringes available for sample injection.
3. Insert the new septum, Teflon face down.
4. Carefully screw the retainer back into place firmly, but without overtightening.

A 10 to 20 minute stabilization period may be required due to a temporary interruption of the carrier gas flow when the septum is changed.

Column Maintenance

The standard Photovac 10A10 is equipped with a 4 foot by 1/8-inch OD Teflon tube packed with 3% SE-30 on 80/100 mesh Chromosorb G for field surveys and analyses requiring detailed separations. Normally the column will be connected for manual operation.

New columns must be conditioned overnight with ultrahigh purity helium (or nitrogen) at a temperature of 100°C and a flow rate of 10 cm^3/min. Reconditioning of older columns is accomplished under the same conditions.

To access the column, utilize the following procedures:

1. Never remove the panel while the instrument is connected to the main power supply.

Table F: Photovac Maintenance and Calibration Schedule

Function	Procedure/Frequency
Battery Charge (when instrument has been operating exclusively on wall current)	Charge for 10 hours on "low" setting; every 3 months.
Battery Charge (when instrument has been operating exclusively on batteries)	Charge for 1 1/2 hours on "high" setting for every hour of use (don't overcharge); after each use.
Calibration	Calibrate after every 24-hour period of use (see section 4.7.2).
Septum Change	Change after approximately every 40 sample injections (see section 4.7.5).
Column Reconditioning	Recondition every 3 months, after heavy use, or whenever installing a new column (see section 4.7.6).

2. Disconnect the AC cord.

3. Disconnect the chart recorder lead.

4. Disconnect the lecture bottle carrier gas supply.

5. Remove the four Phillips screws securing the panel to the case and remove the screw attaching the lid.

6. Grasp the panel assembly by the cylinder clamp. Gently lift the rear of the panel clear of the case rim and ease the panel assembly backward from the front rim. Lift the panel assembly clear.

7. Gently remove the wire harness connection from the circuit board into which it is plugged. Remove the nine Phillips screws from the gold box and lift clear the lid/circuit board subassembly. The interior of the column/ion cell chamber is now accessible.

8. To remove the column, locate the 2 compression fittings at either end of the column (ion cell body and injection port). Using a 5/16-inch, open-ended wrench, loosen these fittings. Unscrew the fitting with your hand and remove column.

9 To replace the column, reverse the previous steps and take special care not to damage the threads on the compression fittings. Fittings are made finger tight and then the 5/16-inch open-ended wrench is used to give an additional 1/8-inch turn to assure fitting seating.

PHOTOVAC 10S SERIES

UV Source

The ultraviolet light source is available to check proper performance. Occasional starting problems can be encountered. After switching the Photovac on, the LCD will respond with "Lamp not ready please wait." This is superseded by "Ready enter command" as soon as the lamp ignites.

Septum

The septum is 6-mm in diameter and composed of silicone rubber with a Teflon face. The Teflon face is always mounted downwards in the injection port.

1. To change the septum, take a spare syringe needle and push it down the septum retainer channel, so that it penetrates the septum.

2. Leaving the needle in place, unscrew the retainer and withdraw it, with the septum still impaled on the needle. Handle the new septum as little as possible between your fingers.

3. Using the left hand, position the new septum, (Teflon face down) at the end of the retainer and push the needle through with the right hand to hold the septum in the correct alignment.

4. Carefully screw the retainer back into position. The needle will maintain the septum in the correct position until it is seated.

The septum retainer must **not** be over tightened, as this will cause unusual resistance to penetration by the needle and may cause needle blockage.

Column Maintenance

The 10S Series Photovac is usually supplied with a 6-inch 5% SE-30 pre-column and a 4-foot 5% SE-30 analytical column suitable for field screening a variety of chlorinated and nonchlorinated alkene and aromatic compounds with adequate resolution. The SE-30 (dimethylsilicone gum) is a packed column. An alternative column, the CP Sil-5 (Dimethylpolysiloxane) capillary column, is also suitable for general field screening analysis.

New packed columns and heavily contaminated columns must be conditioned/reconditioned prior to use, using the column conditioning adaptor and UHP helium or nitrogen, at a flow rate of 5-10 cm^3/min, at 100°C overnight.

