The Uncertainty of a Waterdraw Calibration vs. Gravimetric Calibration on Small Volume Provers

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Introduction

The focus of the API Petroleum Measurement Manuals is to reduce the uncertainty and improve the accuracy of all petroleum measurements. Many recent advances in weighing equipment and research and testing by various groups to improve volume calibrations have provided opportunities to greatly reduce the uncertainty and provide increased confidence in displacement Prover calibrations. Both API and NIST have standards on both volumetric and gravimetric techniques.

The purpose is to review the history, techniques, similarities, advantages and disadvantages, and the uncertainty comparison between gravimetric and the traditional water draw method of Prover volume calibrations by NIST certified volumetric field test measures, focusing on high precision captive displacement flow Provers, known more commonly as SVP's.

Groups, such as American Petroleum Institute Manual of Petroleum Measurements Chapter 4.9.4, and NIST SOP_SVP_15Nov-06 have defined standards for gravimetric displacement flow Prover calibrations.

Volume Measurement Basics

There are 4 basic measurements:

1. Length
2. Time
3. Mass
4. Temperature

Volume is the <u>quantity</u> of three-dimensional <u>space</u> enclosed by some closed boundary. Volume is a <u>derived</u> value, not a basic measurement. A volume of 1 cc of water weighs 1 gram at 4°C.

What is Measurement Uncertainty?

From NIST TN1297:

2.1 In general, the result of a measurement is only an approximation or estimate of the value of the specific quantity subject to measurement, that is, the measurand, and thus the result is complete only when accompanied by a quantitative statement of its uncertainty.

From Tooling U:

The estimate of the difference between a measured value and the true value

From Merriam-Webster:

1: the quality or state of being uncertain: doubt
2: something that is uncertain

## A Brief History of Gravimetric Prover Caibration

Until recently, most displacement Prover volume calibrations in the petroleum industry have been performed by the water draw method using field standard volumetric test measures. With the advent of new high resolution electronic weigh scales, newly defined gravimetric calibration procedures, gravimetric displacement Prover calibrations, especially on SVP's have become common in the industry.

Some of the first commercially manufactured laboratory flow meter calibrators were time/weigh stands manufactured by Cox Instrument Company. These calibration stands contained a reservoir of calibration fluid; a pump, a test section for flow meter installation, and another reservoir with a weighing system using a beam balance weigh scales. They were the standard of the US Government and independent laboratories dating back to the 1950's.

In the 1960's, Ed Francisco, who was the father of the double chronometry technique for pulse interpolation and the flow-through piston, designed and manufactured small volume positive displacement Provers for the rocket industry. Ed calibrated the volumes by displacing the fluid into a container on a high precision beam balance weigh scale. The fluid used by Francisco at his company Flow Technology was Mil-Spec stoddard solvent, which had a known density. In the 1960's Flow Technology developed the first small volume flow Provers for the petroleum industry, and used the same gravimetric technique for the SVP flow Provers. Ed believed it was a far more precise calibration technique than using volumetric containers for calibration.

Comparing Volumetric and Gravimetric Calibration Techniques:

The primary difference between the conventional water draw method and the gravimetric method for flow Prover calibration is that field standard test measures are replaced with a weighing system (weigh scale and container).

