

# ASTM UPDATE to COQA

COQA Meeting Feb 21 2018 San Antonio

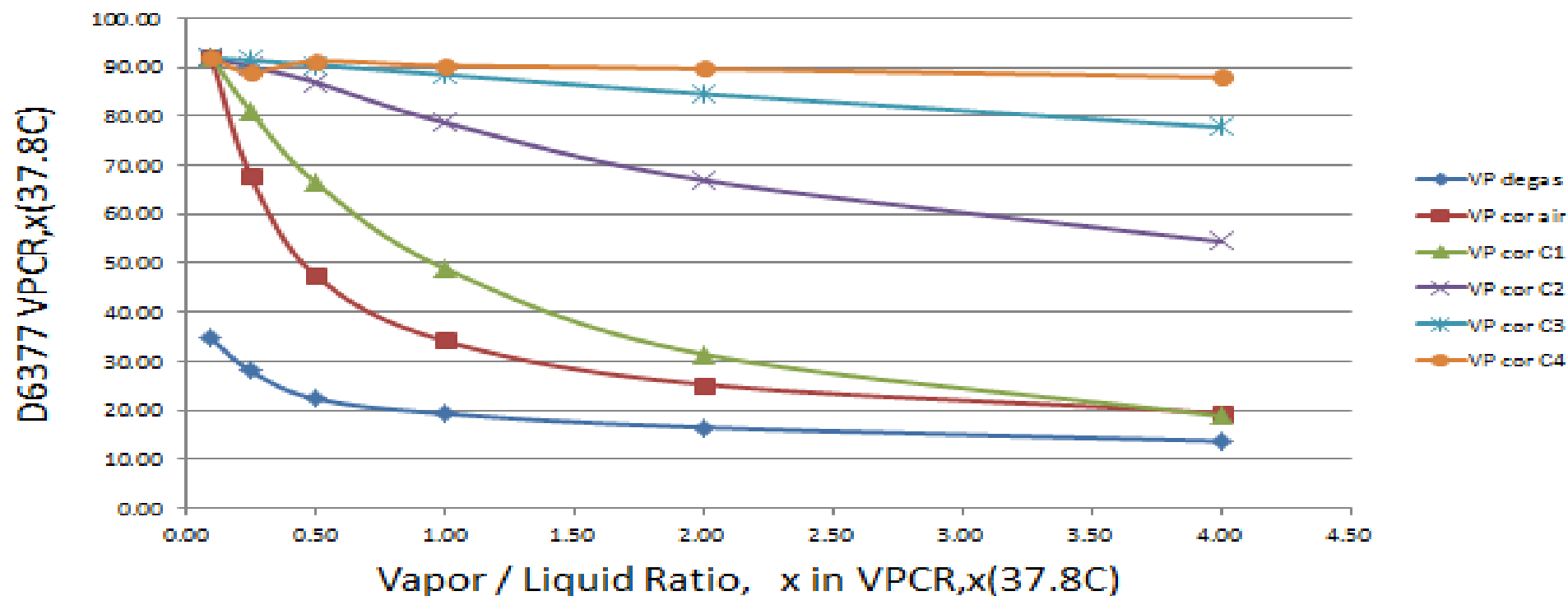
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# WHAT HAS CHANGED IN THE LAST 5 YEARS?

