



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

AUG 3 2011

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

MEMORANDUM

SUBJECT: Test Method for Vapor Pressure of Reactive Organic Compounds in Heavy Crude Oil Using Gas Chromatography

FROM: Conniesue Oldham, Group Leader *Connie Oldham*
Measurements Technology Group (E143-02)

TO: Stanley Tong, Environmental Engineer
USEPA, Region IX

In your June 2, 2011 correspondence, you referred to a request you received from the San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD) to consider a request they received from Chevron U.S.A. Chevron has requested the use of a method, "Vapor Pressure of Reactive Organic Compounds in Heavy Crude Oil Using Gas Chromatography," as an alternative test method to determine vapor pressure. The method would be used for source applicability determination requirements of 40 CFR Part 60, Subpart Kb. The method is dated May 28, 2002, and is attached to this letter as a matter of record.

Based on our previous approval of an earlier draft of this method (as described in a memorandum to you from William Lamason dated September 1, 1999), and the subsequent revisions that have been made, we are hereby approving the May 28, 2002 version of this method for use by Chevron U.S.A. for the purpose of measuring vapor pressure to determine source applicability as described in Subpart Kb. Because we believe that this alternative method is acceptable for vapor pressure determination for any volatile organic liquid storage vessel containing heavy crude oil (with an American Petroleum Institute gravity of 26 or less) that is regulated under 40 CFR Part 60, Subpart Kb, we will be posting this approval on our website at <http://www.epa.gov/ttn/emc/approalt.html> for use by other interested parties.

If you have questions or would like to discuss the matter further, please call William Grimley at (919) 541-1065, or you may e-mail him at grimley.william@epa.gov.

Attachment

cc: William Grimley (E143-02)
Nick Parsons (E143-02)
Leonard Scandura (SJVUAPCD)
John Gruber (Chevron U.S.A.)

Test Method for Vapor Pressure of Reactive Organic Compounds in Heavy Crude Oil Using Gas Chromatography

**David Littlejohn and Donald Lucas
Lawrence Berkeley National Laboratory
Berkeley, California**

May 28, 2002

1. Scope

1.1 This test method describes the determination of the true vapor pressure of reactive compounds in heavy crude oil at the bulk storage temperature of the oil using gas chromatography. Because the method was designed specifically for use with heavy crude oil from heavy oil storage tanks, it is not generally applicable to petroleum distillates or synthetic organic chemicals.

1.2 The useful range of the method extends from an ROC vapor pressure of 0.05 psia to an ROC vapor pressure of 10 psia for crude oil gravities of 26 degrees API or less.

1.3 Using this method, vapor pressures of reactive organic compounds are determined in non-SI units (pounds per square inch), which are regarded as the standard. Nominal dimensions in inch-pound units have been used to specify tubing and fittings used in the construction of the test apparatus. Because the use of SI units is common practice in chemical laboratory analysis, SI units have also been used to specify some analytical parameters.

1.4 Although this method does include some cautions to be considered in sampling and laboratory analysis, it does not purport to address all safety, environmental, and regulatory issues associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to evaluate the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards

D 323 Test Method for Vapor Pressure of Petroleum Products

D 287 Test Method for API Gravity of Crude Petroleum and Petroleum Products E 355
Practices for Gas Chromatography Terms and Relationships

E 516 Practice for Testing TC Detectors Used in Gas Chromatography

E 594 Practice for Testing FID Detectors Used in Gas Chromatography

3. Terminology

3.1 *Definitions:* This test method makes reference to commonly used gas chromatographic procedures and terms. Detailed definitions can be found in ASTM practices E 355, E 516, and E 594.

3.1.1 *Crude Oil, n*—petroleum extracted from the earth that has not been processed in a refining operation.

3.1.2 *Heavy Crude Oil, n*— for the purpose of this method, crude oil having an American Petroleum Institute gravity of 26 degrees or less as measured by ASTM test method D 287.

3.1.3 *Reactive Organic Compound or ROC, n*—any compound present in crude oil having at least one atom of carbon except: methane; ethane; carbon monoxide; carbon dioxide; carbonic acid; metallic carbides or carbonates; acetone; or methyl acetate.

