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ERR/ERP
OZAUKEE CO.

August 1, 1994

Ms. Pamela A. Mylotta
Hydrogeologist, Environmental Repair Program
Wisconsin Department of Natural Resources
4041 North Richards Street
Milwaukee, WI 53212

RE: Tecumseh Products Company
Grafton, Wisconsin, Plant

Dear Pam:

During our meeting with you, Scott Ferguson, and Kerry DeKeyser of Tecumseh Products on July 20, 1994, RMT presented the technical approach and conceptual workscope for evaluating the extent of chlorinated VOCs in groundwater under the Grafton facility. It is our understanding that you verbally approved the scope of the investigation at this meeting, but that we should not proceed with the field program until you have approved the proposed field methods.

As we described to you and Scott, the field investigation will generally consist of a series of soil borings in which vertical profiling of groundwater quality using a portable gas chromatograph (GC) will be performed. The portable GC results will be used in determining the locations and depths of groundwater monitoring wells. The field methods and portable GC procedures for this project are attached for your review. A complete workplan for the site investigation, including a project schedule, will be submitted to you next week.

Because we are making arrangements to begin drilling on Monday, August 15, 1994, we would appreciate receiving your comments on, or your approval of, the field methods and portable GC procedures on or before August 11, 1994. Please call either Kerry DeKeyser, at 414-898-5711, or me if you have any questions.

Sincerely,

Linda Hicken

Linda E. Hicken, P.E.
Senior Project Manager

gjg

Attachment

cc: Kerry DeKeyser, Tecumseh Products
Bruce McCuaig, Tecumseh Products

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FIELD METHODS

FIELD METHODS

1. Drilling and Soil Sampling

Soil borings will be advanced by a truck-mounted drilling rig using 4.25-inch-inner-diameter (minimum) hollow-stemmed augers (HSAs). Samples collected from unconsolidated material will be collected using a 2-inch-inside-diameter, split-barrel sampler (split-spoon) as described in ASTM D1586-84, with the exception that the sampler will be driven 2 feet. Soil samples will be collected at 2.5-foot intervals in the unsaturated zone and at 4-foot intervals below the water table. When the auger is advanced to the top of the desired sampling interval, the decontaminated split-spoon will be lowered into the hollow-stemmed auger on the end of an appropriate drill rod. The split-spoon will be driven 24 inches or to refusal (more than 60 blow counts per 6 inches) using a 140-pound weight. The number of blows required to drive each 6-inch increment will be noted by the driller and also recorded by RMT personnel. Once driven, the split-spoon and rod will be withdrawn from the auger, and the split-spoon will be removed from the rods. The split-spoon will be opened, and the amount of sample recovery will be measured. Samples will be taken from the split-spoon for physical identification and field-screening for VOCs. If a low-permeability clay till is encountered in the bottom 10 feet of the unconsolidated material, samples will also be collected for chemical analysis. The split-spoon will be decontaminated before each sample is collected. (See Subsection 3.2 for decontamination procedures.)

A portion of each sample collected during soil sampling will be retained to develop a log of the borehole. Soil samples will be classified according to the Unified Soil Classification System (USCS), in accordance with ASTM D2488-90. Boring logs will be prepared on WDNR Form 4400-122 in accordance with Chapter NR 141, Wisconsin Administrative Code.

Soil borings that are not converted to groundwater monitoring wells will be abandoned by backfilling the borehole to the ground surface with a bentonite slurry grout using a tremie pipe. Borehole abandonment will be documented on WDNR Form 3300-5B in accordance with NR 141. The area around the borehole will be restored to its original condition.

2. Groundwater Sampling using a Hydropunch Sampler

Groundwater samples will be collected at 4-foot intervals in the deep borings using a Hydropunch II sampler. The groundwater samples will be collected at alternating intervals with the split-spoon soil samples. When the auger is advanced to the top of the desired sampling interval, the Hydropunch II will be lowered into the hollow-stemmed augers on the end of an appropriate drill rod. The Hydropunch II will be driven 24 to 30 inches beyond the end of the augers. The tool will then be pulled back approximately 6 inches to expose the intake screen. From 5 to 15 minutes will be required to collect sufficient groundwater for the in-field GC analyses. The Hydropunch II will be withdrawn and opened, and the groundwater will be transferred to a glass vial with a Teflon® septum seal. The vial will be taken to the in-field GC for immediate analysis.

The Hydropunch II will be decontaminated between each sample using the procedures outlined in Subsection 3.2.

3. Decontamination Methods

3.1 Drilling Equipment

The downhole equipment (both augers and drill rods) will be steam-cleaned before startup and after each boring. Decontamination of the drilling rig and downhole equipment will take place on a temporary decontamination pad constructed at an on-site location specified by the Owner. Decontamination water will be placed in WDOT-approved, 55-gallon drums that will be labeled and stored on-site pending the results of the groundwater analyses.

3.2 Sampling Equipment

Precautions will be taken to minimize the potential for contamination between samples. The split-spoon sampler will be cleaned prior to its initial use on-site and between samples. Cleaning procedures will involve scrubbing away soil material with a stiff brush using a trisodium phosphate soap and water solution, and then double-rinsing in clean, potable water.

At the end of drilling at a borehole, the split-spoons will be steam-cleaned, followed by the washing and rinsing procedures. Other reusable sampling equipment (bowls, spatulas, etc.) will be decontaminated by the washing and rinsing procedures. Spent decontamination liquids from the sampling equipment will be handled in the same manner as the water from the drilling equipment decontamination procedures.

4. Investigation-Derived Wastes

Soil cuttings generated during the performance of the soil borings will be placed in WDOT-approved, 55-gallon drums, and will be labeled and stored on-site. The soil cuttings will be segregated on the basis of the field GC results. A composite soil sample will be collected from the material that had field GC detections and from the investigation-derived soil that was stored on-site from previous field activities. The composite soil sample will be analyzed for the volatile, semivolatile, and metals fractions of the TCLP to assist in determining the disposal requirements for the investigation-derived waste.

