Fundamentals of Liquid Measurement – Part 1
Class Number 2160

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Introduction

Correct measurement practices are established to minimize uncertainty in the determination of the 'custody transfer' volume (or mass) of products.

Understanding and evaluation of the fundamental cause and effect relationships with the liquid to be measured will lead to a volume determination that most closely matches the 'true' volume at the referenced 'standard' pressure and temperature.

When designing a new measurement station it is up to us as measurement people, to understand the product to be measured, apply the correct equipment, and implement the appropriate correction equations.

Proper procedures could implement this process:

1. What is the Composition or Fluid to be measured?
   a. Crude Oil
   b. Light Liquid Hydrocarbon – Condensate – Natural Gas Liquids
   c. Pure Product
      i. Propane
      ii. Butane
   d. Refined Product
2. What is the operating Pressure and Temperature?
3. How does the operating Pressure and Temperature affect:
   a. Density
   b. Expansion/Contraction Characteristics
   c. Viscosity
   d. Vapor Pressure
4. What other operational factors affect proper measurement?
   a. Basic Sediment and Water
5. Based on the answers to the previous questions, what is the best equipment to handle the product?
6. What types of calculations will be implemented to correct the volume, or mass, measured at process conditions to the 'standard conditions'?

The purpose of this paper is to identify these steps and discuss their effects on the determination of standard volumes for Liquid Hydrocarbon Measurement.

MIXTURE COMPOSITION

All Hydrocarbon fluids are mixtures of the same chemical elements. The Basic Elements for all Hydrocarbons, whether in liquid or gaseous state are Carbon and Hydrogen. The number of Carbon and Hydrogen *atoms* joined together will determine the type of *Molecule*. When the Carbon and Hydrogen join together to form a Hydrocarbon Molecule, one Carbon Atom is bonded with more Hydrogen Atoms. Table 1 will detail the number of carbon atoms, hydrogen atoms, and the common name of the molecule.

Common Name	Carbon Atoms	Hydrogen Atoms	Molecular Formula
Methane	1	4	CH4
Ethane	2	6	C2H6
Propane	3	8	C3H8
Butane	4	10	C4H10
Pentane	5	12	C5H12
Hexane	6	14	C6H16
Heptane	7	16	C7H14
Octane	8	18	C8H16
Nonane	9	20	C9H18
Decane	10	22	C10H20

Table 1: Common Hydrocarbon Molecule Names

The Composition of the fluid refers to the percentage of each type of molecules contained in the total volume of the Mixture. Hydrocarbon Liquids are classified as Homogeneous mixtures. This type of mixture has uniform chemical compositions, appearance and properties throughout a sample. A simple example would be Air, which is a homogeneous mixture of gases consisting primarily of nitrogen and oxygen.

A very important consequence of a Homogeneous Mixture is that many of the resulting properties, like Density, Energy Contents, and Vapor Pressures, can be calculated from the sum of the properties of the individual components.

The general composition of the different mixtures will create fluids with different classifications, and very different physical properties. These different fluids will require different measurement equipment and will determine the measurement practices used.

Natural Gas Liquids will typically have a composition that is comprised of Ethane through Decane. Crude Oils and Refined Products (Gasoline, Diesel), on the other hand, will have a composition that is comprised of very heavy molecules: C10 and greater.

Component	Mole%	Weight %	Liquid Volume %
Methane	0.2390	0.0335	0.0835
Ethane	0.2938	0.0773	0.1625
Propane	1.0957	0.4227	0.6230
Isobutane	1.0421	0.5298	0.7034
n-Butane	1.6354	0.8315	1.0639
Neopentane	0.1743	0.1100	0.1378
Isopentane	2.1034	1.3275	1.5887
n-Pentane	1.9377	1.2229	1.4481
2,2-Dimethylbutane	0.1945	0.1466	0.1675
2,3-Dimethylbutane	0.5789	0.4364	0.4894
2-Methylpentane	1.7079	1.2875	1.4624
3-Methylpentane	1.0428	0.7861	0.8779
n-Hexane	2.5077	1.8904	2.1272
Heptanes	23.0747	19.4277	19.3564
Octanes	16.3885	15.0922	14.7522
Nonanes	21.7218	21.8364	20.4648
Decanes plus	24.2353	34.5348	34.4851
Nitrogen	0.0274	0.0067	0.0062
Carbon Dioxide	0.0000	0.0000	0.0000
Total	100.0000	100.0000	100.0000

