Vapor Pressure Best Practice

COQA June 2017 Meeting – St Louis
In this era of “fake” news, our CCQTA/COQA associations seek truth!

The above cartoon is by no means reflective of any producer, midstreamer, refiner or lab or government agency 😊
reminder of Canadian Crude Quality Association (CCQTA) membership and website information

What is the CCQTA?

The Canadian Crude Quality Technical Association membership consists of companies from multiple segments of the Canadian oil industry. The Association is established with the following educational and scientific objectives:

- To facilitate the resolution of common crude oil quality issues by establishing direct lines of communications among crude oil stakeholders.

- To provide a forum for the presentation and consideration of proposals for industry projects related to any aspect of crude oil quality.

- To improve industry knowledge and awareness of crude oil quality through the cooperative exchange of technical information among industry sectors. The CCQTA is careful to stay clear of commercial issues, concentrating instead upon the technical aspects.
‘Just Released June 2, 2017…’

Vapor Pressure Measurement

Best Practice

publication added: 2017-06-02

… factors affecting vapor pressure and the recommended sampling and testing methodologies

… a compilation of the research, understanding and learning gained through the 5 year CCQTA TVP/RVP project and marks the close of the project

… available to the public to promote education around vapor pressure in crude oil
Vapor Pressure Measurement Best Practice Sections

1. Introduction
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5. Summary of Referenced Data Sources
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Introduction

The vapor pressure of a product (crude oil, condensate or other related petroleum products) is an important property that has been regulated for many years.

Vapor pressure specifications are in place for environmental emissions, floating roof tank design limits, pump cavitation avoidance, refinery feedstock limits and refined product requirements.

Vapor pressure provides an indication of the volatility of a product and with the use of correlations, is often used to estimate tank emission limits. The CCQTA TVP/RVP project was initiated with the objective of redevelopment of the correlation between Reid Vapor Pressure (RVP) and True Vapor Pressure (TVPEPA) described by the equations/nomograph published with the API MPMS Chapter 19.2 (Formerly API 2517). The accuracy of the correlation for current market crudes had been under scrutiny since the nomographs and related equations had been developed using “weathered” or “dead” crudes with little or no documented data on how the tests were conducted or the correlations developed. Concerns also relate to other factors affecting vapor pressure measurement, most significantly the sample collection methodologies.
Introduction

The significant increase in light shale oil crude production into the North American market and subsequent incidents that occurred with these high vapor pressure crudes have resulted in added interest and attention on the vapor pressure measurement methods currently in use. In order to evaluate the differences between the testing methods, the CCQTA TVP/RVP project objectives were revised to investigate testing methodologies and sampling techniques. These studies investigated: sampling methodologies, direct vapor pressure measurement methods, compositional analysis methods, and predictive models. Since the project began in late 2012, three ASTM standard practices/methods have been developed as a result of the project work (ASTM D7975, D8003 and D8009).

The goal is providing the industry with information to allow the development/revision of standards and specifications that incorporate sampling, handling and testing standards that provide the representative vapor pressure results using fit-for-purpose methodologies.
4.1. **Dead crude oil, n**— crude oil with sufficiently low vapor pressure that, when exposed to normal atmospheric pressure at room temperature, does not result in boiling of the sample.

4.1.1. *Discussion*—these crudes will have vapor pressures below atmospheric pressure at room temperature.

4.1.2. *Discussion*—A crude oil is normally considered “live” until the vapor pressure can be established using Test Methods D6377, D6378 or D7975. Sampling and handling of dead crude oils can usually be performed without concern in open, non-pressurized sample containers, such as cans, bottles and other atmospheric containers as described in Practice D4057.
Definitions

4.2. **Live crude oil, n**— crude oil with sufficiently high vapor pressure that it would boil if exposed to normal atmospheric pressure at room temperature.

4.2.1. **Discussion**— Sampling and handling of samples of live crude oils will necessitate the use of the closed sample container to maintain sample integrity and preclude the use of open sample containers, such as cans, bottles and other atmospheric containers.

4.2.2. **Discussion**— samples and bulk storage (tank) liquids may or may not appear to boil visibly (rolling) but vaporization (off-gassing) is occurring.
4.3. **Light ends**, n— hydrocarbon components that cannot be maintained as a liquid at atmospheric pressure at temperatures greater than 0 °C.

4.3.1. **Discussion**— This includes any materials that have atmospheric boiling points below 0 °C including methane, ethane, propane, and butane.

4.3.2. **Discussion**— Fixed gases, such as CO, CO2, H2, H2S, N2 and O2, will also contribute to the composition and vapor pressure of the sample.
4.4. **Reid Vapor Pressure (RVP)**— The equilibrium pressure exerted by an air saturated fluid at a 4:1 vapor liquid ratio at 37.8 °C (100 °F).