Typical Calibration (SVP)
Volumetric Calibration Setup

Typical Calibration (SVP)
Gravimetric Calibration Setup
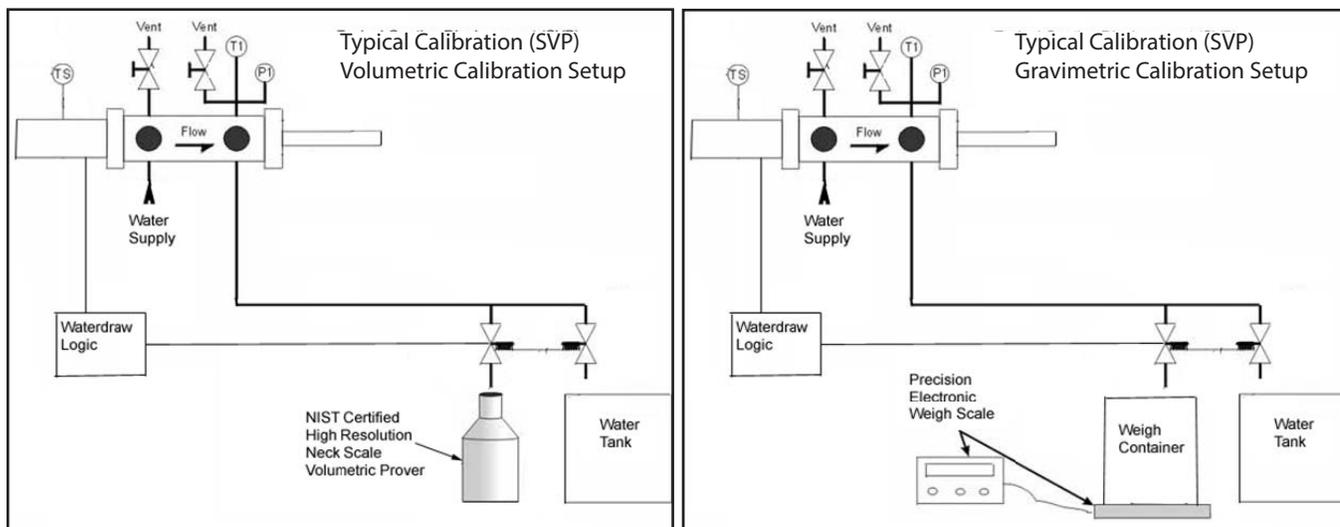
Preparation of the Prover in both cases is identical. Conducting the calibration runs is nearly identical in both cases. Gathering and recording the required data to calculate the base volumes of displacement and tank Provers is nearly identical for the volumetric method and gravimetric methods. Calculations are identical for correcting the Prover volume for pressure and temperature in both techniques.

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Obviously, to be stressed is the importance of proper cleaning of the Prover prior to the calibration process.Contamination can pollute the calibration water and cause serious errors in the calibration results in either volumetric or gravimetric procedures.

Water quality is extremely important. Clean, potable water is required for volumetric water draws. Either deionized or distilled water is highly recommended for gravimetric water draws. Dissolved mineral salts (hardness) affect water density, and can cause errors in the calibration by up to nearly 0.05% if uncompensated. Per API 4.9.4, it is necessary to check the water conductivity using a properly calibrated water conductivity meter.

If, in some circumstances, where distilled water or deionized water is not available or available in the required quantities, clean, potable water may be used. In those cases, the water density must be compensated for by using the conductivity reading from the conductivity meter by using the correction formula from API 4.9.4.

Differences between Volumetric and Gravimetric flow Prover calibrations:

Volumetric Technique:

- Volumetric test measures must be leveled and wetted (wetting of the container is not necessary for gravimetric draws)

- Volumetric test measures should be read by the same person in order to assure consistency - not necessary for a weigh scale reading, as it is digital (digital readings eliminate analog errors of visually reading the sight glass scale)

- Volumetric test measure must be drained for a required amount of time for the same residual water in the can the same as when calibrated (Not necessary for draining of catch container in gravimetric draws, as taring of weigh scale after draining zeroes out any residual water.

- Water temperature in the volume test measure must be carefully and properly read for proper water volume and can corrections. (Not necessary for gravimetric) the mass of the water is not affected by the temperature)

Gravimetric Technique:

Air density must be known for the buoyancy effects on gravimetric calculations. (API 4.9.4 uses altitude of the location where the draw is performed. This method used is taken from API 14.6 densitometers) Not necessary to know the altitude closer than 50'

- Gravimetric calibrations must have a draft-free location for the weigh scale, as air currents can affect the weigh scale readings due to the extreme sensitivity of the high precision weigh scales used for flow Prover calibrations. Uncertainty of the weigh scales is dependent on the scale capacity. Higher capacity precision weigh scales suitable for prover calibrations can have uncertainties of 1-2 grams, and lower capacity weigh scales have uncertainties of 0.1 grams of less. Weigh scales also have linearity uncertainties, but linearity uncertainties are greatly minimized by calibrating the scales to near the weight of the water for the specific Prover volume. This calibration of the scales is defined in API 4.9.4.