Table 2: Composition of typical Product classified as Crude Oil

	1	2	3	4	5
Component	Mole %	Mole Weigh t	Mass-LBM	Weight Fraction	Weight Percent
Methane	**0.0**	16.043	0.0	0.0	0.0
Ethane	**0.2**	30.07	0.0601	0.00078	0.07799
Propane	**2.0**	44.097	0.8819	0.0114	1.1437
Iso-Butane	**7.5**	58.123	4.3592	0.05653	5.6532
Normal-Butane	**7.5**	58.123	4.3592	0.05653	5.6532
Iso-Pentane	**25.5**	72.15	18.398	0.2386	23.8597
Normal-Pentane	**25.5**	72.15	18.398	0.2386	23.8579
n-Hexane	**16.47**	86.177	14.1933	0.18406	18.4066
Heptanes	**7.5**	100.204	7.5153	0.09746	9.746
Octanes +	**7.83**	114.231	8.9442	0.1159	11.5994
Totals	**100**		**77.1099**	**1.00**	**100.0**

Table 3: Typical Composition of a Product Classified as a Natural Gas Liquid

Mole Percent

The term Mole Percent relates the number of Molecules for a particular component to the total number molecules in the liquid. Because Hydrocarbon Liquids are Homogeneous Mixtures, they can be separated into their individual components without requiring any chemical reactions. As a result, the analysis of the individual components can be determined from liquid chromatography.

Weight Percent

Weight percent is the mass of the component divided by the total mass of the composition.

$$\text{Weight Percent} = \frac{\text{Mass of Component}}{\text{Mass of Composition}} * 100 \qquad (1)$$

From Table 3, the Weight Percent of Propane is calculated using Equation 2.

Weight Percent = [0.8819 lbm (Column 3) / 77.1099 lbm (sum of Column 3)] * 100 = 1.1437 (2)

Volume Percent

Volume Percent is the Volume of the Individual Component divided by the total volume of the mixture.

$$\text{Volume Percent} = \frac{\text{Volume of Component}}{\text{Total Volume of Mixture}} * 100 \qquad (3)$$

At this point it is very important to introduce a term: Solution Mixing. Natural Gas Liquid mixtures, especially those containing significant levels of ethane (the lightest-smallest component) experience an error in volumetric measurement called the Solution Mixing effect. This effect causes the total metered volume of this type of mixture to be substantially less than the combined volume of the products. A simple example would be to add one gallon of Sand and one gallon of Gravel together. The total volume does not equal two gallons because the sand will be accommodated between the 'cracks' of the gravel. In natural gas liquid mixtures the smaller molecules of ethane and propane will be contained between the 'cracks' of the larger molecules of Heptanes, Hexanes, and Octanes.

TEMPERATURE / PRESSURE

The physical characteristics of the product will be affected by the operating pressure and temperature. Temperature plays a significant role in volumetric techniques because of the expansion and contraction of hydrocarbons. Using volumetric measurement practices, Volume Correction Factors (VCF) have been determined that relate the amount of expansion/contractions to the type of product being measured. A factor must be determined for temperature correction (CTL), and a factor must be determined for pressure corrections (CPL).

Temperature Correction

In general, when the product is heated, the volume of the product will increase, and when the product is cooled, the volume of the product is reduced. The Industry has determined factors that must be used when correcting Volumes of Liquid Hydrocarbon to standard temperatures. This CTL factor will be a function of the API (American Petroleum Institute) gravity of the product, and the vapor pressure. The American Petroleum Institute in MPMS Chapter 11 has defined tables of temperature corrections. These tables are based on the Gravity Ranges of the product. The API has also defined an algorithm for CTL correction to be used with on-line flow computers.

API Table 6A is to be used for Crude Oils and is an example of the CTL factor developed to correct to the standard temperature of 60 deg F. Table 6B is to be used for Refined Products, and developed in 1998, API/ASTM/GPA Table TP-25 to be used for Volumetric Measurement of LPG/LNG. API/ASTM/GPA table TP-25 replaces ASTM-IP Tables 23/24 and GPA TP-16

Temp Deg F	45.0 API	45.5 API	46.0 API	46.5 API	47.0 API
75.0	0.9920	0.9920	0.9919	0.9919	0.9918
75.5	0.9917	0.9917	0.9916	0.9916	0.9915
76.0	0.9915	0.9914	0.9913	0.9913	0.9913