- CCQTA TVP / RVP PROJECT INITIATED IN FEB 2013
  - GOV'T / INDUSTRY WORKSHOP at AITF EDMONTON WITH REPRESENTATION FROM ACROSS GOV'T, RAIL, PIPELINE, REFINERY & ASTM / API TECHNICAL COMMITTEES
  - GENERAL CONSENSUS ON PATH FORWARD INCLUDING SAMPLING / TEST METHODS
- SEVERAL HIGH PROFILE CRUDE BY RAIL INCIDENTS
- API RP3000 – CRUDE BY RAIL LOADING STANDARD
- DOE / DOT / TRANSPORT CANADA SPONSORED RESEARCH on CRUDE OIL CHARACTERIZATION at SANDIA NATIONAL LABS
- COMMON CARRIER PIPELINE VP SPECIFICATIONS
- NORTH DAKOTA 13.7 psia MAX CRUDE VP REGULATION
- ASTM D7900 – GC SimDist “MERGE” METHOD
- ASTM D7975 - VP FIELD METHOD VPCrF
- ASTM D8003 – HPLIS C1 – C24 GC (SEALED LIQUID INJECT)
- ASTM D8009 – MANUAL PISTON CYLINDER (MPC)
- ASTM Dxxxx – “VLE METHOD” – EQUILIBRIUM VAPOR (in ballot)
- ASTM D6377 - REVISIONS (in ballot)

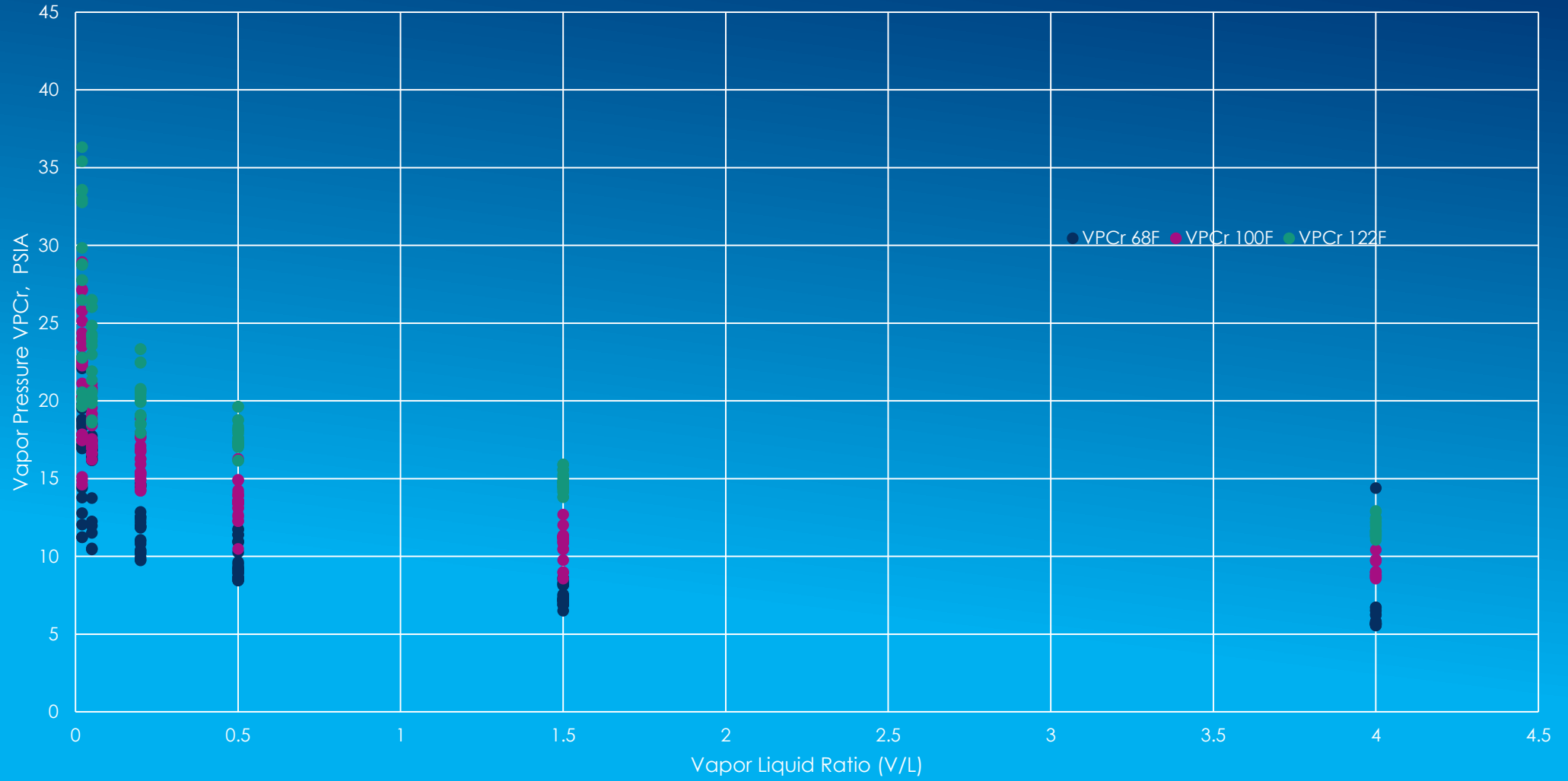
## 2,2,4-Trimethylpentane Blend Comparison