3.1.4 *Reid Vapor Pressure or RVP, n*—vapor pressure determined in accordance with ASTM method D 323.

4. Significance and Use

4.1 The reactive organic compound (ROC) vapor pressure as determined by this method is a measure of the tendency of heavy crude oil to release ROCs during oilfield storage and processing operations. During validation of this test method, the ROC concentration in gases emitted from heavy oil storage tanks was accurately predicted from the measured ROC vapor pressure of liquid samples. This method may be of value in evaluating the potential for ROC emissions from equipment used to store and process heavy crude oil.

4.2 Although this method is similar to ASTM Test Method D 323, which is also used to determine the vapor pressure of petroleum products, there are three key differences that may make this method more specifically applicable to determining the vapor pressure of reactive organic compounds from heavy crude oil. First, this method contains a heavy crude oil sampling procedure designed to prevent the loss of the volatile compounds that affect vapor pressure. Second, the vapor pressure of ROCs is measured at the storage temperature in this method, so it is not necessary to apply conversions to determine the actual vapor pressure of ROCs in the stored oil. Third, the method was designed to measure only the vapor pressure of the ROCs, which are often of specific concern in air pollution control.

4.3 No attempt has been made to correct results for the presence of "exempt compounds". Exempt compounds (e.g. acetone, perchloroethylene, methylene chloride) are organic compounds not included in the regulatory definition of reactive organic compounds. Significant quantities of exempt hydrocarbons compounds (other than methane and ethane) are generally not present in heavy crude oil.

5. Sampling and Test Apparatus

5.1 The test apparatus consists of two parts: the vapor section and the liquid sampler section. The apparatus is shown schematically in Figure 1 (attached). Although the figure clearly shows each component of the apparatus, the true orientation of the apparatus is not properly depicted in the schematic. The ball valve (labeled Valve A) for the sampling port on the left and the pressure gauge are actually assembled perpendicular (i.e. pointing up, out of the page) to the plane created by the vapor and liquid sampler sections. The assembled apparatus has a 4:1 vapor-to-liquid volume ratio, which is the same as that of the Reid vapor pressure apparatus used in ASTM Test Method D 323.

5.2 *Vapor Section* - The vapor section has a volume of 120 mL (+/- 2.0 mL) when attached to the sampling tube and the pressure gauge. It consists of ½" copper tubing, ½" brass pipe thread fittings (4 or 5 nipples of various lengths, 3 elbows, 1 tee, and optionally, a union), a pressure gauge, and a brass, steel, or stainless steel ball valve (Valve A for gas sampling). The outlet of valve A is connected to a 1/16" stainless steel gas sampling line with a stainless steel fitting designed for pressurized gas service (Swagelok ® fittings have been found to be satisfactory for this purpose).

5.3 *Pressure Gauge* - The pressure gauge must be capable of reading pressures from ambient to 15.0 psig in increments of 0.1 psig. Suitable gauges are available from commercial laboratory supply houses.

5.4 *Liquid Sampler Section* - The liquid sampler section has a volume between the ball valves of 30 mL (+/- 1 mL). It is constructed from standard ½" copper tubing, two ball valves with ½" solder fittings and PTFE seats, and a ½" pipe thread - ½" solder fitting adapter. The liquid sampler ball valves (Valves B and C) are commercially available brass ball valves rated at 150 psi for steam.

5.5 *Volume Calibration* - The volumes of the liquid sampler section and the vapor section must be adjusted prior to final assembly. Each volume is calibrated by measuring the amount of water the section holds, and adjusting the length of the copper tubing used in the assembly. The tubing length in the liquid section must be adjusted so that the volume between the ball valves (Valves B and C) is 30 mL (+/- 1 mL). The tubing length used in the vapor section must be adjusted so that the volume contained between Valve A, Valve B, and the pressure gauge is 120 mL (+/- 2 mL).

5.6 *Assembly of Apparatus* - Joints in the liquid sampler are soldered. Pipe joints in the rest of the apparatus are sealed with PTFE tape during initial assembly. After assembly, each valve shall be prominently and permanently labeled.