Table 4: API 6A Generalized Crude Oils Volume Correction Factor to 60 F

In modern Flow Computers it is much easier to calculate the CTL factor without the Tables, but with an equation. The API algorithm uses density, temperature, and thermal expansion factor to determine CTL:

$$VCF = \rho\tau/\rho 60 = EXP[-\alpha\ 60\Delta\tau(1+0.8\alpha\ 60\Delta\tau)] \qquad (4)$$

In which:

VCF = Volume Correction Factor
$\rho\tau$ = density at temperature τ
$\rho 60$ = density at 60˚F
α 60 = thermal coefficient of expansion for that type of liquid at 60˚F
$\Delta\tau$ = τ – 60.0

Proper temperature measurement is key to the proper determination of the CTL factor. In batch tank transfer, mid-level temperature reading is necessary. If a large tank is being used for transfer, an average temperature must be determined by taking measurements at upper, middle and lower levels in the tank.

If the Liquid is being transferred with an Automatic Custody Transfer (LACT) type of system, it is important to use a temperature transmitter in proper calibration and average temperature on a proportional to flow basis. The location of the temperature element should be immediately downstream of the primary flow element.

Pressure Correction

To a certain degree, liquids are compressible and expand and contract with pressure. When pressure is applied to the liquid it will contract. When pressure is decreased, liquids will expand. For Crude Oil measurement the Volume Correction Factor to correct for pressure, or CPL, is determined with API MPMS Chapter 11.2. To correct the CPL of the liquid for elevated pressures, the first step is to determine the Compressibility Factor 'F' using the following equation:

$$CPL = 1/[1(P - Pe) * F] \qquad (5)$$

In Which:

- P = Operation pressure in PSIG
- Pe = Equilibrium vapor pressure at operating pressure (or zero for liquids with vapor pressures less than atmospheric)
- F = Compressibility factor from API MPMS Chapter 11.2.1 or Chapter 11.2.2

API Gravity at 60 Deg F

Temp Deg F	18.0	18.5	19.0	19.5	20.0
99.0	0.434	0.437	0.440	0.444	0.447
99.5	0.434	0.437	0.441	0.444	0.448
100.0	0.435	0.438	0.441	0.444	0.448

Table 5: Compressibility Factor, F, divided by 100,000.

The following is an example to demonstrate the very small effect Pressure has on the VCF.

Crude Oil with a 19.9 API Gravity (at 60.0 F) metered at a pressure of 500 psi and a temperature of 100F, has an 'F' factor of 0.00000448 from Table 5. The corresponding CPL is:

$$CPL = 1 / [1- (500-0) * 0.00000448] = 1.0023 \qquad (6)$$

VOLUME

The Volume of a product represents the amount that will be contained in a previously defined container. Table 6 lists several common units of Volume.

Product	Unit	Country
Oil	Barrel	United States
Natural Gas Liquids	Gallon	United States
Gasoline	Gallon	United States
Propane	Gallon	United States
Oil	Liter	S.I. Units
Additive	Cubic Centimeter	S.I. Units

Table 6: Common Units of Volume

In the United States the standard volume for Oil is the Barrel containing 42 US Gallons. Not only do we need to specify what the Volume refers to but we must also specify at what temperature and pressure we reference a Standard Volume. In the United States, the standard Temperature is 60 deg F. Most everywhere else in the World, the Standard Volume is referenced to 15 deg C.

Liters	U.S. Gallons	Barrels
1	0.26417	6.289×10^{-3}
3.7854	1	2.380×10^{-2}
158.987	42	1

Table 7: Volumetric Conversion Factors

MASS

The mass of a liquid is a term that is a bit less arbitrary than the volume of a liquid. The Mass of a product is determined by the composition of the product. Each component of the product adds to the total mass of the product. Because each component is of known mass, the total mass of the product is the sum of the mass of each component. Table 3 details the calculation process to determine the Weight fraction of each component.

Volume at standard conditions is determined for products such as Natural Gas Liquids (NGL) using Mass methods. Due to Solution Mixing, Standard Tables of Temperature Correction and Pressure Correction used for Crude Oils will not work with NGL. The total mass of the product must be determined and standard volume calculated using the constants in GPA Standard. Table 8 details this calculation procedure when the load consisted of a total mass of 4687 pounds.