- 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

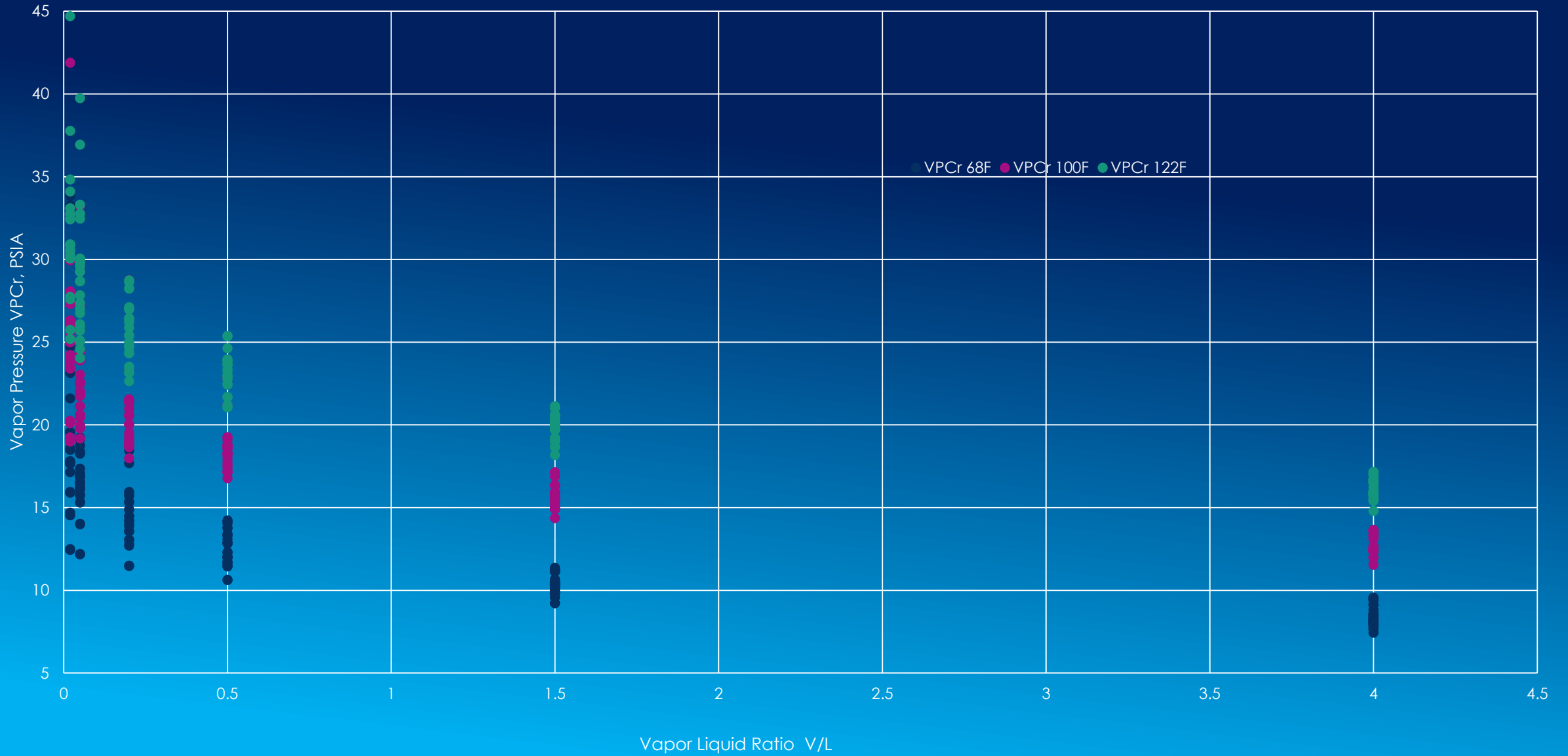


- Data for HC gases corrected for air content, and normalized to 92 kPa (barometric pressure at the time) at V/L = 0.1 to show relative contribution of light gases saturated in iC8 (224TMB) at 37.8C
- Samples prepared and analyzed at Alberta Innovates funded by CCQTA Executive Committee

Vapor Pressure vs. V/L (Eagleford Crude, Sandia Task2 Report)



# Vapor Pressure vs. V/L Ratio (Bakken Crude Sandia Task 2 Report)



## High-Level Findings from Sandia Report SAND2017-12482

- Both open and closed industry standard sampling methods yielded crude oil samples with nearly equivalent VPCR and hydrocarbon content, though important conditions apply:
  - The crude oils have been exposed to atmospheric storage upstream of sampling points
  - For VPCR measurements at  $V/L < 1$ , samples must be introduced from pressurized containers
  - The study was unable to generate reproducible results for VPCR of crude for  $V/L = 0.02$  and  $0.05$ , even with sample preconditioned to same temperature as D6377 injection and measurement temperature (68F, 100F 122F).
- ASTM D6377 VPCR(0.2) compares well to the bubblepoint pressure measured in a flowing separator system at selected temperature
- Commercially available pressurized compositional test methods from spot sampling yielded results that compared well with results from a baseline flowing separator system
- Equation of State Model simulations supplied with the abovementioned compositional data predicted pressure-volume-temperature behavior that compared well with D6377 VPCR
- Inert gas such as nitrogen appears to be common to samples that show higher vapor pressure at low  $V/L$ . The source of nitrogen may come from the sampling system and/or from handling in the field or lab.

## Possible areas for improving understanding and best practice in crude oil sampling, vapor pressure, and light end analysis:

- Improve reproducibility of D6377 VPCR at low V/L for spot sampling. Need to isolate sample handling effects from instrument limitations.
- Reduce frequency/magnitude of introducing inert gas into VPCR and compositional samples that create a lab sample different from the parent material
- Explore the viability of VPCR(0.2) or similar as an estimate for bubblepoint pressure or true vapor pressure
- Determine where in the supply chain open versus closed sampling really does and does not matter for collecting VPCR and compositional samples

# WHAT IS THE CCQTA “VLE METHOD”

## Standard Practice for Preparing an Equilibrium Liquid/Vapor Sample of Live Crude Oil, Condensates and Liquid Petroleum Products using a Manual Piston Cylinder for subsequent liquid analysis or gas analysis by Refinery Gas Analyzer.