5.7 *Water bath* - A temperature controlled water bath large enough to immerse the test apparatus (with the exception of the pressure gauge and gas sampling valve - Valve A) is required. The bath must be capable of maintaining temperatures between ambient temperature and the bulk storage temperature of the oil being tested within +/- 2° F. For higher temperatures, an equivalent bath containing a less volatile heat transfer media may be used.

5.8 *Leak testing of Apparatus*— Each apparatus must be leak tested after initial assembly to ensure that the apparatus is vapor tight. Leak testing is performed by pressurizing the apparatus and submersing the system in a water bath. The apparatus is pressurized to 15 psig by connecting it to a compressed air supply through the fitting on the gas sampling line. If the apparatus is vapor tight no visible bubbling will be observed during submersion.

5.9 *Connection to Gas Chromatographs* —The sampling ports are connected to the two gas chromatographs using 1/16" o.d. stainless steel tubing as shown in figures 2 and 3. The sample tubing is wrapped with electrical heating tape connected to a variable voltage controller to maintain the temperature at least 5 °F above the temperature of the water bath. Two thermocouples are located at distances approximately equidistant along the sample line to measure the line temperature within +/- 2 °F. A vacuum pump capable of achieving a vacuum of 0.001 atm is connected to the sample line as shown in figure 3.

5.10 *Gas Chromatographs* --- Gas chromatographs #1 and #2 shall be capable of operating at the conditions listed in table 1 below:

Table 1 – Operating Conditions for Gas Chromatographs

	Gas Chromatograph #1	Gas Chromatograph #2
Column Type	Porapak Q (1/8"X12ft) (or column with equivalent chromatographic efficiency)	Two 0.32mm Astec Gaspro GSC PLOT columns, 5m and 15m (or columns with equivalent chromatographic efficiency)
Carrier Gas	Helium	Nitrogen
Carrier Gas Flow Rate	20 mL/min	1.8 mL/min
Detector	Thermal Conductivity to Measure air, methane, ethane, and carbon dioxide	Flame Ionization to measure C1 to C10 hydrocarbons
Initial Temperature	70°C for 3 min	50 °C for 3 min
Temperature Ramp	10 °C/min	12°C/min
Final Temperature	120°C for 6 min	230 °C for 7 min
Backflush	NA	Column 1 for 18 min.
Injector	70°C	Pneumatic valve with 0.05 mL sample loop, split ratio 28:1; 120°C
Limit of Detection	100 ppmv hydrocarbons or less	10 ppmv hydrocarbons or less

5.11 *Electronic Data Acquisition System* – The data acquisition and integration system must be capable of recording retention times and adequately quantifying peak areas.

6. Reagents and Materials

6.1 *Carrier Gases* – Helium and Nitrogen carrier gasses with a minimum purity of 99.5%. Oxygen and gas purifiers should be used.

Warning – Helium, Air and Nitrogen as used in this method are compressed gases under high pressure.

6.2 *Detector Gases* – Hydrocarbon-free air, hydrogen and nitrogen with a minimum purity of 99.5%.

Warning – Hydrogen as used in this method is a highly flammable compressed gas under pressure.

6.3 *Calibration Standards* – Calibration standards shall be prepared from chromatographic grade chemicals of known purity.

Warning – Hydrocarbon calibration standards are flammable and may be harmful or fatal if ingested or inhaled.

7. Sampling

7.1 The liquid section of the test apparatus is connected to the tank sampling port by means of the appropriate pipe thread adapters and/or reinforced tubing and hose clamps. The sample is to be taken from the lowest sampling port where the clean oil layer is present.

Warning – Crude oil samples are flammable and may be harmful or fatal if ingested or inhaled. Samples at elevated temperatures may cause severe burns or other harm if they come in contact with skin or eyes. Toxic, corrosive, and flammable gases that may be harmful or fatal if inhaled may be present in oil samples and at oilfield sampling sites. Tanks structures may also present safety hazards. Appropriate safety measures including, but not limited to, the use of insulated gloves, protective clothing, safety glasses, hard hats, safety shoes and respiratory protection may be necessary for sampling.

