MINIVAP ONLINE
Vapor Pressure testing in process

1. *Problem: Preventing damage and optimizing profits by monitoring vapor pressure*

Vapor pressure is an important physical property of volatile liquids especially of gasoline, gasoline-oxygenate blends, crude oil and LPG. Accurate determination of vapor pressure is used because of various – partly overlapping – resasons:

- **Governmental regulations**
  Vapor pressure provides an indication of how a fuel will perform under different operating conditions: Whether a fuel will cause vapor locks at high ambient temperature or at high altitude, or will provide easy starting at low ambient temperatures. Petroleum product specifications are regulated by various governmental agencies and maximum vapor pressure limits for crude oil and gasoline are legally mandated in many areas as a measure of environmental pollution control. Official vapor pressure limits for spark-engine fuels are dependent on ambient conditions, commonly referred to as summergraded or wintergraded fuel. In many countries worldwide it is obligatory to blend gasoline with biofuels, which in turn affects the vapor pressure of the fuel. Maximum vapor pressure limits are controlled according to various ASTM, EN and IP standards.

- **Safety for transportation and storage**
  Pipeline operators, offshore platforms, terminals, fuel depots or oil tankers detect the vapor pressure, before transporting crude oil or other petrochemical products such as Gasoline or LPG for subsequent processing. It is absolutely necessary to know the vapor pressure of the transported substance to prevent costly damage done to the transportation system. Damage prevention is not limited to the supplier only: Customers require their supplier to guarantee a maximum vapor pressure before accepting delivery of fuel.

  The following examples give a better picture, why it is necessary to control the vapor pressure:

  a) Offshore platforms determine the vapor pressure of crude oil to determine the bubble point, before transporting the crude via pipeline or tanker to a distribution terminal/platform.

  Thus excess gas is burned to prevent damage done to the transportation medium. If the vapor pressure of the crude case is too high, pump cavitation during transfer operations might happen. It is therefore advisable for a platform operator to have his platform equipped with a vapor pressure analyzer. Thus the operator is able to provide evidence that the released crude is delivered according to specifications – and to prevent costly damage.

  b) Liquid terminals are used for storage or as a buffer, before petroleum products are transferred or shipped for further processing or delivery. Fuel depots are used, whenever

petroleum products from different oil production sources are transported to a central storage area. Vapor pressure is an important property to determine the quality of the products delivered from different sources.

Safety for the facility and its personnel is a key concern. E.g. most commonly floating roof tanks are used for storage, sometimes fixed roof tanks are used. For fixed roof tanks vapor pressure limits are in place as a means of explosion protection: When gasoline or crude oil is relased, the volume has to be replaced by gases. This is controlled by testing the vapor pressure. In floating roof tanks too high vapor pressure will create bubbles under the roof, which can lead to an overturn of the roof.

Apart from the costs a failure might cause, environmental regulations limit maximum vapor pressure in floating roof tankers, to prevent air pollution control by outgassing of petroleum products.

- ## Profit optimization in refineries and in the pipeline

In the refinery crude oil is processed to gasoline with different quality (octane numbers). Naphta is blended with oxygenates, butane and octane boosters to conform with governmental and environmental regulations, to ensure better performance of the fuels and to reduce production costs. To maintain a certain quality level of the refined product refineries have to watch the vapor pressure closely during the whole refining process.

The following examples show how to profit from precise vapor pressure testing:

a) Refineries: By blending C4-compounds into gasoline, profit margins can be optimized, while

the heat of combustion remains unchainged. C4 like butane is far cheaper than crude oil, but also raises the vapor pressure. Refined gasoline must adhere to maximum vapour pressure limits for summer- and wintergraded fuel, though. Thus the most profit can be made when blending as close as possible to official limits. Which in turn requires an analyzer capable of testing vapor pressure as precise as possible.

b) Pipeline Operators, plants and transportation: Usually supplier and customer agree over maximum vapor pressure limits of crude oil or gasoline delivered to a plant or terminal. This is necessary to ensure safety for transportation and storage, and to guarantee that the customer receives a certain quality of fuel.