The capillary column is conditioned overnight with the same carrier gas. However, the maximum recommended temperature is 50°C if using the plastic encased capillary column supplied by Photovac International.

To access the column, utilize the following procedure:

1. Release the catch of the computer module located at the upper left hand corner of the module.

2. Raise the hinged module and secure in the open position.

3. Carefully unscrew compression fittings and remove the pre-column and analytical column.

4. To replace the columns, tighten the Teflon compression fittings, finger tight, being careful not to strip the threads, as this may result in leakage.

When the Photovac is not in use, it is advisable to maintain a carrier gas flow (2-5 cm^3/min) through the column and Photovac valve system. This will reduce possible contamination from outside sources, and off gassing of possible contaminants which may have accumulated in the detector or injection port. This will also aid in readiness for emergency response operations.

Batteries

The 10S Photovac portable GC uses a single 12V, 6-A rechargeable lead/acid battery. It is usually sufficient for at least 8 hours of continuous operation, depending on the duty cycle chosen for the valves in the case of continuous monitoring. The battery is guaranteed for 300 charge/discharge cycles which is equivalent to a year of very heavy activity.

A battery declining in charge will make itself known to the user by automatically shutting off the instrument. It will require an overnight charge.

In order to re-charge, connect the unit to the AC main. As long as the instrument is connected to the main, the batteries will be trickle charged or in a standby mode. Battery charging and monitoring are matters which are under the control of the computer; to check status, depress the "up arrow" key. Full charge will show 13.6 volts. When charging overnight, leave unit on with carrier flow at 5-7 mL/mm. This is equivalent to a high charge.

Printer/Plotter Service

As a general rule, this device requires little service beyond the timely replacement of pens and paper.

To replace a pen, turn the Photovac on and depress the <PEN> key. The pen turret will move to the right and stop. If the correct color Pen is uppermost, engage your fingernail in the ridges on the little nylon tab, located in the bottom right hand corner of the printer aperture and pull the tab towards you to eject the rear-end of the pen.

If the turret presents the wrong color pen for replacement, briefly depress the <PEN> key and the turret will rotate 90 degrees and present the next color, and so on. Lift the pen out and insert a new one, making sure that the ball tip passes through the tiny aperture in the metal plate located close to the writing surface. Press the rear-end of the new pen into its position in the turret and *briefly depress the <FEED> key to bring the* printer back "on line."

Both paper and pens are readily available from any "Radio Shack" or similar store. In the event of any difficulty in locating a supply, contact Photovac. Troubleshooting information and corrective action procedures can be found in Appendix C.

APPENDIX C

Troubleshooting Guides

Troubleshooting Guide for Photovac 10A10 SOP #2107

	Problem	Probable Cause	Remedy
1	No chromatographic response.	No carrier gas flow.	Check at *Out* port with flow gauge.
		Batteries flat (if on battery operation).	Plug into AC and check again.
		Electrometer saturated.	Turn "attenuation" to set meter to 0, if "offset" reads 10 or more, the instrument is saturated.
2	Unacceptable baseline drift.	Unit has been subjected to large temperature change.	Allow to stabilize until clear.
		A very concentrated sample has recently been introduced, resulting in excessive "tailing".	Allow to self purge until clear.
		Unacceptable contamination levels in carrier gas supply.	Change carrier gas supply and allow instrument to stabilize.
		The unit is charging and the resulting heat is affecting the column.	Turn *Charge* switch to *Off*.
3	Deterioration of sensitivity.	Syringe has leaky plunger.	Try new syringe.
		Column needs conditioning.	Condition column.
		Septum leaking.	Change septum.
		Column fittings leak.	Disassemble and check for leaks around fittings with soap solution, while under pressure.
		Deterioration due to ozone contamination after 1-3 years of operation.	Decrease attenuation; replace detector.
4	Unacceptable low frequency noise.	Column needs conditioning.	Condition column.
5	Peaks elute very slowly.	Carrier flow rate is too slow.	Increase flow rate.
6	Peaks eluting too fast.	Carrier flow rate is too high.	Decrease flow rate.
7	Peak has flat top.	Electrometer has saturated.	Lower injection volume. Pre-dilute sample and repeat.