- Weigh Scales must be leveled and calibrated using certified test weights for every Prover calibration

Gravimetric Flow Prover Dispensed Volume Calculations

This discussion will only cover the calculations for distilled or deionized water (recommended for API, and required per the NIST standards), with a conductivity of less than 50 microSiemens. API 4.9.4 contains a calculation to correct clean potable water to the proper density where there is not an available source of pure water. The procedure for calculating the Base Prover Volume from the data obtained by the calibration is calculated as follows:

Mass = Apparent mass x Air buoyancy correction

where:

M_W = Mass of water, in grams

A_{MW} = Apparent mass of water in grams

C_{BW} = Correction for air buoyancy on weighing

$$C_{BW} = \left[\frac{1-\left(0.0012/\rho_{TWr}\right)}{1-\left(0.0012/\rho_{TWf}\right)}\right]\left[\frac{1-\left(\rho_A/\rho_{TWf}\right)}{1-\left(\rho_A/\rho_{Ftp}\right)}\right]$$

where:

C_{BW} = Correction for air buoyancy on weighting

ρ_A = Density of dry air, in grams/cc

ρ_{TWr} = Density of reference test weights, in grams/cc

ρ_{TWf} = Density of field test weights, in grams/cc

ρ_{Ftp} = Density of fluid at test temperature and test pressure, in grams/cc

Calculation of air density per API 14.6 (USC units)

ρ_A = 0.0012 [1 – 0.032h / 1000)] [520 / (T_f + 460)]

Determination of Dispensed Volume at test temperature and atmospheric pressure in the Container

The volume of water in the container at the test temperature and atmospheric pressure shall be calculated as follows:

$DV_W = M_W / W\rho_{tp}$

where:

DV_w = Dispensed volume of water, in milliliters (ml)

M_w = Mass of water, in grams

$W\rho_{tp}$ = Density of water at test temperature and atmospheric pressure, in grams/cc

Volumetric Field Test Measure to Prover Corrections

$$VCF = [1 + (Tam - Std. Temp) (a)] \rho ms \div [1 + (Tp - Std. Temp) (b)] \rho wp$$

where:

Tam = average temperature in the volumetric test measure

Tp = temperature in the Prover under calibration

a = cubical coefficient of expansion of the volumetric test measure

b = cubical coefficient of expansion of the Prover under calibration

ρms = water density in the volumetric test measure from the Patterson Morris equation

ρwp = Water density in the Prover under calibration from the Patterson Morris equation

Comparing Volumetric and Gravimetric Calibration Uncertainties

For this analysis in the simplest terms, we will compare the uncertainty comparison of only the volumetric test measure vs. the uncertainty of the Prover dispensed volume calibrated by the gravimetric method. In an effort to limit the size of this paper, only 2 sizes of SVP's will be analyzed. A larger 75 gallon and a smaller 5 gallon SVP are used for this analysis. This analysis on the gravimetric are performed using the square root of the sum of the squares of the uncertainties, since all uncertainty related to gravimetric draws are random uncertainties.

The uncertainty of the volumetric test measures used in this analysis is based on an average of a group of NIST certified volume containers provided by NIST. Uncertainty of the example test measures is from the NIST. These containers have been calibrated and uncertainties evaluated by the NIST using SOP-14. These uncertainties are on the can certificates. Per NIST SP 250-72 in description of service, states that typical uncertainties for neck scale Provers, (the field test measure type typically used for calibration of flow Provers) uncertainties range from +/- 0.3% for a 1 gallon can to +/- 0.01% uncertainties for cans of 100 gallons and larger.

The greatest factor for greater uncertainties in smaller test measures versus larger sizes is due to the ratio of the volume of the can to the surface area being less favorable. The above uncertainties are only the uncertainties of the volumetric can certification, and do not include additional uncertainties that must be considered by the customer during subsequent use of the field standard test measures used as a working standard.

Identification of uncertainties during use of the field standard test measures as working standards:

1. Neck scale reading uncertainties
2. Drain uncertainties due to either improper drain times or temperature of use being different than the temperature the test measure was calibrated causing a difference in viscosity of the water. (Per NIST SP250-72, the error for a difference in volume due to viscosity from a temperature change from 15° C to 22° C is a average of 0.02% for a 100 gallon test measure and up to 0.05% for a 5 gallon test measure.)
3. Possible damage to test measure after calibration
4. Cleanliness of the can (scale, rust, or oily films)
5. Poor leveling of the can
6. Incorrect relationship between neck scale increments and neck diameter
7. Temperature measurement error
8. Temperature stratification when the air temperature is significantly different than the water temperature

For a more complete identification and explanation of gravimetric uncertainties of volumetric Provers, see the appropriate section of NIST SP 250-72.

Identification of the magnitude of uncertainties in determining a volume gravimetrically for the following analysis and comparison with uncertainty of a volume determined by NIST certified test measure.

