

Appendix H
Factors to consider when using a triple expansion
method to measure the vapor pressure of heavy refinery
liquids

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Mini method description and variable definitions

The minimethod instruments implemented in this project can be used to perform the automated vapor pressure instruments method ASTM D6378, “Standard Test Method for Determination of Vapor Pressure (VP_X) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method).” In this method, the total pressures at three expansions (three vapor volume to liquid volume ratios) at constant temperature are measured so that the contribution of dissolved gas (air) to total vapor pressure can be calculated. By subtracting the pressure of the dissolved gas from the total pressure, the vapor pressure of the material can be found.

The variables used by instrument manufacturers in their reported results do not necessarily match the variables defined in ASTM D6378, as shown in Table H-1.

Table H-1. Variables for the method and the mini method instruments

Name	ASTM variable	Eralytics variable	Grabner variable	Description
partial pressure from dissolved air	PPA	P_{gas}	p_{Gas}	the pressure exerted in vacuum from dissolved air that escapes from the liquid phase into the vapor phase
total pressure	TP_X	P_{tot}	p_{Tot}	the pressure exerted in vacuum by air- and gas-containing petroleum products, components and feedstocks, and other liquids, in the absence of undissolved water at a vapor-liquid ratio of X:1
vapor pressure	VP_X	P_{abs}	p_{Abs}	the total pressure minus the PPA in the liquid at a vapor-liquid ratio of X:1

In the case of the measurements for this project, the vapor:liquid volume ratio is 4:1, so X in the method's nomenclature is 4. The instruments were used to perform ASTM D6378 as well as variations on ASTM D6378 that were designed to accommodate low vapor pressure, viscous materials such as fuel oil no. 6.

This appendix details a concern about the method and observations related to calculations performed by the instruments.

A concern about the method

Appendix X2 of ASTM D6378 allows for PPA at a given temperature to be calculated based on the triple expansion for PPA at another temperature and the ideal gas law (i.e., by multiplying the PPA at the temperature of the expansion by the new absolute temperature divided by the absolute temperature of the expansion). When operating in "curve" or "multi point" mode, the instruments perform only one triple expansion and use the ideal gas law to calculate PPA at all the other temperatures in the curve. In the case of the Eralytics instrument in "curve" mode, the triple expansion was performed at 100°F. The pressure readings from the triple expansion are

not recorded or reported in the run results. If one of the programmed temperatures is 100°F, a new TP_X reading is made at 100°F.

The flaw in this shortcut for calculating PPA is that it assumes that the equilibrium constant for the solubility of air in the fluid whose vapor pressure is being tested is independent of temperature. In actuality, the equilibrium constant is dependent on temperature, and the expectation is that dissolved air is increasingly driven out of solution at increasing temperatures.

It is unknown how much the results for heavy refinery liquids would be affected by this issue. Once it was discovered that the instruments do not make a separate triple expansion reading at each temperature, single point mode was used instead of curve or multi-point mode. As described later in this appendix, in the case of the Eralytics instrument, all of the results obtained using the curve mode had to be abandoned because of errors in the instrument's algorithms, so there are no curve mode results that could be compared to the single point mode results for that instrument. In the case of the Grabner instrument, only one set of single point readings was obtained and that was for the "known" recipe. It utilized the Grabner's VOC method and the Grabner multipoint runs for the "known" recipe used ASTM D6378, making it impossible to discern the impact of using the curve method instead of the single point method when obtaining vapor pressure results.

Observations related to instrument calculations

The Eralytics instrument and the Eralytics instrument manufacturer provided more information needed to understand the instrument's internal calculations than did the Grabner instrument and the Grabner manufacture. Also, the Eralytics instrument was rugged enough to perform analyses on all of the study materials. As a result, this section is based on calculations using Eralytics instrument readings and results.