7.2 The liquid sampler is held in a vertical position with the inlet to the liquid sampler section at the bottom to ensure no air remains in the sampler during filling.

7.3 A hose is attached to the outlet of the sampler to direct the flow into the drain of the tank sample box.

7.4 The valves of the liquid sampler (Valves B and C) are opened fully and the valve of the tank sample line is slowly opened until a constant flow is established through the liquid sampler.

7.5 A calibrated container is used to measure the sample flow rate (Q_{oil}). $Q_{oil} =$ (volume of oil collected in calibrated container)/(time taken to collect the volume).

7.6 The volume in the tank sampling line V_{line} is estimated using the diameter and length of the sampling line. $V_{line} = (3.14d^2/4)(\text{length of sampling line including sampler})$, where d is the diameter of the sampling line.

7.7 The flow in the sampling line is maintained until the tank sampling line is adequately flushed. At least 3 volumes must flow through the line to ensure that the line is adequately flushed.

7.8 For crude oil stored at an elevated temperature, the temperature of the oil coming out of the drain line must be monitored with a calibrated thermocouple and recorded. The sample must only be taken when the temperature of the oil in the sampler approaches the temperature of the oil in the tank (+/- 5° F).

7.9 To capture the sample, the valves are closed sequentially from downstream. The outlet valve (Valve C) of the liquid sampler is closed first, the inlet valve to the sampler is closed second, and the tank sampling line valve is closed last. After the flow is stopped, the liquid sampler is disconnected from the tank and the sampler valve handles are removed to prevent them from being opened inadvertently.

7.10 A duplicate sample is collected in a second liquid sampler following the same procedures as with the first sample.

7.11 The tank liquid temperature is recorded and the sampler tube is labeled. The label (or a corresponding log) must identify the sample number, tank, tank temperature, sampling date, sampling time, and the person collecting the sample.

7.12 Samples may be stored at ambient temperature for up to 5 weeks before laboratory analysis, but the storage temperature must never exceed the temperature at which the oil was sampled.

8. Gas Chromatograph Calibration

8.1 *Identification* – Peak retention times for carbon dioxide, methane, ethane, and hydrocarbons C3 through C10 shall be established by analyzing calibration standard gas mixtures using the operating parameters defined in Table 1.

8.2 *Calibration* -- Average calibration factors for carbon dioxide, methane, ethane, and C3 through C10 hydrocarbons shall be determined based on the analysis of five standard gas mixtures using the operating parameters defined in Table 1. Propane, butane, ethane, pentane, hexane, heptane, octane, nonane, and decane shall be used for C3 through C10 hydrocarbon calibration. The concentration of analytes in the gas mixtures shall span the range of the concentrations to be tested. The relative standard deviation of the calibration factors shall not exceed 15 percent for any analyte. The calibration shall be repeated at least on a monthly basis. Calibration shall also be repeated whenever changes are made to operating parameters or chromatographic equipment, and whenever the chromatographic system fails daily calibration checks.

8.3 *Daily check samples* – The calibration factors for each analyte shall be checked using a mid-range standard at the beginning and end of each day of operation. The result of each calibration check must be within 20% of the known concentration of the standard, or the test results are not valid.

9. Test Procedure

9.1 The temperature of the water bath is adjusted to the bulk storage temperature of the oil as recorded during sampling. During testing, the water bath temperature must be maintained at the bulk storage temperature of the oil being tested within $\pm 2^\circ \text{F}$.

9.2 PTFE tape is applied to the pipe threads on the liquid sampler. The vapor section of the test apparatus is held with the opening upward and 5 mL of reagent-grade water is added from a graduated cylinder. With the opening of the vapor section elevated so that the water does not run out, the liquid and vapor sections of test apparatus are joined (as shown in figure 1). The connection is tightened and a valve handle is added to the liquid sampler ball valve closest to the vapor section (Valve B).

9.3 With all three ball valves of the apparatus (Valves A, B, and C) closed, the entire apparatus (with the exception of the pressure gauge and gas sampling valve – Valve A) is immersed in the water bath. The immersed apparatus is then visually inspected for bubbles that may indicate leakage. If there are any signs of leakage, the test must be stopped until the leak is fixed.