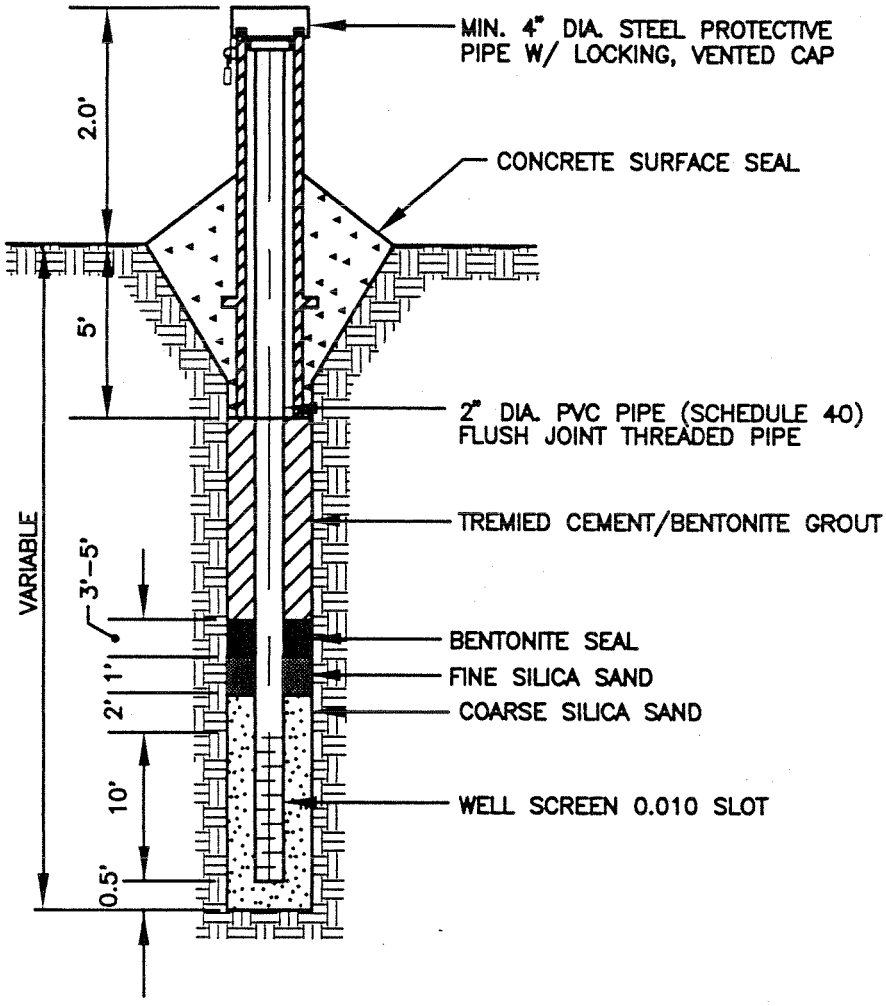
Purge and development water will be placed in WDOT-approved, 55-gallon drums, and will be labeled and stored on-site pending the results of the groundwater analysis.

5. Portable Gas Chromatograph Analyses of Soil Headspace

Soil and groundwater samples will be field-screened for selected VOCs using a portable gas chromatograph (GC). A Photovac® Model 10S50 GC will be used for the VOC screening. The portable GC analysis will be used to characterize the presence and relative concentration of representative VOCs in the soil headspace on a near real-time basis. The soil headspace will be analyzed for trichloroethene (TCE), 1,1,1-trichloroethane, toluene, and total xylenes. Standard operating procedures for the portable GC are included in Appendix B.

6. Groundwater Monitoring Well Installation and Development

The groundwater monitoring wells will be constructed using 2-inch-diameter Schedule 40 PVC with flush-threaded joints. The water table wells will be constructed as shown on Figure 1 and will have 10-foot-long well screens. The piezometers will have 5-foot-long well screens and will be constructed as shown on Figure 2 with the exception of MW-8D, which will have



WATER TABLE WELL CONSTRUCTION DETAIL

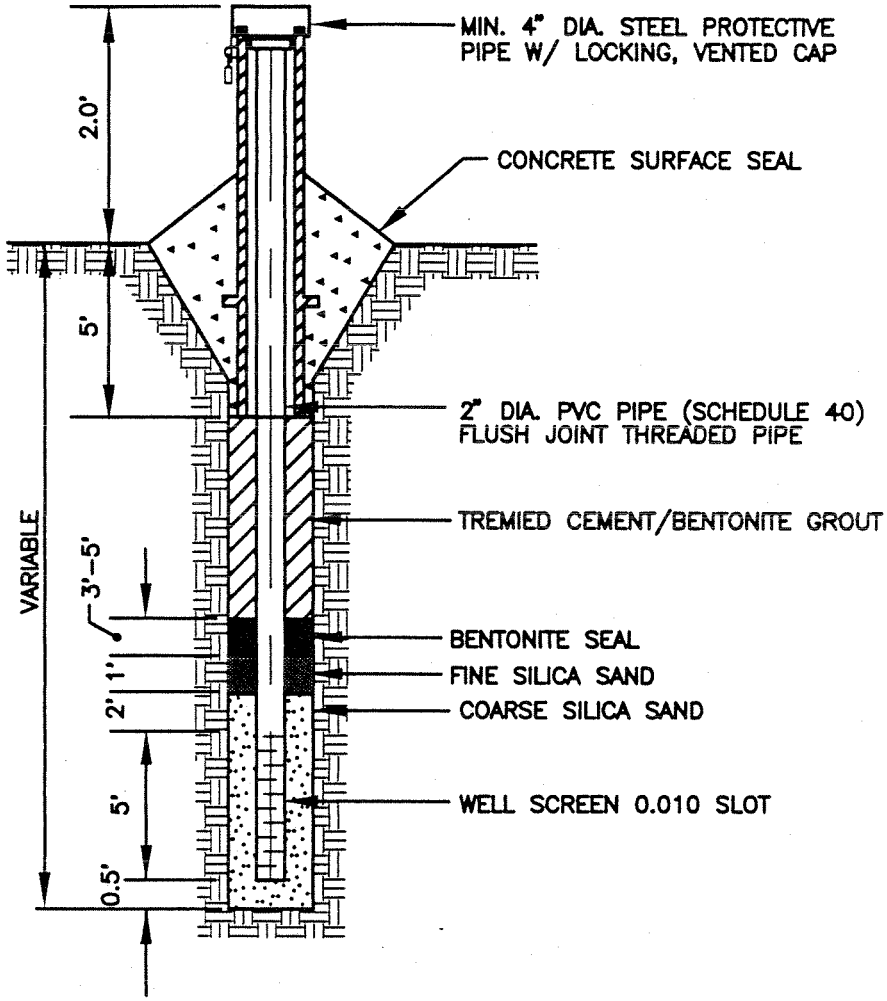
TECUMSEH PRODUCTS COMPANY GRAFTON, WISCONSIN

RMT INC.