4.5. **True Vapor Pressure (TVP)**— Various definitions exist depending on how it is to be used.

4.5.1. **International Maritime Organization**— “The True Vapor Pressure (TVP) or bubble point vapor pressure is the equilibrium vapor pressure of a mixture when the gas/liquid ratio is effectively zero. It is the highest vapor pressure which is possible at any specified temperature. As the temperature of the petroleum mixture increases, its TVP exceeds atmospheric pressure, the liquid commences to boil.” Discussion: A floating roof tank, where the roof is floating directly on the oil, would meet this TVP criteria (V/L = 0)

4.5.2. **US Environmental Protection Agency (40 CFR)**— “The true vapor pressure is the equilibrium partial pressure exerted by the volatile organic liquid, as defined by ASTM D2879 or as obtained from standard reference texts.” This definition excludes the partial pressure contributions of methane, ethane, and fixed gases.

4.6. **Total Vapor Pressure (TVP)**— The total vapor pressure of a crude oil is the equilibrium partial pressure exerted by all the individual components including the partial pressure of all hydrocarbons plus the inclusion of fixed gases such as: CO, CO2, H2, H2S, N2, O2.
ASTM D323, D5191 and D6377 are the three methods most commonly used for vapor pressure measurement of products for transport. ASTM D7975 has also been included in this review since it is applicable to field operations with correlation to D6377.

All the methodologies listed are well suited to the application for which they were developed, however the results from each method are not necessarily comparable to one another.

There are nuances to each method that make comparison inappropriate and often misleading.

*The four methods described are all suitable for the purpose for which they were intended, however the selection of the appropriate method for the application required is often where problems arise. Understanding the nature of the products to which the test is to be used is often overlooked and often coupled with assumptions.*
7.1 ASTM D323—Procedure A

7.1.1 Summary of Test Method (Section 4.1)— “The liquid chamber of the vapor pressure apparatus is filled with the chilled sample and connected to the vapor chamber that has been heated to 37.8°C (100°F) in a bath. The assembled apparatus is immersed in a bath at 37.8°C (100°F) until a constant pressure is observed. The reading, suitably corrected, is reported as the Reid vapor pressure.”

7.1.2 Significance and Use (Section 5.1)— “Vapor pressure is an important physical property of volatile liquids. This test method is used to determine the vapor pressure at 37.8°C (100°F) of petroleum products and crude oils with initial boiling point above 0°C (32°F).

7.1.3 Sampling Requirements— Sampling is performed using atmospheric sample container, such as glass bottles and/or cans, as per ASTM D4057. Sampling takes place by sampling directly from the source into the bottle or can at atmospheric conditions of both temperature and pressure.
Methods (D323)

7.1.4 Sample Preparation Summary— Samples in the laboratory are chilled between 0 °C and 1 °C prior to prepare for transfer for analysis. Once the sample reaches the transfer temperature, the container is opened to allow air to saturate the sample liquid, and then sealed and returned to refrigeration for 2 minutes. This air saturation step is repeated 3 times.

7.1.5 Sample Transfer and Testing Summary— The chilled and air-saturated sample is poured from the sample container into the pre-chilled (0 °C to 1 °C) test liquid chamber until over flowing. The vapor chamber is immediately attached to the liquid chamber and the apparatus is inverted to allow the test liquid to drain into the vapor chamber and then shaken 8 times. The test apparatus immersed (gauge up) in a test bath set at 37.8 °C (100 °F). The gauge is read successively for at least 5 shake and immerse cycles until the last two cycles see a stable pressure reading. The pressure reading is corrected to standard pressure (101.325 kPa) and reported as RVP.

7.1.6 The 4:1 vapor/liquid ratio used in the D323 method is intended to make the almost completely insensitive to air however since methane and ethane have similar thermodynamic properties to air the method is also insensitive to these gases.
7.2 ASTM D5191

7.2.1 Summary of Test Method (Section 4.1)— “A known volume of chilled, air-saturated sample is introduced into a thermostatically controlled, evacuated test chamber, or a test chamber with a moveable piston that expands the volume after sample introduction, the internal volume of which is five times that of the total test specimen introduced into the chamber. After introduction into the test chamber, the test specimen is allowed to reach thermal equilibrium at the test temperature, 37.8° C (100° F). The resulting rise in pressure in the chamber is measured using a pressure transducer sensor and indicator. Only total pressure measurements (sum of the partial pressure of the sample and the partial pressure of the dissolved air) are used in this test method, although some instruments can measure the absolute pressure of the sample as well.