	Problem	Probable Cause	Remedy
8	Peak is misshapen with considerable tailing.	Improper injection.	Repeat.
		Flow is too slow.	Increase flow.
		Improper injection technique.	Repeat.
		Peak is developing from an earlier injection.	Allow greater time between injections or install shorter column.
		Compound is wrongly matched to Column.	Select appropriate column.
		Power supply inadequate.	
9	Source off light stays on after 5 minutes.	Batteries low (if battery operated).	Plug in AC connector.
			Adjust potentiometer under aluminum cylindrical case by 45° clockwise increments.
		Wire attachments to power supply not secure.	Secure wire attachments.
		Tube driver mismatched.	Contact Photovac for advice (516)351-5800.
		Power supply inadequate.	
10	Electrometer does not return to zero.	Electrometer saturated.	Allow carrier flow for extended period without sample injection.

Troubleshooting Guide for Photovac 10S: Supplement to SOP #2108

Lamp won't light

Note: If the lamp won't light, turn the instrument off. If the instrument is left on for more than 3 minutes, the oscillator board will be blown.

1. First try tuning the lamp using the Photovac **plastic screwdriver**, at the detector chamber box. Lamp source tuning and replacement procedures follow.

   a. The Photovac UV source is located inside the black box marked PHOTOVAC, which is situated beneath the hinged electronic module. There is access for a special tuning tool, through an identified hole at the rear of the lid. The tool is provided and is located in a special clip on the front face of the black box. **Do not use a metal tool for this adjustment** as this may cause an electrical short circuit.

   b. Observe the "Lamp not ready, please wait" message seen on the LCD. Engage the tool in the slot of the small screw beneath the hole in the box lid. Rotate the screw slowly in a clockwise direction. You may have to make several slow rotations until the message changes to "Ready enter command." Note the screw repeats its setting every 360° of rotation. Once the "Ready" message appears, turn the instrument off (by pressing <ENTER>) and then turn it on again. After a maximum of 3 minutes the "Ready" message should return. If it does not, repeat the procedure. If unable to achieve the "Ready" state at all, it is probable that the lamp has failed. Proceed as follows:

   c. Turn the instrument off. Remove the four securing screws from the lid of the detector box. Inside you will see a white Teflon cylinder screwed into the right wall of the box. This cylinder is the lamp holder and has a silver wire wound around it in a spiral. There is a connecting wire attached to the free end of the lamp holder. Pull this gently out of its socket. Gently unscrew the lamp holder and withdraw it: you will see the lamp inside as you pull it away from the wall. Be careful not to drop the lamp. Take the new lamp, being very careful not to touch the window end with your fingers. Remove the old lamp and replace it with the new one. The O-ring on the lamp should be positioned about 5 mm from the end face of the window. Screw the holder back into place. **Make sure it goes in straight and is not cross-threaded.** Tighten until resistance from the O-ring is felt. Replace the connecting wire into its socket. Replace the lid and make sure all four screws are returned and are tight.

   d. The instrument is now ready to start; press <ON> and tune if necessary.

   e. Tuning also affects the amount of power consumed by the instrument (lamp). Press <TEST> and <ENTER> to obtain the status report. Check to ensure the value of "POWER" is in the 20 to 50 range (200 to 500 mA). If the power exceeds 50, the battery life will be shortened significantly. Try to aim for a reading of 35 to 40, consistent with a reliable starting.

   f. While you are tuning the lamp, you can also check the power consumption without printing the status report.

   g. Press <TEST> and type in "7853" and <ENTER>. The message "Lamp power" followed by a number, possibly "30," will show. Then you can tune the lamp accordingly.

2. If, after a few tries at tuning the lamp, it still won't light, turn off the instrument. Remove the detector chamber lid, remove the yellow wire from the *S* port on the oscillator board. Now turn on the instrument, and using the plastic screwdriver tune the lamp to its brightest violet color. Replace the yellow wire into the *S* port, and replace the detector chamber lid.