DWN. BY:	DPR
APPROVED BY:	
DATE:	JULY 1994
PROJ. #	3084.01
FILE #	30840105

FIGURE A-1

$$DWG$$
$$PRF$$
$$SCALE$$



PIEZOMETER CONSTRUCTION DETAIL
(STICK-UP SURFACE CASING)
TECUMSEH PRODUCTS COMPANY
GRAFTON, WISCONSIN

RMT INC.	DWN. BY: DPR
	APPROVED BY:
	DATE: JULY 1994
	PROJ. # 3084.01
	FILE # 30840106

FIGURE A-2

$$DWG$$
$$PRF$$
$$SCALE$$

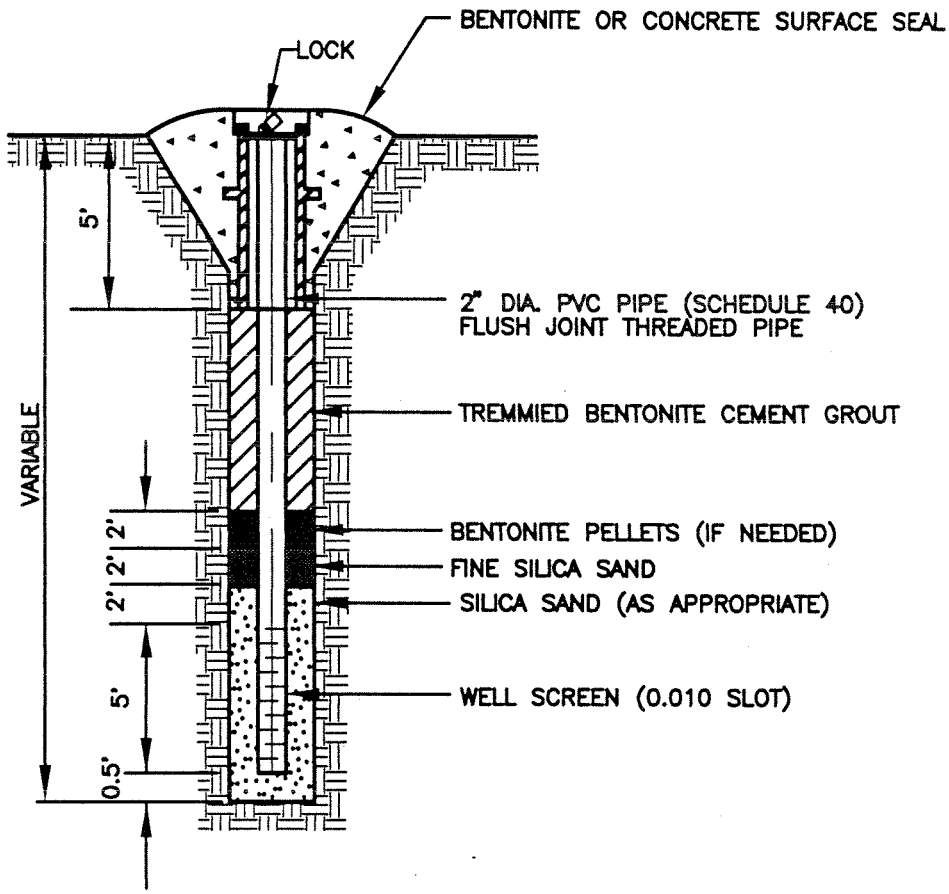
a flush-mount surface cover because of its planned location in the recycling dock area. MW-8D will be constructed as shown on Figure 3. As-built well construction diagrams will be prepared on WDNR Form 4400-113A.

The proposed water table monitoring well (MW-9) will be installed in a soil boring that will extend to approximately 7 feet below the water table. The proposed piezometers will be completed in the zone of highest contamination as determined by the portable GC. If no VOCs are detected with the portable GC, the piezometers will be installed in a sand layer at or near the bedrock surface.

The monitoring wells will be installed through the augers (minimum inside diameter of 4.25 inches). The bottom of the well will be firmly seated on sand, and the sand pack (medium-grained silica sand) will extend approximately 2 feet above the well screen. A 2-foot-thick fine silica sand layer will be placed on top of the filter pack, and a 2-foot-thick bentonite pellet seal will be placed over the fine sand. The remaining annular space above the filter pack seal will be filled with a bentonite slurry grout. A lockable protective steel pipe will be placed over the riser pipe.

After completion of the well installations, the wells will be developed in accordance with NR 141, Wisconsin Administrative Code, to improve the hydraulic connection between the well and the surrounding formation and to reduce the amount of sediment in the groundwater samples. The wells will be developed by surging a dedicated bailer across the screened interval of the well for 10 minutes, and then pumping the well until 10 well volumes have been removed or until the well is bailed dry three times. Well development will be documented on WDNR Form 4400-113B.

The vertical elevation of the top of the PVC casing of each well will be surveyed to an accuracy of 0.01 foot and will be referenced to the National Geodetic Vertical Datum (NGVD). The horizontal location of each well will be referenced to a site datum.



PIEZOMETER CONSTRUCTION DETAIL
(FLUSH-MOUNT COVER)
TECUMSEH PRODUCTS COMPANY
GRAFTON, WISCONSIN

DWN. BY:	DPR
APPROVED BY:	
DATE:	JULY 1994
PROJ. #	3084.01
FILE #	30840107

FIGURE A-3

$$DWG$$
$$PRF$$
$$SCALE$$

7. Groundwater Sampling and Decontamination Procedures

Static water levels will be measured in the monitoring wells prior to purging or sampling. All groundwater level measurements will be made using a reference point established on the well casing. The reference point will be the highest point of the well casing. In order to prevent cross-contamination, the water level measuring device will be decontaminated between wells by rinsing first with a soapy water solution and then with distilled water.

The monitoring wells will be purged to remove stagnant water to ensure that the samples collected are fresh formation water. Before sampling each well, a total of four well volumes will be purged.