This standard is issued under the fixed designation DXXXX; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1. This Standard Practice covers the preparation of an equilibrium gas sample of live crude oil, condensate or liquid petroleum products, using an ASTM D8009 Manual Piston Cylinder (MPC) as a vapor tight expansion chamber to generate an equilibrium vapor/liquid pair at a known temperature and vapor/liquid ratio (V/L). Inert gas such as helium or argon is injected to the equilibrium vapor space of the MPC to provide an equilibrium vapor sample sufficiently above atmospheric pressure for subsequent analysis using a standard refinery gas analyzer (RGA) such as described in D7833. Other gas analysis methods may be used provided they meet the minimum performance criteria stated in 7.4.1.
2. This Standard Practice is suitable for UN Class 3 Liquid samples having vapor pressures between 0 kPa and 300 kPa at 50.0°C, and 0.1:1 to 4:1 vapor/liquid ratio, spanning the nominal range near bubble point (ASTM D6377 VPCr,0.1) to ASTM D323 (RVP), D4593 and D5191 (V/L=4). The temperature may vary over a wide range, provided that the cylinder is maintained at isothermal and isobaric conditions to prevent condensation of equilibrium vapor upon cooling either in the cylinder or in the injection system of the Refinery Gas Analyzer (RGA, D7833). The method is best suited for preparation of an equilibrium Gas/Liquid pair near ambient conditions, typical of routine daily operations in a typical Refinery Quality Assurance or Marine Terminal Laboratory, to routinely monitor the light ends content of crude oil receipts.
3. This Standard Practice is suitable to prepare an equilibrium liquid/vapor sample pair in a sealed sampling system (no light ends loss from either phase). The equilibrium gas phase is suitable for subsequent gas analysis of both hydrocarbon and fixed/inert gases in the sample, including: hydrogen, oxygen, nitrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, C1 to C7 hydrocarbons at levels consistent with the D7833 method used. The equilibrium liquid phase can be subsequently analyzed by D8003 to obtain paired analytical results on both the equilibrium liquid and vapor pair with a sealed sample system.
4. Addition of the diluent gas provides a positive pressure sample to allow the use of a typical RGA type gas injection system that operates only slightly above barometric pressure. The preferred diluent gas shall be the same as the carrier gas used in the RGA (typically helium or argon). Choice of diluent or carrier gas may affect the ability to detect some inert gases (especially O<sub>2</sub> or H<sub>2</sub>) in some RGA configurations conforming to D7833.
5. The values stated in SI units are to be regarded as standard.

This practice is under the jurisdiction of ASTM Committee [D02](#) on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee [D02.08 on Volatility](#).