		Weight Fraction	Weight Percent	Component Mass	lbm/bbl from GPA Tables	Net BBLS	Net GALS
Methane	**0.0**	0	0	0	105	0	0
Ethane	**0.2**	0.00029284	0.02928402	1.37254208	124.723	0.01100472	0.46219837
Propane	**2.0**	0.00429444	0.42944379	20.1280307	177.526	0.11338075	4.76199141
Iso-Butane	**7.5**	0.02122641	2.12264114	99.4881902	197.093	0.5047779	21.2006717
Normal-Butane	**7.5**	0.02122641	2.12264114	99.4881902	204.498	0.48649958	20.4329822
Iso-Pentane	**25.5**	0.08958676	8.95867553	419.893122	218.744	1.91956407	80.6216908
Normal-Pentane	**25.5**	0.08958676	8.95867553	419.893122	220.991	1.90004626	79.8019427
n-Hexane	**16.47**	0.06911181	6.91118092	323.92705	232.445	1.39356428	58.5296999
Heptanes	**7.5**	0.03659431	3.65943142	171.517551	240.979	0.7117531	29.8936303
Octanes +	**7.83**	0.04355249	4.35524943	204.130541	247.498	0.82477653	34.6406141
Totals	**100**	1	100	4687		**19.4446**	**816.673**

Table 8: Calculation of Standard Volume using Mass measurement techniques

To some degree (with gravity a standard), the Mass of the Product can also be referred to as the weight of a product.

DENSITY

The Density of the product is the term that relates the Volume of the Product to the Mass of the Product. It is defined as the Mass of the Fluid per Unit Volume. Like Volume, Density must also be referenced to a Temperature. This temperature can be operating temperature, or standard temperature.

Relative Density

Relative Density is the ratio of the density of a liquid at a given temperature to the density of pure water at a standard temperature.

Specific Gravity

Specific gravity of the liquid is the ratio of mass of a given volume of a substance to that of an equal volume of another substance used as a standard. Water is used as a standard for liquid. The volumes of comparison are referenced to 60 deg F and atmospheric pressure in PSIA.

API Gravity

API Gravity is a special gravity scale used exclusively in the Petroleum Industry to characterize the density of Crude Oils. The reporting of density in Degrees API dates back to the use of Hydrometers for density determination.

API gravity is related to relative density by the following formula:

$$\text{Degree API @ 60 deg F} = \frac{141.5}{\text{Relative Density}} - 131.5 \qquad (7)$$

It is important to note that API Gravity is inversely related to relative density. Liquids that are commonly called ‘heavier’ have low API Gravities and have ‘high’ Relative Densities

Petroleum Liquid	Relative Densities	API Gravity Range
Crude Oil	1.00 – 0.78	10 - 50
Fuel Oils, Jet Fuel	0.875 – 0.780	30 - 50
Gasoline	0.780 – 0.685	50 - 75
Natural Gas Liquids	0.50 – 0.68	75 - 110
Butanes - Propane	0.695 – 0.505	75 - 115

Table 9: Typical Ranges of Densities

S & W

Sediment and Water (S & W) is the collective term for non-hydrocarbon materials that are often included in crude oil as it leaves the production area. Crude oils may contain significant amounts of S&W as the product from from the wells, and are treated on-site to reduce S&W. The concentration, which is set by the pipeline is typically 1.0% or less. More often S&W content may be regulated by state agencies, such as the Texas Railroad Commission, which sets a maximum of 2.0% on S&W. S&W are usually in the form of tiny droplets which are suspended in the oil, and generally will not settle out from the oil phase.

The most common method for measuring S&W is the centrifuge method. This method uses a measured (typically 50 ml) sample of crude oil placed in a cone-shaped glass centrifuge tube. An equal amount of solvent is added, and then heated to 140 deg F – 160 deg F. Several heated tubes and their contents are spun in a high-speed centrifuge for an amount of time during which the sediment, water, and heavy elements are driven to the bottom of the tubes. The amount of S&W is read from a scale (calibrated in milliliters), which is etched on the side of the tube. This quantity of S&W is related to the original quantity of sample before dilution.

It is very important in this process that the S&W sample is representative of the crude oil that has passed through the meter. A crude oil sampling system will be installed to automatically take a small amount of product on a proportional to flow basis. This small sample is injected into a receiver vessel. At the end of the month, the receiver vessel is circulated with a small pump to mix the composite sample.

S&W determination using the centrifuge method usually relay on a ‘batch period’ of a month. This correction is then applied to the monthly volume ticket with the other correction factors (CTL and CPL).