When the Eralytics instrument returned negative values for Pabs for two of the fuel oil no. 6 samples in late July, it was noted that the Ptot values were fairly stable for all the readings but the calculated Pgas showed a great deal of variation, sometimes exceeding the Ptot value. Per the method,

$$P_{abs} = P_{tot} - P_{gas}$$

In this equation, Pabs is the vapor pressure, Ptot is the total pressure, and Pgas is the partial pressure of the dissolved air in the sample.

These inconsistent Pgas values and the resulting negative Pabs values sparked a deeper investigation of the method's formula for calculating Pgas. This is when it was discovered that the curve methods perform only one triple expansion per curve and apply the Pgas at that temperature along with the ideal gas law to get Pgas values for other temperatures in the curve. Because this simplification does not take the dependence of the equilibrium constant of air in solution on temperature into account, and there was no means of assessing the reasonableness of the results from the simplification, curve methods were not subsequently used for either of the minimethod instruments.

It was observed that the calculated P_{gas} value at the lowest temperature for each curve was higher than the second lowest temperature. This turned out to be the result of an error in the instrument's algorithms. The original triple expansion result for each curve was not stored and could not be retrieved, so getting corrected values for the curve methods on the Eralytics instrument was not possible.

The instrument manufacturer pointed out that while the P_{tot} value for the third expansion was lost when applying the curve method, the P_{tot} values from the first and second expansions are recorded by the instrument and could be accessed. The instrument manufacturer also stated that the nominal vapor volumes for a 1:4 liquid:vapor ratio are 0.7 ml, 1.5 ml, and 4 ml for the first, second, and third expansion, respectively, and that the triple expansion whose results were not recorded was measured at 100°F. The actual expansion volumes used by the instrument in calculating P_{gas} differ from the nominal expansions due to corrections for dead space and other effects, and the instrument manufacturer shared the corrected vapor volumes on the condition that this information remain confidential. These corrected volumes were used when conducting the sensitivity analyses described later in this appendix.

Calculations of P_{gas} from the newly accessed P_{tot} values for the first two expansions and the nominal vapor volumes revealed that the results at all of the curve temperatures were not consistent with a reasonable estimate of P_{tot} for the triple expansion that was not recorded. These calculated P_{gas} values were three to six times smaller than the results reported by the instrument. This turned out to be the result of a second error in the instrument's algorithms for calculating P_{gas} .

In any case, going forward, single point mode was applied instead of curve mode and the results of the curve methods obtained on the Eralytics instrument had to be abandoned. At first, using the low VP single point method appeared to be very promising. The results for the "known" recipe using this method were consistent with modeled expectations of vapor pressure. Two pairs of readings were taken at each of three temperatures and each pair returned results so similar it is difficult to ascertain that they are not just one point when charted. In addition, the vapor pressure values formed an ever-increasing curve with increasing temperature, as vapor pressure values are expected to do.

However, when the low VP single point method was applied to the MM fuel oil no. 6 sample, the pairs of readings at 120°F and 140°F disagreed by a factor of three to four. For the BT fuel oil no. 6 sample, the vapor pressures, if anything, declined with increasing temperature, and the results from the pair of readings at 140°F disagreed by more than an order of magnitude. Only three readings, one at each temperature, could be obtained from one syringe for the MB fuel oil no. 6 sample and those three readings did not increase with increasing temperature.

A deeper investigation of the results was conducted in order to develop an understanding of the factors that could lead to poor repeatability and physically insensible results. This helped identify some tactics for conducting quality control checks of mini method instruments when measuring the vapor pressure of heavy refinery liquids. It also showed that calculated P_{gas} values are very sensitive to pressure readings and vapor volume values when the vapor pressure of a heavy refinery liquid is being measured.

In order to conduct this investigation, intermediate values such as the equilibrium constant k for air in solution and the P_{gas} and P_{abs} values at all three expansions had to be calculated. ASTM D6378 (2010) does not provide the equations for calculating these intermediate values, it only provides the final result for calculating P_{gas} at the third expansion.

The equations for the intermediate values were derived by solving a system of 14 equations and 14 unknowns. This introduces new variables and a different nomenclature than the ones expressed in Table H-1.