3. As a last resort, change the lamp. See procedure 1.c above.

No Flow -- Valves are Open

1. Check the carrier gas cylinder and regulator to ensure all valves are open.

2. Check flowmeter and injection port. If the injection port is over-tightened, the flow will be cut off.

3. Check column fittings (should only be finger tight) and check the plumbing configuration. If the GC is set up for serial flow, then either the green or black carrier gas tubing, the tee port on the capillary column, and the clear tubing coming from the top right side of the column chamber will be closed off. With the backflush setup the black carrier gas tubing will be going into the first port in valve 3. The green or blue valves 4 & 5, and the tee port on the capillary column will be hooked up to the last port in valve 3 via clear tubing.

Low Sensitivity

1. Leak in system.

2. Plugged syringe.

3. Gain too low.

No Peaks Appear

1. Plugged syringe.

2. Leak in system/no flow.

3. Check events (*Test* key) and all parameters; press <CHART ON WITH SETUP>, then press <START/STOP> and <ENTER>.

Keyboard Jam

1. A key is jammed when it won't respond to any commands. If one key is jammed the whole keyboard is jammed. To fix, lift off key with needle-nose pliers and lift up the metal tab with the needle-nose pliers. Replace the key and press down on the key, a clicking noise should be heard. Usually the last key pressed is the key that is jammed, also check the most frequently used keys.

2. As a last resort, hit the red reset button underneath the green piece of cardboard near the detector chamber. Re-enter all parameters.

Instrument Shuts Itself Off After Printing the Message, "Batteries low, AC power required"

1. This can be avoided two ways; first use a power surge cord, and second allow the GCs to run off their internal batteries for four (4) hours then charge overnight prior to taking the instruments out in the field. This will keep the batteries from going into deep discharge.

2. If the instrument does this out in the field, then run the GC using the Photovac external battery. (Note: it must be recharged every six hours.)

Pens won't Print

1. Check to make sure the paper is fed properly.

2. Check the metal tables in front of the printer barrel; they may be bent. With needle-nose pliers or tweezers, push the metal tabs towards the keyboard (away from the pen tips).

3. Make sure the metal pen holder on the pen barrel is not bent. Use a paint brush to brush away any dust from the printer.

Negative Baseline

1. Regular pressure is too low. Pressure should be 20-30 psi.

2. Check for a leak in the system.

3. Compounds from last run are going past the detector which causes the baseline to go negative, or the column needs more purging. An immediate fix is to put in two septa.

"Valve Remains On" Indicated on LCD.

"On" time greater than "off" time. Check "list" or "event" status on LCD.

Sensitivity Too Low

1. Calibration is wrong. Check.

2. Syringe is leaking. Check.

3. Probable leak in system. Finger tighten all suspect fittings. Check column attachments and injection port. **Do not over tighten fittings.**

4. Gain setting is too low. Increase.

5. Valve timing is wrong. Check EVENTS, it is possible that the backflush is too fast -- see above. It is also possible that injection time is too short.

6. Lamp is failing. Replace with spare and try again.

Peak appears but is not recognized

1. Peak not calibrated. Do qualitative calibration; see Exercise (8) in User's Manual.

2. Increase subsequent calibration frequency.

3 Check peak in library for proper ID, RT, and plotter numbers.

Peaks appear too slowly

Flow rate is too low.

Peaks appear too quickly

Flow rate is too high.

Battery life too short

Lamp power is too high. To get a status report, press <TEST> + <ENTER>. If "source power" is greater than 50, see Corrective Procedure 1 in Users Manual.

Printer/valve cycle is too frequent

If cycle time is 2 minutes you are using frequent full printout; battery life is reduced. Use external battery pack (Cat. No. SA202) or minimize print format.

Instrument uses carrier too fast

1. Flow rate is too high. Check flow rate.

2. Carrier gas is leaking. Tighten all fittings (especially on column). **Do not over tighten valve fittings.**

Troubleshooting Guide for the Micromonitor: Supplement to SOP #2111

If the ready asterisk (*) won't come on, perform the following:

1. Press the <METHOD> button. Note the temperature setpoint for column A. Press the <A/B> button. Note the temperature setpoint for column B.