Groundwater samples will be collected from the monitoring wells immediately after purging. The procedures for the sampling of the monitoring wells are as follows:

- Set up and prepare meters.
- Prepare bottles by writing the date, the sampler's name, and the time of day in the sampler section.
- Collect a sample from the monitoring well using a pre-cleaned PVC bailer and a bottom-discharging device to prevent excessive amounts of agitation and aeration. The bailer will be dedicated for use in only one well.
- Place the samples on ice immediately.
- Perform field measurements for pH, temperature, and specific electrical conductance.
- Complete documentation of the sample collected in the sample log book and on the chain-of-custody forms.

The tests conducted in the field and the instrument calibration procedures are described below:

- ***Temperature*** - The temperature of the groundwater sample will be recorded immediately after the sample is removed from the well.
- ***Specific Conductance*** - The specific conductance of the liquid will be measured in the same groundwater sample used for the temperature measurement. A portable specific conductance meter will be used to measured the specific conductance of the groundwater sample.

- ***pH*** - The pH measurements will be made electrometrically using a combination electrode and portable pH meter. Portable meters with provisions of temperature compensation will be used. The meter and electrode will be checked against standard buffer solutions of known pH values (4 and 7).

All equipment used for sampling that is not dedicated (e.g., bailers, water level measuring devices, etc.) will be decontaminated prior to initial use by the following methods:

- Prepare a soapy water bath using laboratory-grade detergent.
- Unwind and soak water level measuring devices in soapy water, and wipe clean with a cloth.
- Rinse all equipment with tap water.
- Rinse all equipment, except water level measuring devices, inside and outside with diluted 1:1 nitric acid.
- Rinse all equipment with deionized water.
- Dry all equipment, except water level measuring devices, in the oven at 105°C, and seal in polypropylene plastic to prevent contamination.

The procedures to be followed for cleaning equipment in the field between wells are as follows:

- Rinse all equipment with soapy water.
- Rinse all equipment with distilled water.
- Place rinseate in WDOT-approved 55-gallon drums, and store at an on-site location specified by the owner.

8. Hydraulic Conductivity Testing

In-field hydraulic conductivity testing will be performed on monitoring wells completed in sandy soil. If visual observations of the soil suggest that the hydraulic conductivity of the soil is greater than 10^{-4} cm/s, a pressure transducer coupled to a data logger will be used to record the recovery of hydraulic head following an instantaneous head change produced by a solid PVC slug. Lower permeability soil will be tested by removing water from the monitoring wells with a bailer and recording recovery rates with an electric water level indicator and clock.

The recovery data obtained by either of the methods described above will be analyzed using the methods described by the following:

Bouwer, H., and R.C. Rice. 1976. A slug test for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells. *Water Resour. Res.*, 12: 423-428.

Hvorslev, M.J. 1951. Time lag and soil permeability in groundwater observations. U.S. Army Corps of Engineers, Waterways Expt. Sta. Bull 36.

9. Chain-of-Custody Procedures

The possession of samples will be traceable from the time of collection through the use of chain-of-custody procedures. Specific chain-of-custody forms will accompany all sample shipping containers to document the transfer of the shipping containers and samples from the field collection point to the laboratory receiving the samples for analysis. The procedures to be implemented are as follows:

- Properly identify and label the samples in the field.
- Complete a chain-of-custody form in the field, indicating sample identification, containers filled, sampling date, sampling time, and sample collector's name.
- Pack shipping container with samples, chain-of-custody forms, and ice. The sample container should be assigned a chain-of-custody form, which travels with the container.
- Seal, date, and ship the coolers to the appropriate laboratory using an overnight delivery service or via RMT field vehicle.
- Receive and check shipping containers in the laboratory for broken seals or damaged sample containers.

RMT STANDARD OPERATING PROCEDURE FOR PORTABLE GAS CHROMATOGRAPH ANALYSIS

RMT STANDARD OPERATING PROCEDURE FOR PORTABLE GAS CHROMATOGRAPH ANALYSIS

1. Parameters To Be Analyzed

The four parameters to be analyzed by the portable GC are trichloroethene, 1,1,1-trichloroethane, toluene, and total xylenes. These parameters were selected on the basis of previously identified constituents in groundwater and soil, and on the sensitivity of the portable GC to these parameters. The peak area of targeted parameters will be determined for each sample. Quantitation of the specified compounds is determined by comparing peak areas of standards to those of samples.

2 & 3. Range of Measurement and Limits of Detection

The anticipated working linear range and limits of detection are presented in Table 1. These detection limits are based on the concentration represented by the minimum recorded peak area for the GC (0.1 v-sec) at normal operating conditions. The maximum measurable concentrations for the different parameters are around 1,000 μL/L (parts per million by volume). The μL/L (or ppm) units will be used to avoid confusion between concentration units in water and air.

4. Sample Matrix

As a means of screening soil samples for VOC contamination, the headspace over the soil sample is measured for the VOCs. Thus, the sample matrix is air that has been contacted with the sample. Headspace measurement evaluates soil concentrations indirectly by determining the parameter concentration in the air in contact with the soil (i.e., the headspace). Parameter distribution between the soil and headspace is affected by a number of soil and parameter properties, including the parameter Henry's Law constant, and soil organic and water content and consistency. Since some of these properties can vary between samples, the parameter distribution between the soil and headspace can vary between samples. Headspace measurement thus does not give a direct measurement of parameter concentration in the soil, but rather gives a qualitative indication of the soil concentration.

TABLE 1

DETECTION LIMITS FOR CHLORINATED AND BTEX COMPOUNDS ANALYZED BY PORTABLE GC

Parameter	µL/L
Trichloroethene	0.01
1,1,1-Trichloroethane	0.3
Toluene	0.03
m,p-xylene	0.03
o-xylene	0.04

VOC concentrations in water can be estimated by measuring the headspace concentration over the water in a VOA vial. At equilibrium, the VOCs partition between the headspace and water in accordance with Henry's Law, as follows:

$$H = (\text{concentration in air})(\text{concentration in water})$$

where H is a constant

Standards will be prepared using the procedures suggested by Photovac® Technical Bulletin #27 (Attachment 1). The standards are analyzed at the same time as the samples, and each parameter's operational partitioning coefficient is calculated. The operational partitioning coefficient is the reciprocal Henry's Law constant, with the effects of temperature, equilibration time, kinetics, and relative volumes of water and headspace included.