These equations are applied to a single temperature at a time, so the equilibrium constant k for dissolved air in the sample is constant and the vapor pressure of the material P_{VOC} (which is corrected for the effect of dissolved air) is also constant. It is assumed that the liquid volume is essentially constant. R is the ideal gas law constant, T is the constant absolute temperature, V is vapor volume, V_L is liquid volume, P_{TOT} is the total pressure, n_{TOT} is the total number of moles in the vapor phase, n_{gas} is the number of moles of air in the vapor phase, P_{gas} is the partial pressure of the dissolved air in the vapor phase, and $n_{\text{gas(l)}}$ is the number of moles of air in the liquid phase. The subscripts 1, 2, and 3 indicate the expansion number. The equations are:

From the ideal gas law:

$$P_{\text{TOT3}} V_3 = n_{\text{TOT3}} RT$$

$$P_{\text{TOT2}} V_2 = n_{\text{TOT2}} RT$$

$$P_{\text{TOT1}} V_1 = n_{\text{TOT1}} RT$$

$$P_{\text{gas3}} V_3 = n_{\text{gas3}} RT$$

$$P_{\text{gas2}} V_2 = n_{\text{gas2}} RT$$

$$P_{\text{gas1}} V_1 = n_{\text{gas1}} RT$$

From the conservation of mass (in terms of moles of air):

$$n_{\text{gas(l)1}} + n_{\text{gas1}} = n_{\text{gas(l)3}} + n_{\text{gas3}} = n_{\text{gas(l)2}} + n_{\text{gas2}}$$

From the equilibrium relationship for dissolved air:

$$n_{\text{gas1}}/V_1 = k n_{\text{gas(l)1}}/V_L$$

$$n_{\text{gas2}}/V_2 = k n_{\text{gas(l)2}}/V_L$$

$$n_{\text{gas3}}/V_3 = k n_{\text{gas(l)3}}/V_L$$

From the definition of P_{VOC} :

$$P_{\text{VOC}} + P_{\text{gas1}} = P_{\text{TOT1}}$$

$$P_{\text{VOC}} + P_{\text{gas2}} = P_{\text{TOT2}}$$

$$P_{\text{VOC}} + P_{\text{gas3}} = P_{\text{TOT3}}$$

This system of equations solves to the result given in equation 2 of ASTM D6378 (ASTM 2010), which yields P_{gas3} (PPA_t of the method) and P_{VOC} ($VP_{X,t}$ of the method). Intermediate solutions of interest are:

$$k = (P_{\text{gas1}} V_L - P_{\text{gas2}} V_L) / (P_{\text{gas2}} V_2 - P_{\text{gas1}} V_1)$$

$$P_{\text{gas1}} = P_{\text{TOT1}} - P_{\text{VOC}}$$

$$P_{\text{gas2}} = P_{\text{TOT2}} - P_{\text{VOC}}$$

$$n_{\text{gas3}} = P_{\text{gas3}} V_3 / RT$$

$$n_{\text{gas2}} = P_{\text{gas2}} V_2 / RT$$

$$n_{\text{gas1}} = P_{\text{gas1}} V_1 / RT$$

Quality checks on the results include a finding that

- k is reasonably constant at constant temperature
- k is positive
- k increases with increasing temperature
- $n_{\text{gas3}} > n_{\text{gas2}} > n_{\text{gas1}}$ (assuming $V_3 > V_2 > V_1$)
- P_{VOC} increases increasingly with increasing temperature.

For the fuel oil no. 6 samples of the study, P_{gas} is often a large contributor to P_{TOT} . This is not the case for pentane, which is the material the study team used as an operational check for the minimethod instrument and which more physically resembles the materials that the minimethod instruments were originally designed to analyze. For the study's fuel oil no. 6 samples, P_{gas} from the low VP single point method at the third expansion is between 21% and 99.6% of the total pressure reading. At the second expansion, it is between 38% and 99.7% of the total pressure reading, and at the first expansion it is between 52% and 99.7% of the total pressure reading. For pentane, P_{gas} from the ASTM D6378 single point method at the third expansion is only about 2% to 3% of the total pressure reading. At the second expansion, it is about 6% to 7% of the total pressure reading, and at the first expansion it is 12% to 14% of the total pressure reading.