2. Press the <STATUS> button. The display should show the status at the same value as the setpoint for B.

3. Press the <A/B> button. The display should show the status at the same value as the setpoint for A.

4. Press the <ENTER> button. The display should show a reading between 5 and 45 psig.

5. Press the <A/B> button. The display should show a reading in the same range of between 5 and 45 psig.

6. Press the <ENTER> button. The display should show a reading between +420 mV and -445 mV for the autozero voltage.

7. Press the <A/B> button. The display should still read in the above range.

8. If the temperatures are not correct, try waiting until they heat up or cool down.

9. If the pressures are not correct, check the supply or change the setting at the back.

10. If the autozero range is not correct, you may have a slowly eluting peak coming through the system.

11. Try increasing the temperature for a while to purge the column.

APPENDIX D

Figures

Figure 1: Pneumatics of Photovac 10S Series

SOP #2108

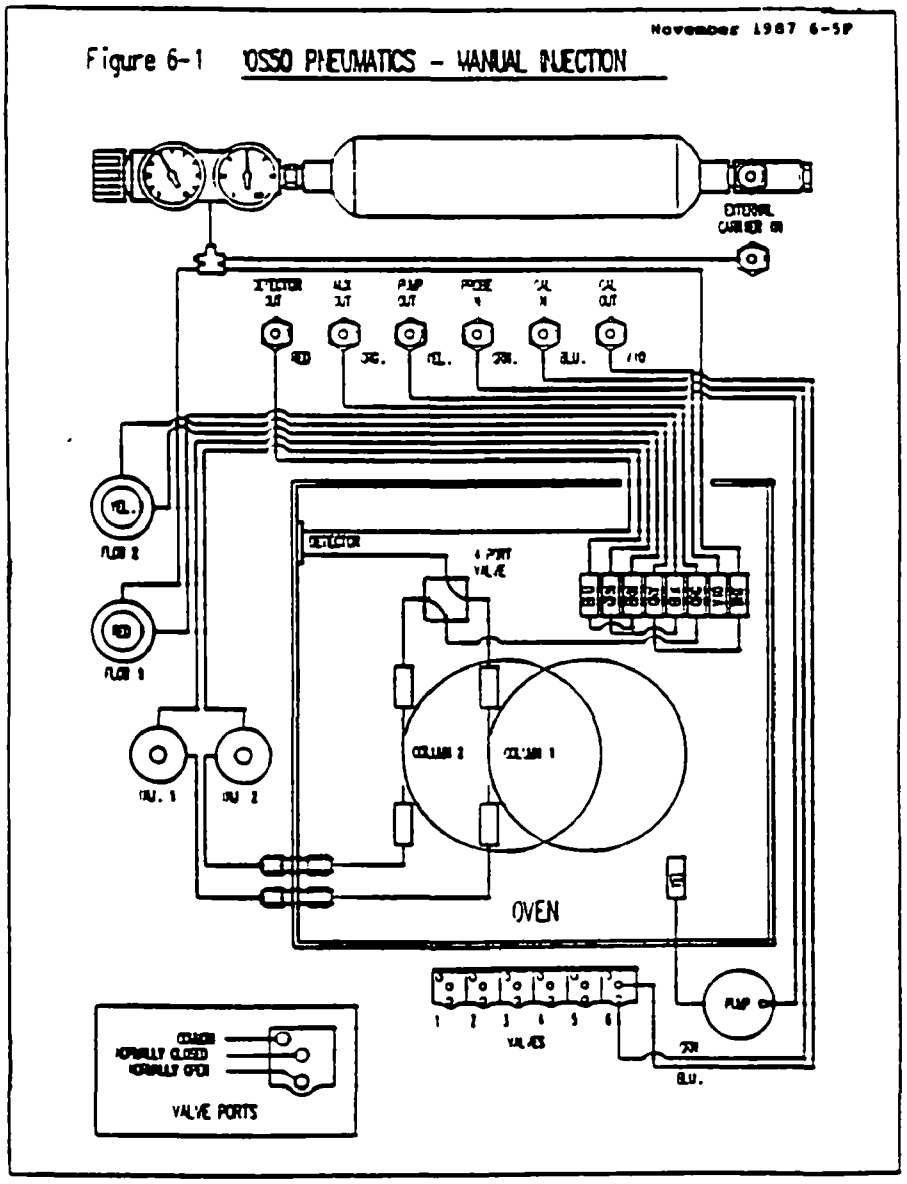