7.2.2 Significance and Use (Section 5.3)— “Specifications for volatile petroleum products generally include vapor pressure limits to ensure products of suitable volatility performance.”

7.2.3 Sampling Requirements (Section 8.1.2)— “Obtain a sample and test specimen in accordance with Practice D4057, except do not use the “Sampling by Water Displacement” section for fuels containing oxygenates. Use either a 250-mL or 1-L (1-qt) sized container filled between 70 and 80 % with sample. For best testing precision (reproducibility), it is recommended that a 1-L sized container be used.”
7.2.4 Sample Preparation Summary— Samples in the laboratory are chilled between 0 °C and 1 °C prior to prepare for transfer for analysis. Once the sample reaches the transfer temperature, the container is opened to allow air to saturate the sample liquid, and then sealed and returned to refrigeration for 2 minutes. This air saturation step is repeated 3 times.

7.2.5 Sample Transfer and Testing Summary— The chilled and air saturated sample is opened and the instrument sample introduction tubing is inserted into the sample. Using an internal pump, a volume of sample is drawn into the instrument then purged to a waste container to flush the measurement chamber. Fill/purge cycles will be dependent on the instrument manufacturer. Following the final purge, a known volume fresh sample is drawn into the measurement chamber to begin the test. The measurement chamber is heated to 37.8 °C and expanded to a 4:1 vapor:liquid ratio and allowed to equilibrate until a stable pressure is reached. The pressure is reported as $P_{tot}$ and a correlation used to report the dry vapor pressure equivalent (DVPE).
Methods (D6377)

7.3 ASTM D6377

7.3.1 Summary of Test Method (Section 4.1)— “Employing a measuring chamber with a built-in piston, a sample of known volume is drawn from the sample container into the temperature controlled chamber at 20° C or higher. After sealing the chamber, the volume is expanded by moving the piston until the final volume produces the desired V/L value. The temperature of the measuring chamber is then regulated to the measuring temperature.”

7.3.2 Significance and Use (Section 5.3)— **Chilling and air saturation of the sample prior to the vapor pressure measurement is not required.**

7.3.3 Sampling Requirements (Section 8.1.1)— The extreme sensitivity of vapor pressure measurements to losses through evaporation and the resulting changes in composition requires the utmost precaution and the most meticulous care in the drawing and handling of samples.

Sampling of live crude oil shall be performed in accordance with Practice D3700.

Sampling in accordance with Practice D4057 shall only be used for dead crude oil and if Practice D3700 is impractical.
Methods (D6377)

7.3.4 Sample Preparation Summary—The floating piston cylinder (FPC) sample is brought to room temperature and then pressure is applied to piston and the fluid is pressurized above the sample source conditions. The sample is shaken to ensure the sample is single phase prior to beginning testing.

7.3.5 Sample Transfer and Testing Summary—The sample cylinder is connected to the instrument inlet and sample is transferred and maintained under single-phase conditions. Using the displacement of the internal piston, a volume of single-phase sample is drawn into the instrument then purged to a waste container, via a control valve, to flush the measurement chamber. Fill/purge cycles will be dependent on the instrument manufacturer. Following the final purge, a known volume fresh sample is drawn into the measurement chamber to begin the test. The measurement chamber is heated to a known temperature and expanded to a known vapor:liquid ratio and allowed to equilibrate until a stable pressure is reached.

This method allows any combination of V:L and temperature to be used depending on the requirements for testing. For comparison to RVP the test is performed using a vapor:liquid ratio of 4:1 and a temperature 37.8°C. VPCR... VPCR results compared to RVP results use the following factor: [VPCR4(37.8°C) * 0.834 = RVPE].
7.4 ASTM D7975

7.4.1 Summary of Test Method (Section 4.1) — “Using a portable variable volume measurement chamber with a built-in piston, a sample of crude oil of known volume is drawn from the sample point or sample container into the field test apparatus. After sealing the chamber, the volume is expanded by moving the piston until the final volume produces the desired V/L value.”

7.4.2 Summary of Test Method (Section 4.2) — “After temperature and pressure equilibrium, the measured pressure is recorded as the VPCRX-F(Tm°C) of the sample. The test specimen is mixed during the measuring procedure by shaking the measuring chamber to achieve pressure equilibrium in a reasonable time of 1 min to 5 min.”
7.4.3 Significance and Use (Section 5.3) — “The direct sample collection and subsequent, in place, vapor pressure measurement without the need for further sample handling eliminates the potential for light hydrocarbon material from the sample. The combination of sampling and handling may produce higher results than Test Method D323.”