The operational partitioning coefficient (OPC) is calculated as follows:

$$OPC = \frac{(\text{original concentration in water, } \mu g/L)(\text{gain})(\text{injection volume})}{\text{concentration in headspace, v-sec}}$$

Water concentrations are determined by preparing samples and standards, and then multiplying the sample concentration by the OPC and dividing by gain and injection volume, as follows:

$$\text{Water concentration, } \mu g/L = \frac{(OPC)(\text{GC response, v-sec})}{(\text{gain})(\text{injection volume, } \mu L)}$$

5. Principle, Scope, and Application

Headspace analysis is a convenient means of screening for VOC contamination. In principle, VOCs contained in soil or water will partition between the matrix and any air in contact with the matrix, with partitioning dependent on the VOC concentration in the matrix as well as on several other factors (Devitt, et al., 1987). Analysis of the soil headspace can be done in the field using a portable gas chromatograph, and can provide near real-time screening analysis of VOCs. Due to the variety and variability of factors that influence VOC partitioning between the matrix and air, headspace analysis is best used for screening VOC levels rather than for quantitatively analyzing the VOC content in the field. However, measurement of the VOC concentration in the gas itself is a quantitative measurement.

Headspace screening is useful for locating areas of contamination and relative levels of contamination, for selecting samples for further laboratory analysis, and for determining the areas that should be further investigated (e.g., soil borings or monitoring well installation).

6. Interferences and Corrective Action

Interferences are uncommon in the analysis for the parameters analyzed under standard operating conditions. However, components of gasoline coelute with di- and trichloroethlene and, if gasoline is present, it is difficult to quantify di- and trichloroethlene. Generally, however, gasoline and the chlorinated ethylenes are not found in the same sample. In addition, ethylbenzene and m- and p-xylene peaks overlap. If both peaks are present, the peak is calculated as if it contained the constituent giving the large peak, and a note is made that both compounds were present.

Dirty apparatus can cause problems with a portable GC, since many surfaces (notably teflon) can adsorb and desorb gaseous constituents. Several precautions and cleanup steps are used to avoid such cross-contamination. First, standards are transported separately from the syringes, septa, etc., so that no cross-contamination during transport occurs. Second, column and syringe blanks are run whenever contamination is suspect. Third, syringes are cleaned between each run by removing the plunger and allowing the contamination to disperse, or by purging the syringe or plunger with compressed air from the air cylinder. If syringe contamination is suspect, a syringe blank is run in which room air or compressed air is injected into the GC with the syringe in question. Syringes that remain contaminated after purging are baked overnight in a portable oven. Typically, ambient air contamination has not been found to be a problem.

7. Safety Precautions

Samples are contained in 40-mL VOA vials, and the analyst does not come into direct contact with the soil. If soil needs to transferred from one vial to another, or if a vial breaks, then the analyst will take the normal precautions used when working with chemicals, e.g., washing hands after working with the material, not eating while handling the material, etc. All pure solvents used for making standards are likewise kept in 40-mL VOA vials, and the analyst does not come into contact with the solvents.

Standard laboratory practice precautions are taken when working with the gas cylinders used for gas supply to the GC. The cylinders are either secured to the wall by chains or, in places where no wall mountings are available, supported by a gas cylinder stand.

8. Sample Size, Collection, Preservation, and Handling.

Water and soil samples are collected in 40-mL VOA vials with a septum top. If the samples are analyzed in the field, the vials are filled approximately half full with soil when the sample is collected. If the samples are analyzed in the laboratory, the vials are filled completely in the field, and a second vial is then filled half full in the laboratory. The vials are then allowed to equilibrate at room temperature for at least 30 minutes. No preservatives are used in the samples. After the equilibration time, an aliquot of the headspace is removed with a syringe through the septum, and is injected into the GC for analysis. Injections are repeated until the peaks of interest are on scale. The sample is discarded by either returning the vials to RMT Laboratories or by returning the soil to the sampling area. At RMT Laboratories, the vials are opened in a hood, and the VOCs are allowed to volatilize, after which the soil is discarded. After the soil has been removed from the vials, the empty vials are discarded.

9. Apparatus

The GC used is a Photovac® Model 10S50 Portable Gas Chromatograph. Other sampling equipment used for the headspace analysis is listed in Table 2.

10. Routine Preventive Maintenance

The routine preventive maintenance procedures used in day-to-day operation of the GC are described in section 14 below. The procedures include running column and syringe blanks at the start of a day's operation, and when syringe or instrument contamination is suspected. The injection port septa is changed after 50 to 75 injections. VOA vial blanks are run if vial contamination is suspected. Vial contamination would be suspected if similar peak patterns were found in several soil samples from different areas.

TABLE 2

PORTABLE GC FIELD EQUIPMENT CHECKLIST

EQUIPMENT	# NEEDED	CHECKOFF
INSTRUMENTS		
Photovac® 10S50		
Battery pack for oven		
Electrical cord for using GC with 110 V		
Electrical cord for charging battery pack		
Electrical cord for GC from battery pack		
Gas flow meter and connecting gas lines		
Gas tank regulator and connecting lines or internal tank refill gas line		
0.1-ppm grade air tank		
GC SUPPLIES		
Plotter pens		
Plotter paper		
Extra UV lamp		
White Teflon®-coated septa for GC		
PAPERWORK		
Field GC logbook		
Field notebook		
Photovac® GC instruction manual		
SYRINGES		
10 µL		
25 µL		
100 µL		
250 µL		
1,000 µL		
Syringe needles		

TABLE 2 (CONTINUED)

PORTABLE GC FIELD EQUIPMENT CHECKLIST

EQUIPMENT	# NEEDED	CHECKOFF
SAMPLE CONTAINERS		
VOA vials		
1-L gas sample bottles		
250-mL gas sample bottles		
Green septa for sample bottles		
Labels for vials/sample bottles		
Standards (pure solvent/gas STD)		
TOOLS		
Adjustable wrench for gas cylinder		
Small wrench for gas line fittings		
Slotted screwdriver		
Phillips head screwdriver		
MISCELLANEOUS		
Kim Wipes®		
Paper hand towels		
Markers		
Pens		
Calculator		
Knife		
Rubber bands		
Paper clips		
Water bottle		

The neat solvents used for preparing standards are stored and transported separately from the other GC equipment to avoid cross-contamination. Septa, syringes, and the plastic portions of the gas sample bottles are stored in organic contamination-free areas.