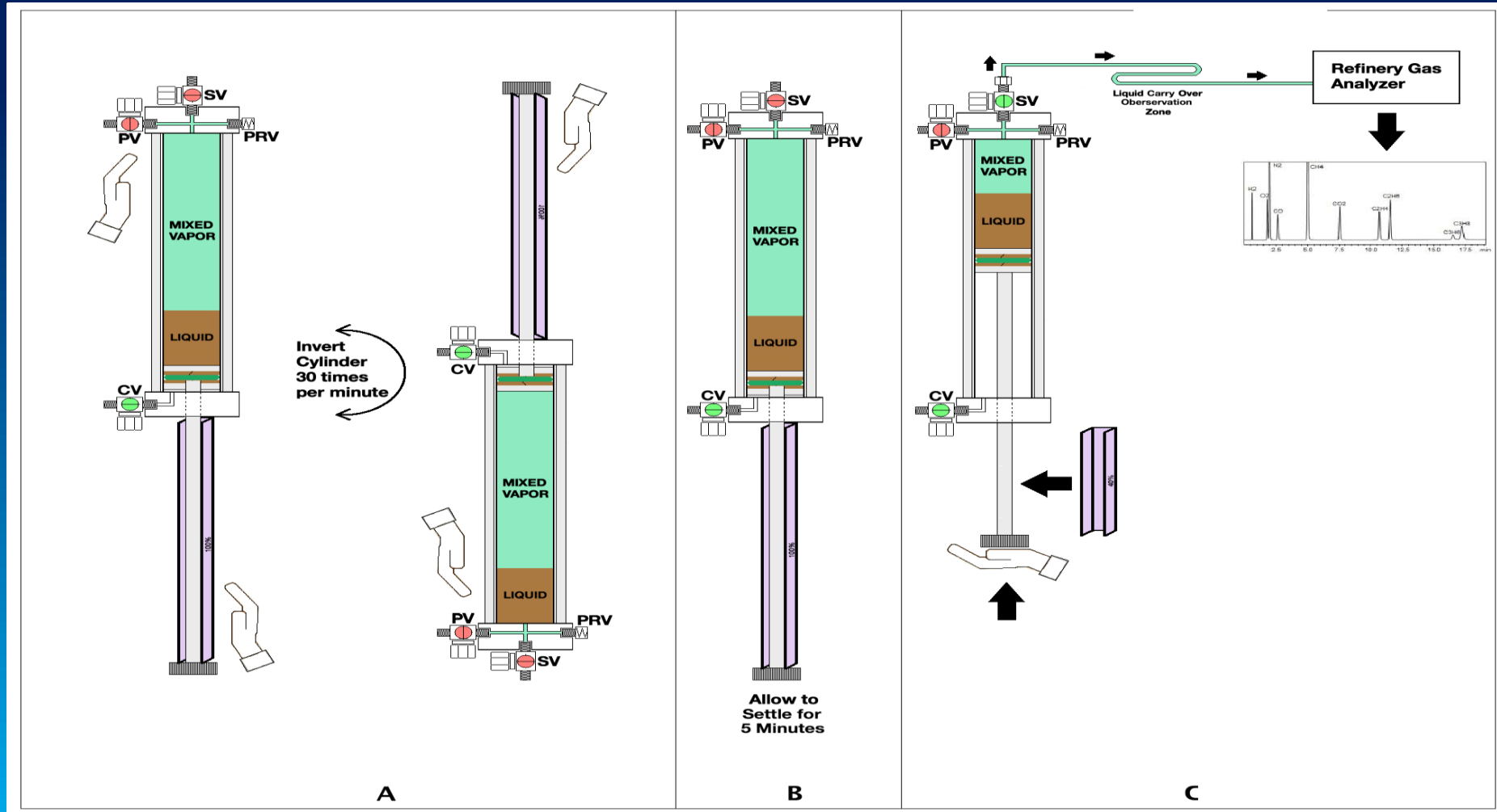
**CURRENTLY IN SUBCOMMITTEE BALLOT AT ASTM**



# WHAT IS THE CCQTA “VLE METHOD”

- MEASURE THE D6377 VP AT A KNOWN T AND V/L (eg 70 F, V/L = 4)
  - $PV = nRT$ , so number of moles in vapor space is known from VP
- USE THE D8009 MPC TO DUPLICATE THE T & V/L CONDITIONS OF THE D6377 VP MEASUREMENT
  - Same number of moles in vapour space as in the VP measurement
  - Generates an equilibrium LIQUID & GAS paired sample at known T & P
- BACKFILL THE MPC WITH GC CARRIER GAS ~ 10 PSIG
  - Inert gas at low P does not change the composition of the phases
  - Now have sufficient vapor sample > atmospheric pressure to inject into GC
- INJECT VAPOUR SAMPLE INTO STD. ASTM D7833 REFINERY GAS ANALYSIS (RGA) GC
  - Commonly referred to as Refinery Fuel Gas or Green House Gas Analysis
  - Measures HC light ends AND inerts (O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, “pad gas”)
  - CAN USE EOS to CORRECT VP FOR PRESENCE OF INERTS AND OBTAIN HYDROCARBON TVP
- **FEASIBLE FOR REFINERIES TO MONITOR / TREND CRUDE LIGHT ENDS ROUTINELY (for the first time)**
  - in house, fast, low cost, standard methods, existing equipment
  - easily done in refinery QA Lab
- CCQTA PLANNING TO FIELD TEST SUMMER 2018

# WHAT IS THE CCQTA "VLE METHOD"



Graphics and ASTM formatted text courtesy of Dave Murry for CCQTA TVP/RVP Project