7.4.4 Sampling and Testing Summary — The apparatus is connected directly to a suitable sample point. Sample is drawn into the apparatus either via source pressure or by pulling on the piston handle. The sample is filled and purge a number of times to ensure a representative sample has been captured then sealed from the sample point. The piston is then drawn back to the appropriate vapor/liquid ratio and fixed in place while the apparatus is shaken to agitate the contents and accelerate equilibrium between vapor and liquid phases. After agitation the pressure gauge is opened to the measurement chamber and the pressure and temperature is recorded. Correlation charts can then be used to correct the value to other temperature conditions for comparison to historical results or D6377 specifications. The temperature correlation curves are included in the appendix.
Method Comparison

D323 scope lists an initial boiling point (IBP) greater than 0 °C as the criteria for use, meaning a fluid containing no butane or lighter components (n-butane BP = -1 °C at atmospheric pressure) however it is often used for condensate and crude oils with initial boiling points well below 0 °C. The scope of ASTM D323 states it is suitable for crude oils and is also cited in many pipeline specifications and tariffs.

What the scope fails to define is what kind of crude oil; live or dead?

A live crude oil will contain butane and lighter components making the IBP below 0 °C therefore outside of the scope of the test method.

A dead crude oil will not contain butane and/or lighter components making the IBP above 0 °C and therefore the scope is applicable and the method is suitable for use.
Method Comparison

ASTM D5191 is intended for use with finished products, such as gasolines, to ensure cold weather start characteristics at atmospheric conditions. This method is common in finished product specifications.

The D5191 method is essentially a miniaturized and faster version of the D323, using the same sample preparation, vapor/liquid ratio and temperature condition but on a 1 to 10 mL sample size.

As with the D323 method the IBP limitation of greater than 0 °C limits this method to dead crudes and or finished products above this boiling point.
Method Comparison

**ASTM D6377** is the most flexible and is suitable for use with all products, including: finished products, crude oil, condensate and LPG/NGL. D6377 is prescriptive in its use of floating piston or manual piston cylinders for sampling and the method requires transfer of the sample into the apparatus via single-phase transfer. This ensures the sample is tested at the conditions in which it was sampled, providing unbiased results.

The D6377 method allows the user to test multiple V/L ranges within a single test to develop a vapor pressure versus V/L plot that can be used to characterize how a product will behave under various conditions.

The D6377 apparatus can also be used to perform the D5191 test when used with the appropriate sample collection and preparation.
Method Comparison

ASTM D7975 is intended as a field level vapor pressure tester incorporating both sampling and testing into a single apparatus. The results of D7975 are comparable to D6377 provided the measurement temperature is equivalent or adequate temperature correlations are applied.

This method is ideal for locations where the use of D6377 instrumentation is not practical such as oil batteries or loading/off-loading facilities. The apparatus is well suited for connection to a treater outlet sample point for incremental monitoring of treater performance and sales oil vapor pressure. This test method is also very sensitive near barometric pressure and provides a tactile response to the operator by means of the “feel” of the piston handle during measurement. The operator can easily identify the difference between incompressible liquid filled (solid response) and compressible vapor (spongy response).

Note: This test method is not recommended for custody transfer applications and is best suited as a screening method for identifying potential out of specification product.
The bias between the sampling and testing methods is well documented. Prior to the CCQTA study, an ASTM inter-laboratory study (ILS) was conducted in 2005 to compare ASTM D6377 to ASTM D323 using both FPC and 1 L atmospheric sample containers. Based on that study, a sample collected in a FPC and run by ASTM D323 would be **16.6% lower** than the same sample run by ASTM D6377. A sample collected in an atmospheric container and run by ASTM D323 would be **8.5% lower** than the same sample run by ASTM D6377. This study was performed under a strictly controlled protocol and would provide the likely best-case scenario for bias measurement.

The ASTM ILS clearly illustrates the bias resulting from both sampling and testing methods.

![Vapor Pressure Comparison by Testing & Sampling Method](image)

**Figure 1 – Theoretical Vapor Pressure Comparisons based on D6377 Appendix X1**
Effect of Sampling and Handling Methods on VP Measurement

Since the partial pressure of the butane and lower compounds contribute the most to overall vapor pressure, the sampling methods were also compared directly with the composition of the material. Figure 2 illustrates the compositional difference between a sample collected via FPC (original) versus the same sample collected in an atmospheric container (weathered). Note the significant loss of butane and lower components.