A common analytical problem is clogging or partial clogging of the injection syringe needles. Occurrence of partial clogging is determined by running replicate samples. If the results cannot be replicated after several runs, the syringe needle is changed. Clogged syringes are detected by injecting air into a water-filled vial. If no bubbles are observed, then the needle is changed.

11. Reagents and Calibration Standards

Pure solvents and calibration standards are purchased from chemical supply companies. Commercially prepared gas standards are purged into the gas sample bottles from pressurized gas cylinders. An example of standard concentrations is shown in Table 3. Water standards are prepared by appropriate dilution of pure solvent. Water standards are prepared in 40-mL VOA vials using methanol and water as dilutents. The final working solution contains 20 mL of liquid in the 40-mL VOA vial. The constituents in water are allowed to come into equilibrium with the headspace of the VOA vial prior to injection of this headspace to the GC. A new standard is prepared when the septum on the gas bottle becomes too perforated, or when the solvent volatilizes through the septum. A Photovac® Model 10S50 can analyze only phase-phase samples, so all samples and standards must be in the gas phase prior to injection.

Chromatograms of the standard are compared with previous standard chromatograms to ensure that the standard was prepared properly.

12. Calibration Procedures

A. Standards should be prepared according to the protocol given above.

TABLE 3

EXAMPLE OF A COMMERCIALLY PREPARED STANDARD

Compound	Gas Concentration ppm (μL/L)
Trichloroethene	15.4
1,1,1-Trichloroethane	150.0
Toluene	19.9
Total xylenes	82.0

B. A standard should be run after the column blank when starting the instrument. For the most accurate results, standards should be prepared daily. The standard can be used for calibrating the instrument response factor on the first run or runs, and then for peak identification for the rest of the day.

C. After the instrument is calibrated, a second standard should be run to verify that the first standard is reasonable. If the results differ by more than 5 percent, rerun and recalibrate (if necessary) the instrument using a different syringe or a different needle.

D. Record on the strip chart both the V-sec and ppm readings on standards that are used for calibration, so that the calibration factor the instrument is using can be calculated.

E. If there is a question on the identity of a given peak in a sample run, run a standard to determine the retention time of the compound of interest. Peak identification by the GC can be in error if the airflow rate or column temperature drift. The analyst should be familiar with the peak patterns of the compounds of interest, check to ensure that the GC is correctly identifying peaks, and check retention times against standards if any questions arise.

13. Sample Preparation

Sample preparation is discussed in Section 8 above.

14 & 15. Step-by-Step Analytical Methodology

The daily operation of the GC, including routine procedures, preventive maintenance, and daily quality control procedures, is described below:

A. Connect the power supply for the GC (unless using the internal battery).

B. Connect the battery for the column oven to the external DC input connector. Set column to the desired temperature, and allow to heat for approximately 30 minutes to reach operating temperature.

C. Connect the exhaust gas lines to the gas flow meter. The left side of the flow meter measures flow through the detector and is connected to the "Detector Out" port, while the right side is connected to the needle valve on the "Aux Out" post.

D. Connect the input gas lines, turn the gas flow on, adjust the flow through the column, and backflush to the appropriate values. The backflush flow should be set slightly higher than the column flow. If using the internal tank, fill the tank before adjusting the flow. The gas flow through both the detector and backflush lines is set by the "A + B" valve at the center left of the front panel. The backflush flow is also controlled by the "Aux Out" needle valve. Note that the internal gas pressure should be set at 40 psi.

E. Turn the instrument on (Note: gas must be flowing past detector before the lamp is turned on). The instrument will read "LAMP NOT READY. PLEASE WAIT" for a few minutes after turning the instrument on. If the lamp does not come on after several minutes, as indicated by the instrument reading "READY," turn the instrument off ("OFF", then "ENTER") and then back on, and wait for a minute. If the lamp still does not turn on, use the special Teflon® screwdriver to adjust the lamp power supply on the lamp box inside the unit. If the lamp still does not light, change the detector bulb.

F. Set daily information, using USE button. Also enter project information, if necessary, using INFO button.

G. If you are not sure of the GC's valve timing, press "TEST" then "ENTER." The GC will print out the Event timing. Event 1 should be set for an ON time of 8 (sec) and one OFF time of 10 (sec). Event 1 controls the buzzer for sample injection, and the injection port sequence. Event 3 controls the backflush start time. The ON time should be 0 (sec), and the OFF time should be one-fourth to one-fifth of the retention run time of the slowest analyte of interest. The run time is set by the CYCLE button.

H. Set gain to desired value. (Note: Gain defaults to 2 when instrument is turned off.)

I. Change septum on injection port, if necessary (septa are good for approximately 50 injections).

J. Prepare daily injection log. All runs should be recorded on log.

K. Run a column blank (no injection) and a syringe blank.

L. Prepare appropriate standards (if necessary). Directions for standards preparation are given in Section II.

M. Run standard. Recalibrate instrument, if necessary (see Calibrating the GC in Section II-12). If possible, obtain the peak areas in V-sec as well as ppm-V, so that the instrument calibration factor (in (μL/L)/V-sec) can be determined.

N. If time permits, run a syringe blank (an injection of room air or 0.1 air) to ensure syringe cleanliness using the syringes that will be used in the day's work.

O. Run samples. Adjust the injection volume until the peaks of interest are on scale and preferably more than 1/4 of maximum size for chart paper. If time permits, runs should be duplicated and average values should be used for quantification.

P. Record sample ID, injection volume, and gain on the injection log. Also record sample ID and injection volume on chromatogram at the start of the run.

Q. Record the results of the run on the calculation sheet for the project. Correct the GC output for injection volume (and gain if results are in mV or V-sec) to those values used for standard. When two replicate runs are made, calculate for both separately, and then average the results.

R. Record the corrected results on the results sheet for the project. One copy of the results sheet should be given to PM/person-in-charge, and one copy should be placed in the project notebook.

S. Clean syringes by removing the plunger after an injection and letting the plunger air.

T. If replicate runs are not satisfactory (< 10 percent difference is a suggested guideline), reinject sample. If third run is still inconsistent, replace the needle on the syringe, and then rerun the sample. Also check for syringe contamination by running a syringe blank. Check for plugged syringes by injecting air into a vial filled with water.