9.4 The apparatus is agitated periodically (approximately every 2 min) and the pressure is monitored. Once the pressure stabilizes (less than 0.1 psi change in 5 min), the pressure is vented by opening the gas sampling valve (Valve A) while the apparatus is still immersed.

9.5 When the gauge pressure returns to 0 psi, the vapor sections gas sampling valve (Valve A) is closed. The valve between the liquid and vapor sections (Valve B) is then opened. The apparatus is agitated intermittently (approximately once every 2 min) and the pressure is monitored. Once the pressure stabilizes (less than 0.1 psi change in 5 min), the temperature has reached equilibrium and testing may proceed.

9.6 The gas sampling port is connected to the sample loops using the 1/16" o.d. sample heated line as shown in figures 2 and 3. The line is heated to at least 5°F but no more than 10°F above the water bath temperature. The line is then evacuated to 0.01 atm (as measured by the pressure gauge).

9.7 The valve between the vacuum pump and the sample line (Valve D) is closed and the vacuum pump is turned off. Then the ball valve for the sampling port (Valve A) is opened to expand gas into the line and fill the sample loops (which are still isolated from the chromatographic columns).

9.8 The pressure on the gauge is monitored. If the pressure is greater than 1 atmosphere, the excess pressure is vented by opening Valve D so that the sample is at atmospheric pressure. If the pressure is less than 1 atmosphere, the value is recorded so that concentration measurements can be appropriately scaled.

9.9 With the gas chromatographs set to operate at the parameters specified in Table 1, the samples are injected from the sample loops into the columns. Data from the gas chromatograph detectors is collected using the electronic data acquisition system.

9.10 A blank sample of reagent grade water shall be analyzed with each set of samples. The result of each blank test shall be an ROC vapor pressure of less than 0.1 psia or the tests shall not be considered valid.

9.11 After the tests are completed, the system is drained of oil. After draining, with the vapor section immersed in the heated water bath and blanked off, the vacuum pump is used to evacuate the vapor section for at least five minutes and remove any remaining volatile compounds. All liquid sampling sections that contained crude oil with significant ROC vapor pressure (above 0.5 psia), must be thoroughly cleaned and baked dry for a period of at least one hour at a temperature of 100°C. Solvent cleaning should not be performed on the apparatus.

10. Calculations

10.1 The uncorrected ROC concentration is the sum of the measured concentration of each ROC component, C3 through C10, in ppmv.

10.2 If the pressure in the sample line measured during the test was below 1.0 atm, a pressure correction factor (F_{pc}) must be calculated. The pressure correction factor is determined by simply dividing the atmospheric pressure (P_{atm} or 14.7 psi) by the measured pressure in the sample line P_{line} in psi.

$$F_{pc} = P_{atm} / P_{line}$$

10.3 The corrected ROC concentration ($C_{ROC,1 atm}$) is calculated by multiplying the ROC concentration at test pressure ($C_{ROC,test P}$) by the pressure correction factor (F_{pc}).

$$C_{ROC,1 atm} = C_{ROC,test P} \times F_{pc}$$

If the pressure in the sample line was not below 1.0 atm, no correction is needed.

10.4 As a final step, the corrected ROC concentration is converted to pressure units (psi) by multiplying the result by 14.7 psi/atm and dividing the concentration by 10^6 ppmv/atm.

$$P_{ROC,1 atm} = (C_{ROC,1 atm} \times 14.7 \text{ psi}) / 10^6 \text{ ppmv/atm};$$

where $P_{ROC,1 atm}$ is the ROC vapor pressure for the sample.

11. Precision and Bias

11.1 *Precision* – The precision of this method was determined by performing seven consecutive analyses of actual heavy crude oil samples with vapor pressure well below common regulatory limits (0.34 psia). The relative standard deviation for the seven test results was determined to be 14.7%.

11.2 *Bias* – The bias of the method was determined by using the method to determine the vapor pressure of a pure substance (water) of known vapor pressure. The bias of the method was determined to be +0.9%.