Thus, for the fuel oil no. 6 samples, P_{VOC} is more sensitive to the calculated value for P_{gas} and thus more sensitive to the pressure readings and volume values than it is for a material like pentane. In the case of the MM and BT fuel oil no. 6 samples, P_{gas} values were similar to P_{gas} values for pentane, but P_{TOT} was far less. The BT fuel oil no. 6 samples had much higher P_{TOT} readings than the other two fuel oil no. 6 samples, but the P_{gas} values returned by the instrument were also much higher.

As mentioned previously, in order to best conduct sensitivity analyses of the calculated P_{gas} and P_{VOC} results, corrected vapor volumes were needed (as opposed to nominal vapor volumes of 0.7, 1.5, and 4.0). These were provided by the instrument manufacturer on the condition that they be kept confidential. For the fuel oil no. 6 samples, the P_{gas} values calculated using these corrected vapor volumes were within -0.0003 and +0.0005 psi of the values returned by the instrument (it may be they were not identical because the instrument carried more significant figures when it did the calculations than were provided in the instrument output).

Table H-2 and Table H-3 show that the sensitivity of the vapor pressure results ($P_{\text{abs}} = VP_{X,t} = P_{\text{VOC}}$) to perturbations in the reading for P_1 and in the value of V_1 . Table H-2 shows the deviation in the P_{gas} and P_{tot} results when the P_1 reading is raised by 0.03 psi, with no other changes. Table H-3 shows the deviation in the P_{gas} and P_{tot} results when V_1 is increased by 1%, with no other changes.

Table H-2 shows that the deviation in vapor pressure due to a small perturbation in the first expansion pressure measurement can be very large for the fuel oil no. 6 samples. The deviation in the vapor pressure of the “known” recipe and nonane was smaller than the deviation for most of the fuel oil no. 6 readings. For pentane, which was tested using the instrument’s ASTM D6378 single point method, the perturbation results in a negligible deviation in vapor pressure.

Table H-3 shows that a very small perturbation in the value used for V_1 impacts one of the vapor pressure values for the BT sample substantially.

Table H-3 includes a column that shows the fraction of the total pressure at the third expansion that is due to the contribution of air. The sensitivity of the vapor pressure results to perturbations in the first expansion total pressure and perturbations in the vapor volume ratio correlate with the values in this column: the closer the contribution of air gets to the total pressure, the more sensitive the vapor pressure results are. This would apply to all of the expansions, not just the third expansion. This shows that extra care must be taken in obtaining the total pressure readings and vapor volumes at each expansion when using a triple expansion method to obtain the vapor pressure of heavy refinery liquids.

References

ASTM International (ASTM), 2010, ASTM D6378-10, Standard Test Method for Determination of Vapor Pressure (VP_x) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method), West Conshohocken, PA, www.astm.org.

Tables

Table H-2. Sensitivity of measured vapor pressure to a perturbation of the total pressure reading for the first expansion (an increase of 0.03 psi) for the Eralytics mini method instrument.