U. If instrument is not recognizing obvious peaks, recalibrate the known peak. If unsure of peak ID, run standard for peak identification. (Note: Once the septa is punctured in the gas sample bottle, the VOCs are slowly lost from the bottle. Therefore, the standard should be used for calibrating the concentration only shortly after the standard is prepared. The standard can still be used for peak identification until the peaks disappear.)

V. Standards should be run periodically throughout the day, for peak identification (not for recalibration of concentration) and at any time when questions on peak identification arise. At least three standards should be run each day.

W. Column and syringe blanks should be run periodically throughout the day, and if any questions of syringe contamination arise. Column and syringe blanks are particularly important when the sample concentration is low, or if there is a sharp drop in sample concentration (< factor of 5 change in concentration).

X. Under normal operation, the maximum gain is 20, and under all conditions, the maximum injection volume is 1,000 µL.

Y. After 50 to 60 injections, change the injection septum.

Z. After the last run has been completed, disconnect the oven battery from the instrument, and then shut the power off to the instrument. After the instrument has turned off, turn off the airflow, either by closing the tank or decreasing the regulator (if using an external tank). If using the internal tank, turn off the flow by using the instrument flow control knob.

AA. At the end of a day's run, tear off the chart paper and mark the end with the date, project name and number, and if possible, the samples run.

BB. If the instrument is using the internal power supply, then it should be recharged overnight. Fill the internal gas tank in the instrument, and bring the GC to a place where there is a 110 v power supply. Plug the instrument in, turn the airflow to a very slow rate (5 to 10 mL/min), and then turn the instrument on overnight. Be sure the air tank is full or that it has sufficient air to keep air running through the detector throughout the night.

16. Data Treatment

The Photovac® measures the area under peaks for the compounds in the injected gas sample. When using a "Library," the area, in V-sec or MV-sec, is converted to µL/L (ppm-V) in the gas phase by calibrating the instrument using a known concentration of the compound in question (with gas standards). The instrument compares areas of standards with sample peak areas to determine the concentration of the unknown. The instrument corrects for gain, but not for injection volume. The instrument's concentration output should be corrected for injection volume as follows:

$$(\textit{actual conc.}, \mu L/L) = (\textit{instrument reading}, \mu L/L)\left(\frac{\textit{injection volume of standard}}{\textit{injection volume of sample}}\right)$$

If the reading is given in V-sec, a correction needs to be made for gain as well as for injection volume, i.e.,

$$(\textit{actual conc.}, \mu L/L) = (\textit{instrument reading}, V\text{-sec})\left(\textit{response factor}\ \frac{\mu L/L}{V\text{-sec}}\right)$$

$$\left(\frac{\textit{injection volume of standard}}{\textit{injection volume of sample}}\right)\left(\frac{\textit{gain setting for standard}}{\textit{gain setting for sample}}\right)$$

where the injection volume and gain are the values for the standard at the time the instrument was calibrated.

The response factor is the conversion factor for the V-sec given by the detector at a given standard concentration, i.e.,

$$\textit{response factor} = \left(\frac{\textit{standard concentration}, \mu L/L}{\textit{instrument reading}, V\text{-sec}}\right)$$

The response factor is specific for the injection volume, gain, and detector response.

Gas measurements are commonly reported in ppm or $\mu g/m^3$. A gas phase unit of ppm is a $\mu L/L$. To avoid confusion between measurements made on different matrices (air, water, or soil) units of $\mu L/L$ are used in the calculations.

17. Data Deliverables

Portable GC Results Notebooks will be prepared. The notebook will consist of the following sections:

A. Project information

B. Standards preparation and SOP for the sample handling and GC operation

C. Injection logs

D. Calculation sheets

E. Results summary sheets

F. Replicate comparison and standards results sheets

G. Chromatograms

After the fieldwork, the chromatograms are xeroxed and placed in the appropriate section. Replicates are recorded separately, and compared in a separate section of the notebook. The calculation and results summary sheets should be checked by the QC reviewer. The notebook should be comb bound and placed in the project file. The calculation and results summary sheets can be xeroxed and stored at the GC operator's desk for later reference, if appropriate.

The notebooks contain the information required to follow the results from the original chromatogram to the final results sheet. Standards are included so that retention times can be checked. However, syringe or column blanks, runs that went off-scale, and other miscellaneous runs are not included. The original chromatograms are stored in the RMT Applied Chemistry Laboratory.

18. Quality Control

The degree of QA/QC for the portable GC use is dependent on the use of the results, and should be adjusted as appropriate. It should be recognized that the GC itself is a precise analytical instrument, capable of providing as consistent and reliable results as a laboratory GC, if used under optimum conditions. However, use in the field under less controlled conditions increases the analytical variation in the results. Further, and more important, soil headspace analysis is designed to be a screening method, giving approximate indicators of soil concentrations. There is inherent variability in a soil headspace measurement due to changes in the soil itself that cannot be eliminated by QC procedures during the analysis. The extent of QC should be appropriate to the end use of the results.

During field operation of the GC, the operator checked for syringe clogging or contamination, machine malfunction, and miscalibration as discussed in Sections 14 and 15. If replicate runs vary by more than 10 percent difference between the results, the sample is reanalyzed by repeating the injections until the results do replicate or the cause of the poor replication is identified.

The purpose of the QA/QC procedures can be divided into three areas, as follows:

A. Verification

Much of the verification of peak identification, syringe cleanliness, and proper operation is done during machine operation, and is discussed in Section 12, Calibration Procedures. During the QC check of the results, the following steps are needed:

i. Sample and standard peak retention times and peak patterns are compared. GC identification of the peaks is checked. Incorrect GC peak identification is noted on the chromatogram.

ii. If a question of peak identification arises that cannot be resolved by comparing sample peak retention time with that of the standard, relative retention times for the unknown and for a known compound are calculated and compared between the sample and standard.

iii. If a question of peak identification arises after a relative retention time check, the peak is identified as the compound of interest with a note saying "Tentative Identification."

