Combining Vapor Pressure & Density:

Simultaneous measurement of ASTM D5191 vapor pressure and ASTM D4052 density with highest accuracy and precision



Introduction

Vapor pressure and density are amongst *the* most important quality parameters of gasoline and its intermediates. Testing according to ASTM D5191 (vapor pressure) and ASTM D4052 (density) is carried out in fuel testing laboratories of refineries as well as throughout the complete distribution chain, like at terminals, storage facilities and even directly at gas stations using mobile laboratories.

Our Approach: A Revolutionary 2-in-1 Instrument

eralytics' latest groundbreaking innovation – the integrated density meter module DENS4052 for ERAVAP – allows the simultaneous determination of vapor pressure and density for liquid samples in full compliance with ASTM D4052 & ISO 12185 ($r = 0.0001 \text{ g/cm}^3$)



Advantages of the density meter module DENS4052:

- The integration of this ASTM D4052 density meter module in our ERAVAP makes it the only vapor pressure tester on the market allowing the simultaneous measurement of two parameters listed in international fuel specifications like ASTM D4814 and EN 228, namely the vapor pressure according to ASTM D5191 and the density according to ASTM D4052.
- ➤ Filling, rinsing and measurement are **fully automated** → **no operator bias**, no cumbersome cleaning with solvents or drying of the cell and no need of consumables like syringes.
- > The oscillating U-tube is **vertically oriented**, **minimizing the risk of trapping a bubble** inside the U-tube during filling.
- ➤ ERAVAP features a unique two stage FillingProofTM procedure (patent pending), employing the change in density as a function of pressure to detect any gas bubble in the U-tube and to quantify its maximum impact on the measured density result.
- With less than 1 kg the module DENS4052 is not only the worlds lightest ASTM D4052 density meter module, but due to its metal design (Hastelloy U-tube) it is also highly resistant against shocks and vibrations, making it ideal for the use in harsh operating conditions and inside mobile laboratories.

The Challenge

In practice, most petroleum-based products are kept in a refrigerator at 0°C to ensure long-time stability and to avoid the loss of volatile material. While ASTM D4052 does not specify any specific sample preparation, the vapor pressure standard test method ASTM D5191 requires "chilled, air-saturated samples". This raises essential questions:

- 1. Is there a density bias between cold and (ambient) warm samples due to dissolved air?
- 2. Will the dissolved air lead to degassing and to the formation of bubbles inside the U-tube oscillator, thereby diminishing the precision of the density measurements?

Experimental

To investigate this challenge, several different samples were measured under real conditions.

The cold samples were pre-cooled in an ice bath and air saturated prior to the measurement as required by ASTM D5191. Additionally, a 'spiked' sample had been prepared to mimic gasoline with a high content of volatiles: a FPC filled with gasoline to 80% of its capacity was pressurized with n-butane and thoroughly homogenized. To prevent degassing this sample was then kept in the FPC at a constant back pressure of 350 kPa.

Cold and spiked samples were measured according to ASTM D5191 or ASTM D6377 (total vapor pressure), for the other samples triple expansion methods were applied to determine the absolute vapor pressure. eralytics' Low VP method (based on ASTM D6378) was used for Isopropanol and Cyclohexane due to their significantly lower vapor pressures compared to n-pentane or gasoline.

To prove the performance, especially the consistency of the analyzer, each substance was measured 5 times at 37.8°C (vapor pressure) and 15°C (density), respectively. The standard deviation for each series of measurement is shown in brackets:

| Sample | | Density | | Vapor Pressure | | | |
|-------------|--------|---------|-----------------------|----------------|----------|----------------|------|
| Substance | Info | T [°C] | Density [g/cm³] | Method | T [°C] . | VP [kPa] | Туре |
| n-Pentane* | cold | 15.0 | 0.63123 (± < 0.00001) | D5191 | 37.8 | 112.7 (± 0.15) | Ptot |
| | cold | 15.0 | 0.63123 (± < 0.00001) | D6377 | 37.8 | 112.8 (± 0.07) | Ptot |
| | warm | 15.0 | 0.63124 (± < 0.00001) | D6378 | 37.8 | 107.8 (± 0.07) | Pabs |
| | | | | | | | |
| Gasoline | cold | 15.0 | 0.75755 (± 0.000011) | D5191 | 37.8 | 61.4 (± 0.12) | Ptot |
| | warm | 15.0 | 0.75761 (± 0.000017) | D6378 | 37.8 | 58.1 (± 0.03) | Pabs |
| | spiked | 15.0 | 0.72477 (± < 0.00001) | D5191 | 37.8 | 134.6 (± 0.02) | Ptot |
| Cyclohexane | warm | 15.0 | 0.78332 (± < 0.00001) | Low VP | 37.8 | 22.7 (± 0.01) | Pabs |
| Isopropanol | warm | 15.0 | 0.78933 (± < 0.00001) | Low VP | 37.8 | 12.3 (± 0.02) | Pabs |

^{*} References n-pentane: Ptot = 112.8 ± 1.2 kPa (ASTM D5191 & ASTM D6377) Pabs = 107.9 ± 1.2 kPa (ASTM D6378)

Conclusion

- > No significant density bias could be observed between cold and warm samples due to dissolved air.
- Chilled and air saturated samples do not have any visible impact on the precision of density measurements for ERAVAP.
- > Even high n-butane level gasoline can be measured with excellent precision.
- The repeatability **significantly outperforms the limits stated in ASTM D4052** (gasoline: r = 0.00045; distillates: r = 0.00016).
- Due to the rugged design of the DENS4052 module even the shaker motor can be used during density measurements (ASTM D6377 and Low VP).
- > The simultaneous density measurement does not have any impact on the vapor pressure results.

Combining vapor pressure and density testing in a single, portable analyzer saves costs without affecting the performance of both results – on the contrary, especially for density testing eralytics' unique new density meter module DENS4052 even outperforms established U-tube density meters.