Vapor Pressure

The true Vapor Pressure of a liquid is the pressure at which the fluid is in equilibrium between its liquid and gas state. Looking at GPA Standard 2145-03 for example, the Vapor Pressure of Propane at 100 deg F is stated as 72.484 psia. This means that it will take 72.484 psia to liquefy the gaseous state, and maintain two-phase (liquid and gas) equilibrium. Practically this means that the measurement system must maintain greater than 72.484 psia or the system will experience flashing.

A common term for a liquid at its ‘flash point’ is a ‘Bubble-point liquid’. An example of this measurement problem exists at the inlet of a Gas Processing Plant. Condensate liquid from a producing gas field will be collected at the inlet to the plant in a large vessel called a ‘Slug Catcher’. This liquid is in equilibrium with the produced gas, and is referred to as a bubble-point liquid. Typically this liquid is the property of the owners of the producing gas field and as a result, must be measured at the inlet of the plant. A pump must be implemented to ‘boost’ the pressure of these liquids, or flashing will occur in the measurement equipment.

Another common example of Vapor Pressure considerations occurs with the sampling of Natural Gas Liquids. Unlike sampling of Crude Oils, the containment system for Natural Gas Liquids must be pressurized above the vapor pressure of the product. If the containment pressure does not exceed the product vapor pressure, when a sample is injected, it will flash, and the composite sample will not be representative of the liquid composition at the primary measurement element.

Equilibrium vapor pressure enters into the calculation of CPL as the factor ‘Pe’ in Equation 5. There are a variety of laboratory methods that measure vapor pressure. ASTM method D 86 uses laboratory distillation data. True vapor pressure for Natural Gas Liquids, Ethane/Propane mixes and other light products can also be calculated from a Chromatograph Analysis.

Another form of vapor pressure, which is used for many purposes, is the Reid Vapor Pressure (RVP). RVP is the vapor pressure of a liquid at 100 deg F as determined by the testing procedures in ASTM D323-28 standard test method for vaporization of petroleum products. RVP is used to set safe operating specifications. For example, crude oils or other petroleum stocks may be accepted for transportation only if the RVP is less than 10 psia. This limit is set to prevent excessive losses due to evaporation, damage to tanks or marine vessel compartments due to excessive pressure or boiling or inaccurate measurement due to flashing in meters.

Viscosity

Viscosity is the characteristic of a fluid that causes it to resist flow. Viscosity is measured in several ways and is reported in a varity of units. The fundamental unit of absolute viscosity is the Poise. The Poise is the force measured in dynes to effect a tangential displacement over one square centimeter in one second.

Kinematic viscosity is defined as absolute viscosity divided by density. Kinematic viscosity is measured in Stokes. Because it includes the density term, kinematic viscosity is more useful in predicting the effect of viscosity on meters, pumps, and pipe friction loss. The measured value of both Poise and Stokes is too large for practical reporting, so the Centipoises (Cp) and Cenitstoke (cSt) are used.

Higher values of centipoise or centistokes indicate greater resistance of the fluid to flow. The viscosity of many common petroleum products ranges from about 0.5 Cp to about 2 Cp, whereas viscosity of crude oils ranges from a few hundred Cp to thousands of Cp.

Viscosity is very sensitive to temperature. Table 10 demonstrates the effect.

	60 deg F	210 deg F
Fuel Oil	13,000 cSt	45 cSt
Diesel Fuel	750 cSt	30 cSt
SAE 40 Motor Oil	1,000 cSt	14 cSt

Table 10: Temperature effects on Viscosity

Effects on Liquid Turbine Meters

While not entering into any correction factor for net volume, or mass calculations, the viscosity of the fluid must be considered when the density of the measurement station occurs.

The viscous drag on the rotor of a liquid turbine meter is related to the fluid viscosity. As the viscosity of the fluid increase the drag increases. The result of this drag will be a shift in the turbine meter’s performance curve to ‘the right’. As a result, the original ‘K Factor’ (the factor that relates output pulses of the meter to the volume flow rate) will shift.

Another way to look at the effect of viscosity is in terms of slippage. The Viscosity of the product will have an effect of the product slippage in both a Liquid Turbine Meter and a Positive Displacement Meter. High viscosity oil reduces slippage in positive displacement meters, which results in a lower meter factor. Higher viscosity will reduce the linearity of the meter and may increase the minimum flow rate rating.

If the liquid turbine meter installed is a system where the viscosity of the fluid is different for the original calibrated fluid, an in-situ calibration (meter proving) must be performed.

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