B. Data and Calculation Checks

i. All results to be reported should be recorded on the calculation sheet.

ii. The results should be corrected for injection volume and gain. Note: the Photovac® automatically corrects for gain if the reports are presented in ppm, but does not correct for gain if the results are presented as V-sec.

iii. Further calculations should be recorded on the DATA CALCULATION SHEET.

iv. The corrected results should be recorded on the sample results sheet. All results should be reported as µL/L (ppm-V).

v. All data transcriptions and calculations should be checked by a QC person, unless otherwise instructed. The QC person should check the results for accuracy of transcription, and spot check the calculations. Furthermore, the QC person should compare the final results for reasonableness, based on previous results or anticipated results.

vi. A xerox of the chromatograms used for calculation should be made. The xerox facilitates QC checking and project file documentation. If duplicate injections were made, both chromatograms should be recorded. Further, if there is any uncertainty about peak identification, then the standards used for retention time calibration should be xeroxed also.

vii. The QA/QC person should initial and date each page of data calculation or results sheet checked and any corrections that are made. Corrections should be in a different color ink (e.g., blue or red) than the original.

C. Documentation

i. A portable GC project notebook should be used unless there are instructions not to. The project notebook should consist of the following sections:

Section Topic

a. General Project Information

- Includes the proposed Scope of Services if available

b. Standard Operating Conditions

- Standards preparation forms
- Standards chromatogram
- Calculation equations
- Sample handling instructions (if prepared)

c. Results summary forms

d. Daily injection log

e. Calculation sheets and chromatograms

ii. While the project is active, the notebook should be kept in a 3-ring binder (unless otherwise specified).

iii. After the project is completed, the notebook should be comb bound, with a cover page, and stored in the project files. The GC operator is responsible for putting the final notebook together.

iv. The original chromatograms should be stored in the Applied Chemistry Laboratory. The chromatograms should be organized by project and date.

19. References

Devitt, D.A., R.B. Evans, W.A. Jury, T.R. Starks, B. Eklund and A. Gnolson. 1987. Soil gas sensing for detection and mapping of volatile organics. EPA 600/8-87-036, USEPA, Las Vegas, Nevada.

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ATTACHMENT 1

PHOTOVAC® TECHNICAL BULLETIN #27

PHOTOVAC

Technical Bulletin

27

PREPARATION OF AQUEOUS STANDARDS FOR GROUNDWATER ANALYSIS

For further information on contents of this bulletin or on Photovac products, please contact:

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PREPARATION OF AQUEOUS STANDARDS FOR GROUNDWATER ANALYSIS

This procedure is based on an actual site investigation conducted with E.P.A. approval and is intended to provide a guide for similar investigations. Local site conditions and the type of compounds present will abviously be different and approval of the planned procedure will need local E.P.A. approval.

PREPARATION OF WATER STANDARDS

This is a general guideline to be used when making water standards of volatile compounds. The example given is for Benzene and TCE, two compounds commonly found in groundwater contamination. The volumes used for generating the initial stock solution and subsequent dilutions are readily dispensable to allow the preparation of low concentration standards.
The accuracy of the standards is dependent on the precautions taken in the transfers of liquids and care taken to prevent headspace loss. Cross contamination by using contaminated syringes must also be avoided.

APPARATUS: The following apparatus is required, with care being taken to decontaminate the various items using only spectroscopic grade solvents:

1. 40 ml. VOA bottles
2. Gas tight syringes (50 ul to 100 ul).
3. Volumetric pipettes to measure 20 ml and 40 ml volumes. (Other glassware of compatible accuracy can be used as alternatives).
4. Analytical balance (and pan balance if available).

REAGENTS

1. 100ml Methanol
2. Approximately 20 ml each of other desired reagents.
3. Organic-free water.

PROCEDURE

If analytical balances are available, then the preferred method of making standards is to weigh small quantities of the volatile organic compounds in gas-tight syringes. These quantities are transferred to 20 ml of Methanol and the whole reweighed (See appendix A "Procedure for weighing liquids with a syringe"). Concentration is then calculated directly on a wt/wt basis (ppm = ug/g).

If analytical balances are not available, the densities of the compounds are used to determine the weight of known volumes. The following is an example for making water standards at low ppb concentrations of Benzene and TCE. Theprocedure consists of 3 parts: A) Making a stock solution in Methanol (approx. 1000-5000 ppm), B) 1/800 dilution in water, C) 1/500 dilution in water.

A) STOCK SOLUTION IN METHANOL

1. Using a 20 ml volumetric pipette, transfer 20 ml of Methanol

Let the solution sit 30 minutes to equilibrate before using.

Concentration : $\frac{40\ \mu l\ Solution\ B}{20\ ml\ water}$ =

$\frac{.40\ ml}{20\ ml}$ = $\frac{1}{500}$ dilution = 9.2 ppb TCE + 8.3 ppb Benzene (Solution)

Solution C is the working Standard.

NOTE: Follow chemical manufacturer's recommended safety information for the reagents used.

Precautionary Notes

1. Care should be taken not to inject liquid into the G. C.

2. When using a 10S50 or 10S70 G. C. use a separate library for water standard data. By listing the headspace concentration as the liquid concentration, from the standards, the G. C. will then print results based on liquid concentration for field samples. This approach will prevent confusion with air calibration data and negates the need for using Henry's Law to calculate vapor concentrations with respect to liquid samples.

3. When working with samples in the parts-per-billion concentration range, freshly prepared aqueous standards should be used on a daily basis. The standards should be stored with the septum screw capped VOA vial inverted.

4. Depending upon the volume of headspace used for injection into the G. C., using a clean gas-tight syringe, transfer the same volume of UZ air to replenish the headspace. Allow the standard to equilibrate for approximately 1/2 hour.

5. Typically, injection volume of headspace range from 100-500 µl.

APPENDIX A

PROCEDURE FOR WEIGHING LIQUIDS WITH A SYRINGE

Cautions/Limitations:

1. The minimum amount of liquid to be weighed is 20 µl.

2. Use only about 50-60% of the capacity of the syringe, therefore, the minimum size syringe that can be used is 50 µl.

3. Perform procedure as quickly as possible to avoid exposure and possible volatilization.

4. For liquids that are very volatile, it is neccessary to draw total sample back into syringe barrel, before weighing, to prevent liquid volatilization during weighing procedure.

Procedure

1. Use a 50 µl syringe and withdraw at least 20 µl of liquid.

2. Carefully wipe the needle and syringe dry.

3. Place syringe on analytical balance and weigh. (Tare and sample).

4. Depress plunger to empty syringe into a suitable flask containing solvent. To prevent volatilization of liquid, be sure to empty contents of the syringe under the surface of the solvent.

5. Reweigh syringe (tare), and by difference calculate the weight of the liquid taken.