Measurement temperature, °F	Increase in the first expansion's total pressure (a.k.a. P_{TOT1} , $TP_{X,1}$, or P_1) due to perturbation	Decrease in the contribution of air to the total pressure reading for the third expansion (a.k.a. P_{gas} , P_{gas3} , or PPA_t) due to perturbation	Increase in vapor pressure (a.k.a. P_{abs} , P_{VOC} , or $VP_{X,t}$) due to perturbation
Using the low VP single point method:			
nonane:			
100.04	0.66%	0.88%	3.0%
100.04	0.66%	0.90%	2.9%
100	0.67%	0.88%	2.8%
100	0.66%	0.89%	3.0%
"known" recipe			
100.04	1.0%	1.2%	3.8%
100	1.1%	1.2%	4.0%
120	1.0%	1.2%	3.0%
120	0.99%	1.2%	2.9%
140	0.93%	1.1%	2.1%
140	0.94%	1.1%	2.1%
BT fuel oil no. 6			
120	1.3%	8.9%	8.5%
120	1.3%	11%	16%
140	0.85%	12%	2380%
140	0.85%	11%	43%
160	0.54%	9.0%	79%
MB fuel oil no. 6			
120	2.6%	5.1%	5.6%
140	2.1%	4.1%	12%
160	1.2%	2.5%	5.8%
MM fuel oil no. 6			
120	2.0%	5.9%	1.6%
120	2.5%	5.2%	9.6%
140	1.6%	4.3%	1.1%
140	1.8%	5.3%	11%
160	1.0%	2.8%	2.4%
160	1.0%	3.0%	3.8%

Measurement temperature, °F	Increase in the first expansion's total pressure (a.k.a. P_{TOT1} , $TP_{X,1}$, or P_1) due to perturbation	Decrease in the contribution of air to the total pressure reading for the third expansion (a.k.a. P_{gas} , P_{gas3} , or PPA_t) due to perturbation	Increase in vapor pressure (a.k.a. P_{abs} , P_{VOC} , or $VP_{X,t}$) due to perturbation
Using the ASTM D6378 single point method:			
Pentane			
100	0.17%	1.43%	0.04%
100	0.17%	1.44%	0.04%
100	0.16%	1.27%	0.04%
100	0.17%	1.36%	0.04%
100	0.17%	1.41%	0.04%
100	0.17%	1.38%	0.04%
100	0.17%	1.35%	0.04%
Nonane			
100	0.66%	0.61%	1.48%

Table H-3. Sensitivity of measured vapor pressure to a perturbation in the first expansion's vapor volume of +1% for the Eralytics minimethod instrument. No other changes were made.

Measurement temperature, °F	Fraction of total pressure (a.k.a. P_{TOT3} , $TP_{X,3}$, or P_3) due to contribution of air (a.k.a. P_{gas} , P_{gas3} , or PPA_t) for the third expansion before perturbation	Decrease in the contribution of air to the total pressure reading for the third expansion (a.k.a. P_{gas} , P_{gas3} , or PPA_t) due to perturbation	Increase in vapor pressure (a.k.a. P_{abs} , P_{VOC} , or $VP_{X,t}$) due to perturbation
Using the low VP single point method:			
nonane:			
100.04	77%	0.9%	3%
100.04	77%	0.9%	3%
100	76%	0.9%	3%
100	77%	0.9%	3%
"known" recipe			
100.04	76%	0.8%	3%
100	77%	0.8%	3%
120	72%	0.8%	2%
120	72%	0.8%	2%
140	65%	0.8%	2%
140	64%	0.8%	2%
BT fuel oil no. 6			
120	49%	1.2%	1%
120	60%	1.3%	2%
140	99%	1.8%	354%
140	80%	1.6%	6%
160	90%	1.8%	16%
MB fuel oil no. 6			
120	52%	0.9%	1%
140	74%	0.9%	3%
160	70%	0.9%	2%
MM fuel oil no. 6			
120	21%	0.9%	0%
120	65%	0.9%	2%
140	21%	0.9%	0%
140	67%	1.0%	2%
160	46%	1.0%	1%
160	56%	1.0%	1%
Using the ASTM D6378 single point method:			
Pentane			
100	2.5%	0.8%	0.02%
100	2.5%	0.8%	0.02%
100	2.9%	0.8%	0.03%
100	2.5%	0.8%	0.02%
100	2.5%	0.8%	0.02%
100	2.5%	0.8%	0.02%
100	2.9%	0.8%	0.03%
Nonane			
100	71%	0.8%	1.99%