12. **Keywords**

12.1 Vapor Pressure, Crude Oil, Petroleum

**Test Method for Vapor Pressure of Reactive Organic Compounds
in Heavy Crude Oil Using Gas Chromatography – Q.C. Records**

Sampling Record

Sample Date _____ Time _____ ID No. _____

Facility Name _____

Sample Collector (Name) _____ Device Prepared By: _____

Sampling Device ID _____

Tank ID _____ APCD Permit No. _____

Sample Description _____

Sampling Flow Rate _____ in³/min

Volume of Sample Line _____ in³

Flush Time _____ sec.

Calculated Flush Volumes _____

Tank Temperature _____ °F

Sample Temperature _____ °F

Approx. Tank Fill Level _____ ft.

Location of Sample Port _____

Tank Operation During Sample Collection (*Check One*):

- Filling
- Draining
- Constant Level (w/flow)
- No Flow

Notes (*Special Circumstances; Procedural Deviations; etc.*)

**Test Method for Vapor Pressure of Reactive Organic Compounds
in Heavy Crude Oil Using Gas Chromatography – Q.C. Records
Analysis Record**

Sample ID _____ Analysis Date _____ Time _____

Laboratory _____

Analyst Name _____

Sampling/Test Device ID _____

G.C. Calibration Date _____

	GC #1	GC #2
Carrier Gas	_____	_____
Carrier Gas Flow	_____ mL/min	_____ mL/min
Initial Temperature	_____ °C	_____ °C
Temperature Ramp	_____ °C/min	_____ °C/min
Final Temperature	_____ °C	_____ °C