Figure 2: Micromonitor M200 Front Panel

SOP #2111

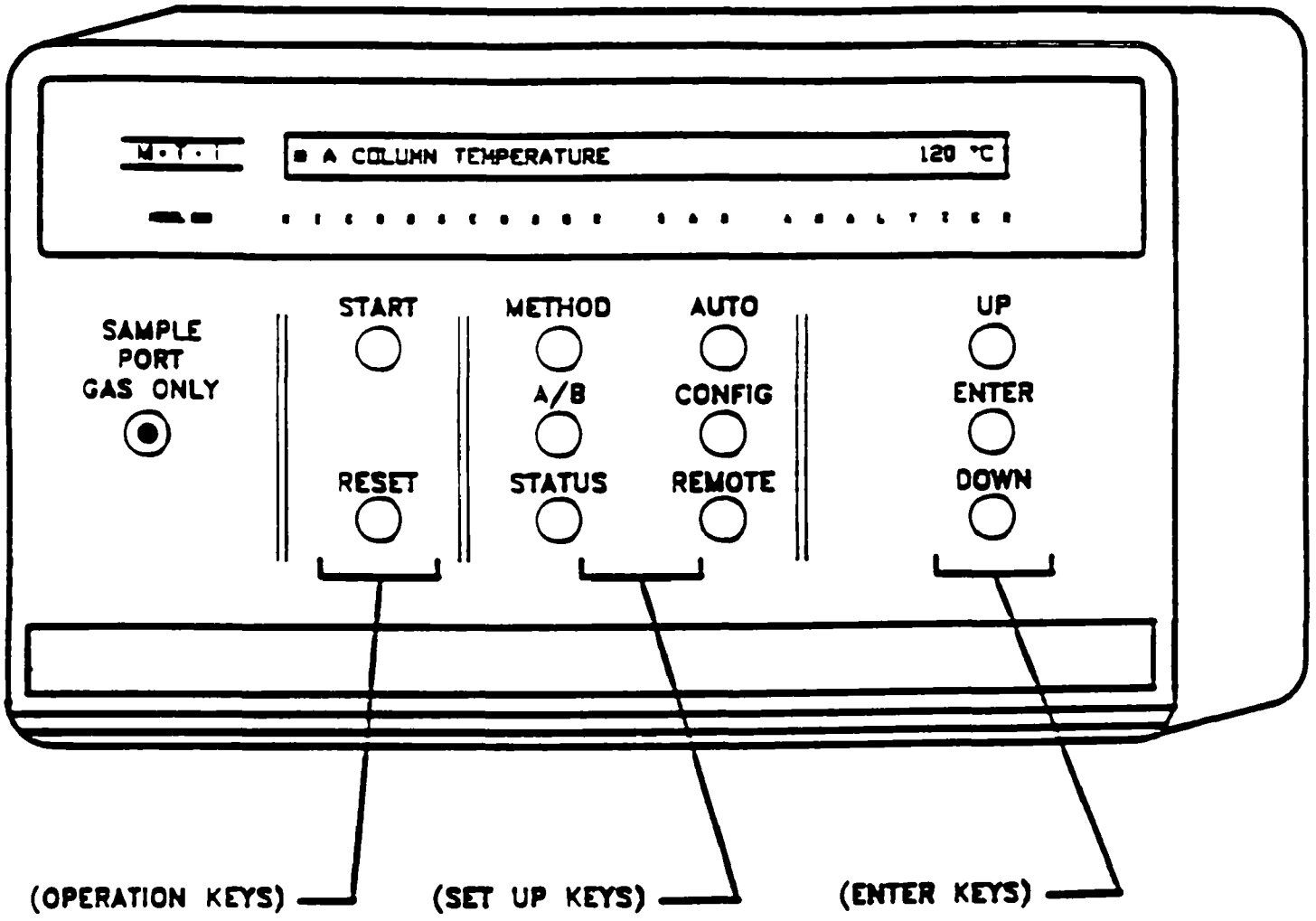


Figure 3: Systems Setup Diagram

SOP #2111

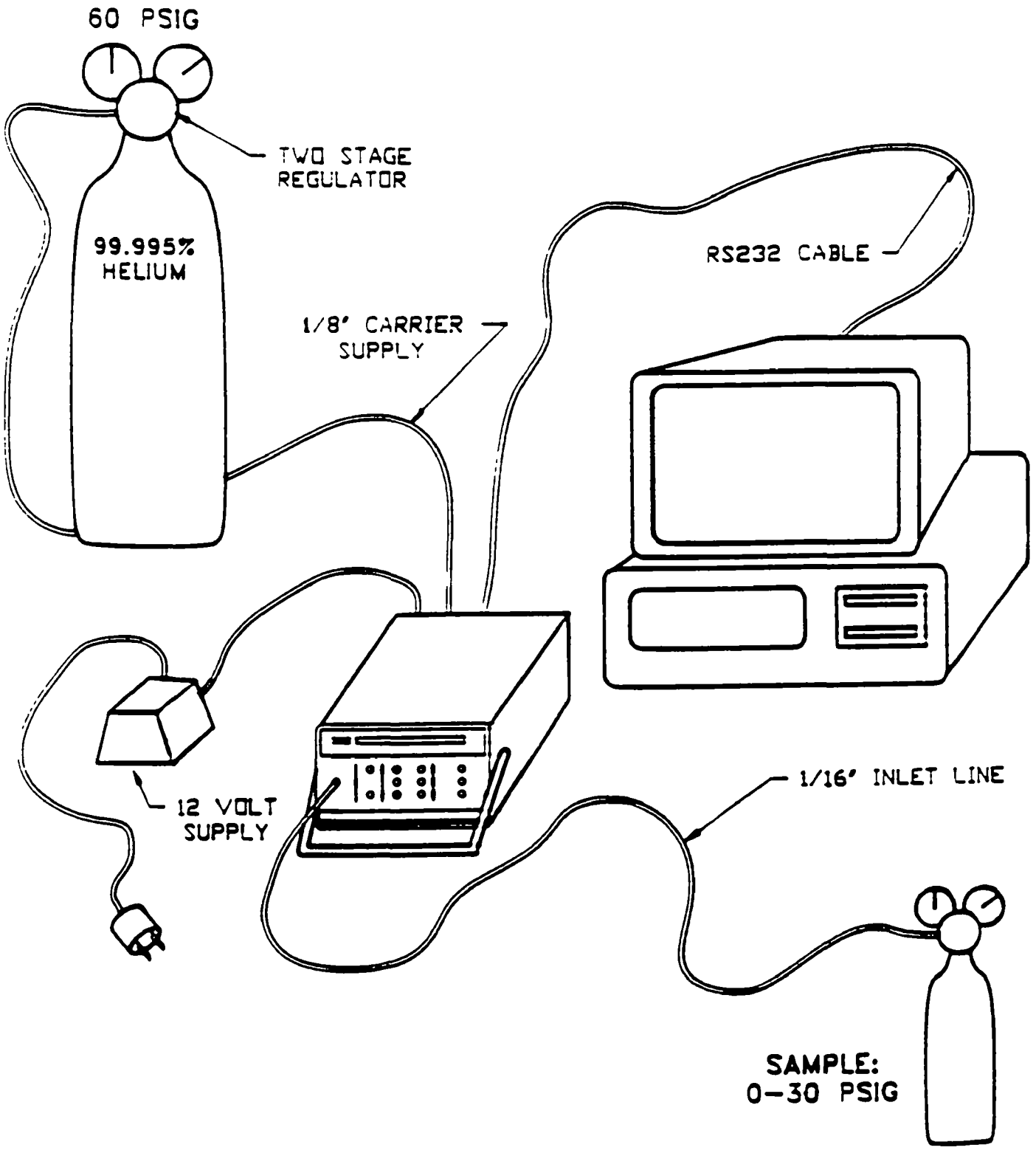
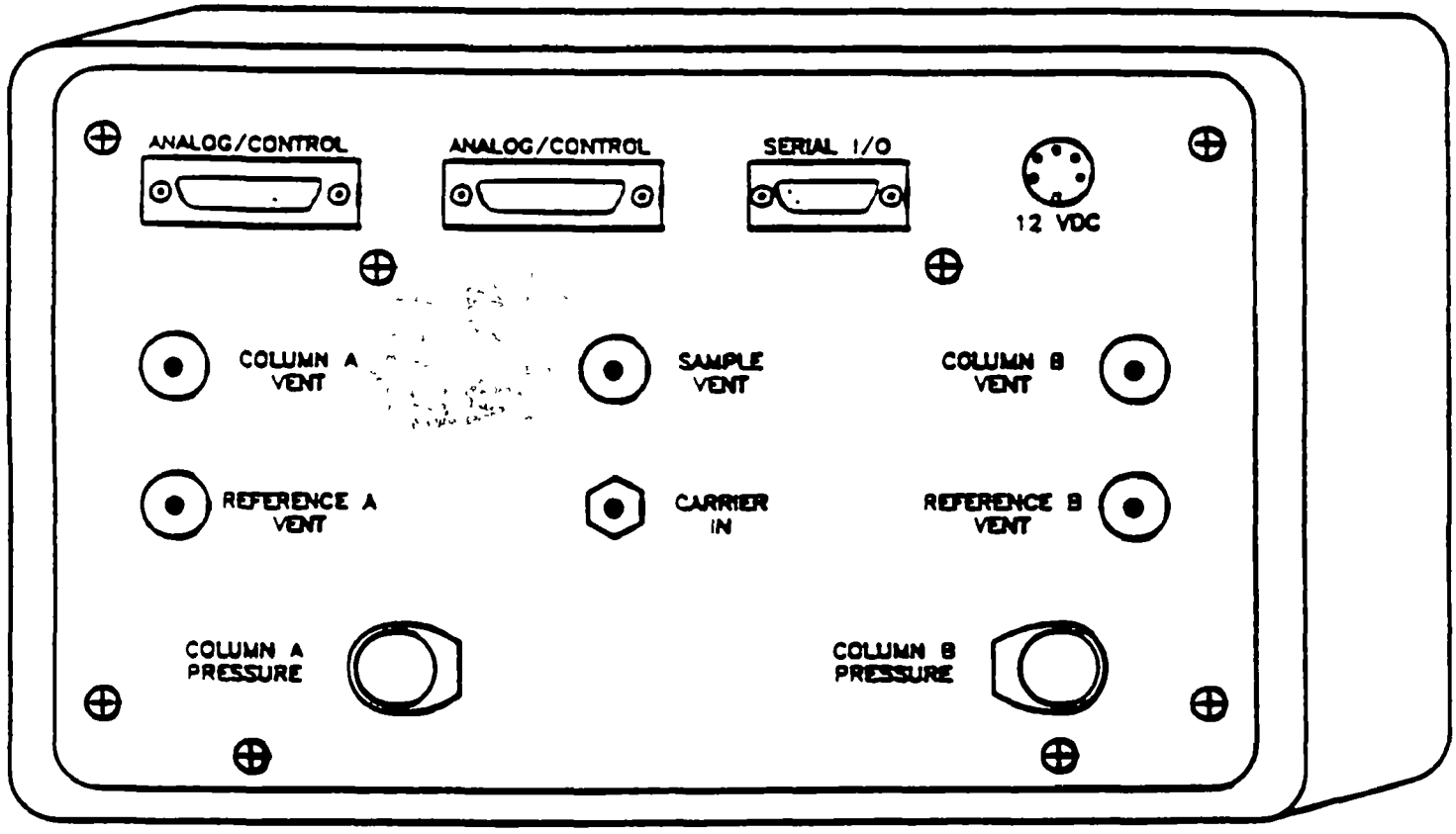


Figure 4: Micromonitor M200 Back Panel

SOP #2111



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