Uncertainty of test weights from certification:
 - 25 KG ASTM Class 1 test weights (25,000 grams) with 12 mg uncertainty = +/- 0.00005%
 - Uncertainty of scale reading: = (percentage of error based on weight measured and weigh scale uncertainty)
 - Uncertainty of distilled or deionized water assuming 0.1° F uncertainty = +/- 0.0018%
 - Uncertainty of air density assuming a ten (10) foot altitude uncertainty with an effect of 0.0012: = +/- 0.00004%

Air density is measured using dry air density corrected for altitude per API 4.9.4 and API 14.6
Weigh scale linearity errors assumed to be insignificant if scales are calibrated at near the weight of water draw.

Uncertainty comparison between volumetric and gravimetric calibration on a 75 gallon SVP
This comparison uses a 3,000 Kg weigh scale with an uncertainty of +/- 1 gram. Because of the size of this unit, 2 dispenses were performed since the total weight of water and container exceeded the scale capacity. 6 each 25 Kg test weights each with an uncertainty of +/- 0.00005% were used to calibrate the scales at near target weight.

      1. Uncertainty of 6 ea 25 Kg test weights: = +/- 0.00012%
      2. Uncertainty of scale reading: = +/- 0.00071%
      3. Uncertainty of water density: = +/- 0.00180%
      4. Uncertainty of air density: = +/- 0.00004%
      5. Gravimetric uncertainty per dispense   =
                    $\sqrt{(0.00012\%^2 + 0.00071\%^2 + 0.00180\%^2 + 0.00004\%^2)}$
                    = +/- 0.00190%
    Gravimetric uncertainty for 2 dispenses   = +/- 0.00268%

This example uses a 25 gallon test measure. 3 fillings are required per run to obtain the 75 gallons.

High resolution 25 gallon can uncertainty average of 6 NIST certified cans was = +/- 0.03%
      1. Uncertainty of 25 gallon neck Prover: = +/- 0.03000%
      2. Uncertainty of temperature: = +/- 0.00186%
      3. Uncertainty of water density: = +/- 0.00180%
        25 Gallon neck Prover uncertainty: = $\sqrt{(0.03000\%^2 + 0.00186\%^2 + 0.00180\%^2)}$
                    = +/- 0.03111%
     Neck Prover uncertainty for 3 fillings: = +/- 0.05215%

Uncertainty comparison between volumetric and gravimetric calibration on a 5 gallon SVP

The example of the uncertainty presented here used a 35 Kg weigh scale with an uncertainty of +/- 0.1 gram. 1ea. 25 Kg test weight is used to calibrate weight scale, being close to the water target weight.

1. Uncertainty of 25 KG test weight: = +/- 0.00005%
2. Uncertainty of scale reading: = +/- 0.00029%
3. Uncertainty of water density: = +/- 0.00180%
4. Uncertainty of air density: = +/- 0.00004%
5. Gravimetric uncertainty $= \sqrt{(0.00005\%^2 + 0.00029\%^2 + 0.00180\%^2 + 0.00004\%^2)}$
        = +/- 0.00182%

High resolution 5 gallon test measure uncertainty average of several NIST certified cans was = +/- 0.15%

1. Uncertainty of 5 gallon neck Prover: =+/- 0.15000%
2. Uncertainty of temperature: =+/- 0.00186%
3. Uncertainty of water density: =+/- 0.00180%

5 Gallon test measure uncertainty: $= \sqrt{(+/-0.15000\%^2 + +/- 0.00186\%^2 + +/-0.00180\%)}$
        = +/- 0.15002%

Note: Please refer to additional uncertainties that may be incurred in volumetric water draw calibrations in a previous paragraph, and also in NIST SP 250-72

Results

The results show a dramatic improvement (decrease) in uncertainty by using the gravimetric method, especially as the Prover volumes get smaller:

75 Gallon SVP nearly 20 times
5 Gallon SVP over 80 times

Conclusion

Manufacturers of captive displacement (SVP) Provers have recognized the importance of accurate volume calibrations, and have employed the gravimetric method in their final acceptance testing for years. The above comparison indicates the gravimetric method has a significant improvement (decrease in value) in uncertainty over volumetric water draws. The values also show an improvement that is at much greater than an order of magnitude (a factor of 10) better than the volumetric method.

In order to obtain the required or to significantly improve the uncertainty of custody transfer measurement applications, it would seem to be imperative to utilize the gravimetric method for Prover calibrations, especially for SVP's. Remember, volume is a derived value.

Always check the uncertainties of all measurement components used for flow Prover calibrations to be certain they meet the API requirements.

References
API MPMS: 4.9.4, 4.9.2, 12.2.4, 11.2.3, 11.4.1
NIST Publications: SP 250-72, NISTIR 7383, Technical Note 1297
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