Note that in Table 1. C1 is 100 times lower in concentration than C4 but exerts the same partial pressure. These results are illustrations of the significant effect light end components (C4 minus) have on vapor pressure and how sampling, handling and testing can bias vapor pressure results.
2,2,4-Trimethylpentane Blend Comparison

- Difference between TVP and RVP is LARGE for Air, Methane and Ethane, SMALL for propane, butane and heavier
- Shape of the VP vs V/L curve can alert operator that an unknown sample received in the lab contains light dissolved gases

Figure 4 — Illustration of vapor pressure curves for each component
Recommendations

Current specifications citing ASTM D323 or D5191 for use with crude oil are not suitable for custody transfer for “live oils”.

This is based on both the sampling and testing methodologies.

Results of “live” oil samples tested via either D323 and D5191 are potentially biased low.
Recommendations

Prior to sampling, handling and testing of any product it is important to understand if the product is considered “live” or “dead” at the sampling conditions as well as the anticipated conditions in the laboratory handling the sample (e.g., room temperature).

If this is not already established then a method such as ASTM D7975 or D6377 must be employed to characterize the product for proper sampling, handling and testing.

It is also critical to understand the conditions that the testing will be run to ensure appropriate sampling is performed. Samples taken for the purpose of V/L curve development must not be exposed to atmosphere since equilibrium air can affect the vapor pressure measurements at low vapor/liquid ratios.
Recommendations

If the sample is “live” then either ASTM D8009 (MPC) or D3700 (FPC) must be used.

The sample point and product conditions will dictate which of these two methods is most applicable.

Lower pressure sample points including but not limited to: atmospheric tanks, tank trucks, rail cars, low pressure pipelines, or any low pressure sample points should employ the D8009 (MPC) practice. This method allows the sampler to draw the low-pressure product into the chamber without the reliance on source pressure to drive the product into the cylinder.

Higher-pressure sample points including but not limited to: downstream of pumps, high-pressure pipelines, and/or process streams should employ the D3700 (FPC) practice. These sample points have sufficient pressure to drive the product into the cylinder and overcome any piston friction and allow displacement of the pre-charge fluid (gas or liquid).
Recommendations

Sampling Method

Prior to sampling an unknown product the state of the product should be confirmed as “dead” or “live” by D7975 or D6377. Always assume a product is “live” unless testing results deem otherwise.

If the product is “dead” then atmospheric sampling practices such as those found in ASTM D4057 are suitable.
Recommendations

Vapor Pressure Testing Method
It is important to ensure that the reported vapor pressure includes the test conditions (V/L and temperature) to avoid confusion between results.

“Dead” crude oils may be tested by any of the test methods listed (D323, D5191 and/or D6377).

“Live” crude oils must be tested by D6377. D7975 may also be used with the appropriate temperature correction but should not be used for custody transfer applications.

Compositional Analysis Method
When coupled with a single-phase sampling technique, ASTM D8003 is recommended for compositional analysis of hydrocarbon components (C1-C24).

Regulation and/or Specifications
Regulations and or specifications should always reference both the sampling and testing methods to avoid confusion to the user. A referee method should also be included in case of dispute. In the case of vapor pressure dispute, ASTM D6377 should be considered the referee method. This includes sampling via D3700 or D8009. Other single-phase sampling methods are not permitted within D6377 and therefore they are not suitable for dispute resolution.
The next round of project meetings will be held June 20th and 21st hosted by Kinder Morgan Canada in the Stock Exchange Tower at 300-5 Ave SW, Calgary, AB in the Edmund Taylor Room on the 2nd Floor.

We have scheduled an Open Forum Lunch on Tuesday the 20th to give members an opportunity to chat about issues they may be facing outside of our current ongoing projects as well as discuss any new project ideas. Based on our last two open forum meetings two projects have surfaced that are likely to become projects: (Water Content Test Methods / Amines in Crude)

Project meetings this term, with the exception of the TAN Phase IV, are open to all CCQTA members. For the TAN Phase IV project if you are not a member and wish to attend as a guest please contact the project manager prior to the meeting. You may be asked to leave the meeting if you are not invited or a participant.

June 20th, 2017
Pipeline Sour Service 9:00-11:30 (Open to all CCQTA Members)
Open Forum(Lunch provided) 12:00-16:00 (Open to all CCQTA Members)

June 21st, 2017
TAN Phase IV 9:00-11:00 (Participant Only – Contact Project Manager Randy Segato for access)
CCQTA Executive Meeting (Lunch provided) 11:30-13:00 (Open to all CCQTA Members)
Properties of Thermally Processed Materials 13:30-16:30 (Open to all CCQTA Members)

Please visit the website often as events, agendas and schedules may be subject to change. http://www.ccqta.com/allevents.php
Come visit Alberta… where we work hard 😊
# PROJECTS LIST

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