Bath Temperature _____ °F Line Temperature _____ °F

Any Device Leakage?: Yes No

Corrective Action for Leakage

Pressure Stabilized (<0.1 psi/5 min.)? Yes No

Pressure Line Evacuated: _____ psi

Sample Vapor Pressure (*Initial Gauge Reading*) _____ psi

Pressure Correction Factor _____

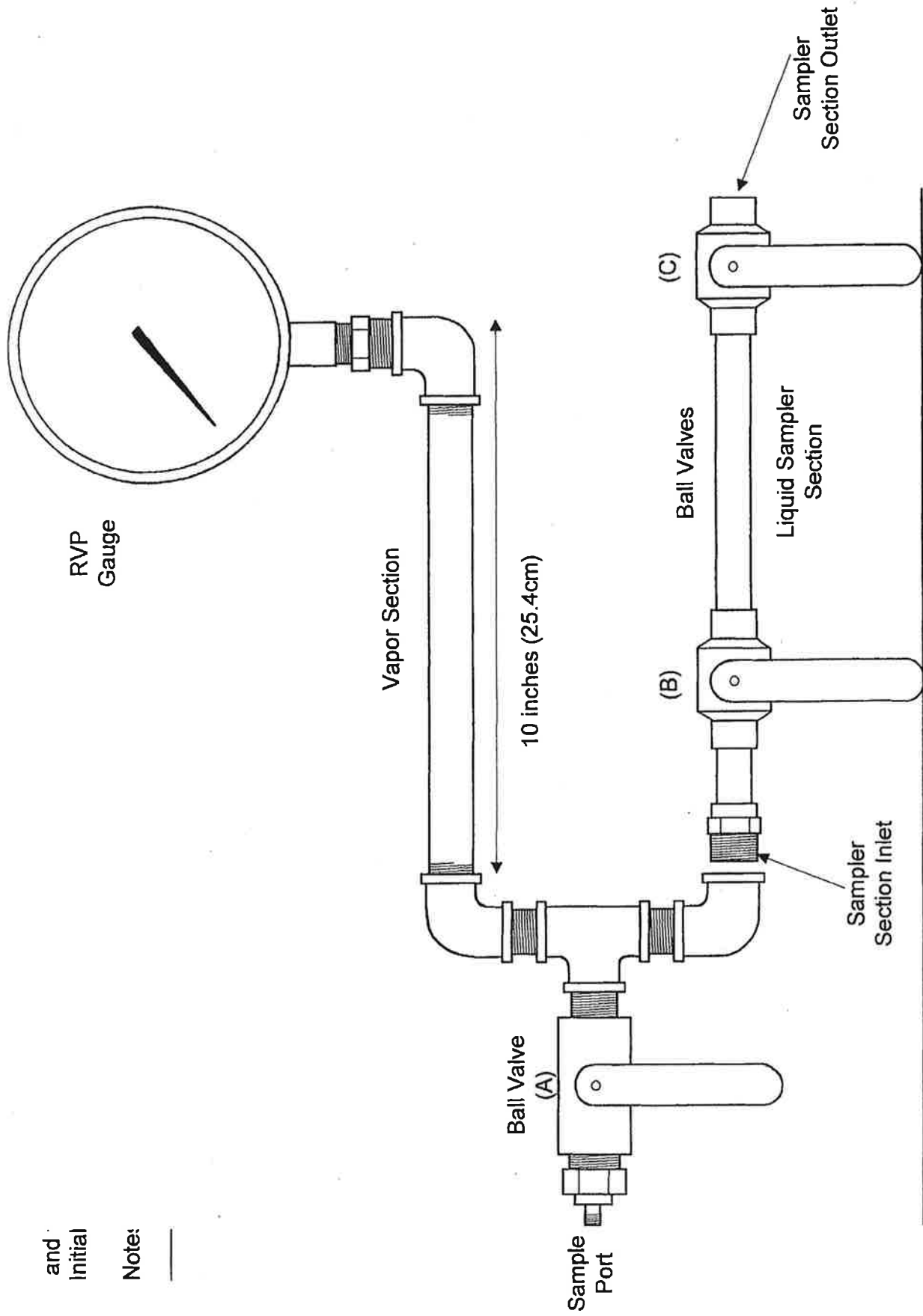
ROC VP Result _____ psi

Blank GC Result _____ psi

Device Cleaned and thoroughly dried?: Yes No

Initials of Person Cleaning Device after Analysis _____

Notes: _____



and
Initial
Note:

Figure 1

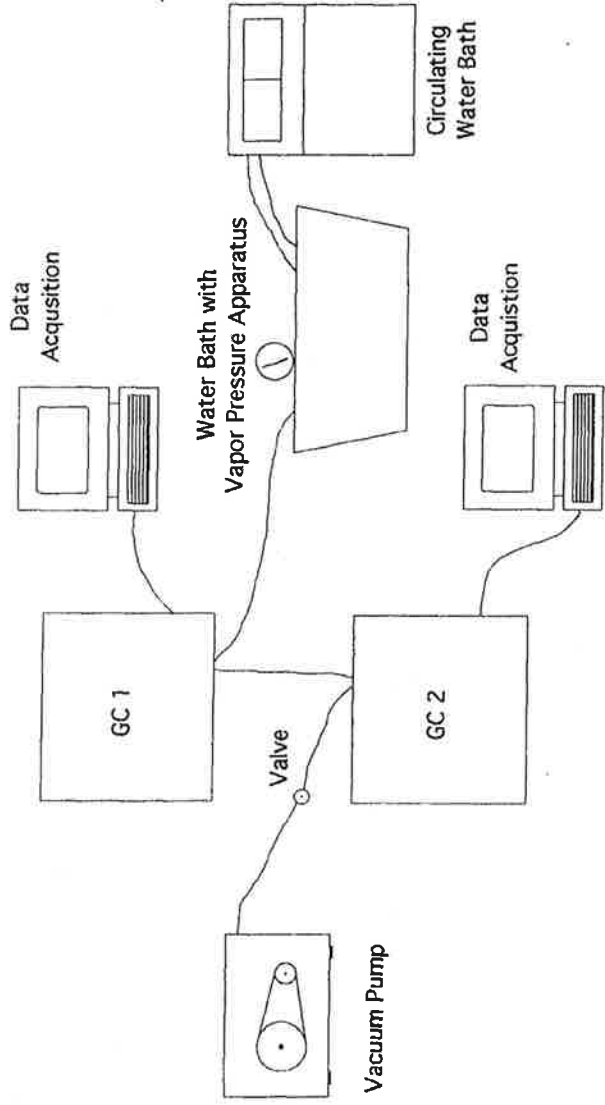


Figure 3
Figure 2