One of the most prominent applications for vapor pressure testing is C4-blending: The price valutation of crudes can be increased significantly, when butane or propane is blended into the crude. The addition of these hydrocarbons is limited by the maximum Reid Vapor Pressure (RVP). Depending on the RVP prior to blending, typically ratios of 1 to 5% of hydrocarbons are blended into the crude. Thus even a small plant handling some 10,000m3 per month can expect up to $50,000 through C4-blending.
So accurate blending of cheap butane into crude oil, while monitoring product quality via vapor pressure detection, can significantly improve profit for pipeline operators and plants, paying down vapor pressure analyzer equipment costs in short term.

2. Method / Solution

a. Method

Grabner Instruments MINIVAP ONLINE works with the same smart, fast and precise method for vapor pressure determination as the Grabner Instruments laboratory vapor pressure testers. MINIVAP laboratory testers are US EPA reference instruments for highest precision. Based on the fact that the vapor pressure of liquids remains constant and that all components - like dissolved air - follow the ideal gas equation, an expansion is performed in three steps at constant temperature. Three total pressure values are determined. From these three total pressure values the partial pressure of the air, the solubility factor of the liquid, and the absolute vapor pressure of the liquid are calculated.

MINIVAP ONLINE is the only vapor pressure process analyzer fully compliant with all relevant ASTM, EN and IP specifications for Crude Oil, Gasoline and LPG. MINIVAP ONLINE conforms to ASTM D5188, D5190, D5191, D6377 & D6378, D 6897, EN 13016 1+2, IP 394, 409 and 481 and offers ASTM approved correlations for D323, D1267, D4953, and D5482.

b. Measuring principle

The stream product is conditioned in the sample conditioning system that allows the measuring system to operate. Pressures up to 70 bar in stream are brought down between 0 and 7 bar filling pressure adjustable by a pressure regulator depending on the applied sample. The filling pressure must be higher than the vapor pressure of the sample in order to get proper filling of the system. The sample conditioning system guarantees a representative sample in the measuring unit like in the stream line.

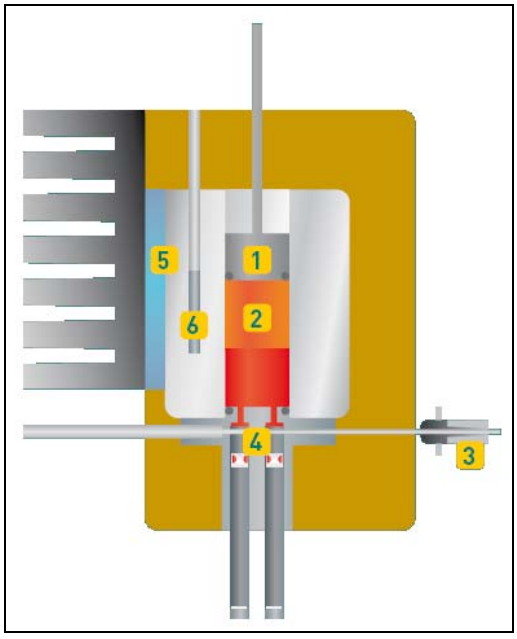

Figure 1: Measuring Cell of MINIVAP ONLINE

The sample is introduced through the Luer sample inlet (3) and the sample inlet valve (4) into the measuring chamber. The automatic sample introduction and the volume adjustment is accomplished by a piston with an integrated pressure transducer (1). The measuring chamber (2), with a total volume of 5 mL, is rinsed with 3 x 2.5 mL and filled with the appropriate amount of sample. After

closing the valve (4), single or triple expansion to 5 mL (with vacuum created by piston withdrawal) is obtained by additional piston strokes. The temperature of the measuring cell is controlled by a high-power thermoelectric module (5) and measured with a precision Pt100 RTD sensor (6).

Data is output via standard MODBUS digital signal or standard 4-20mA analog signal, the analyzer incorporates an ExplosionproofClass I housing and is ATEX and UL certified.

The MINIVAP ONLINE analyzer can handle up to two different sample streams, both controlled by an automatic sample conditioning system. Accuracy allows blending as close as 0.3 kPa (0.05 psi) to official limits within 7-minute cycle time.

c. Analytical Performance

The excellent performance of the MINIVAP ONLINE has been proven in various round robins in refineries and independent laboratories. The following figures show the results of measurement of gasoline and pure components.

Accuracy of MINIVAP ONLINE vs. ASTM D5191 standard:

Per Standard ASTM D5191 cooling and air saturation of the sample is required prior to the measurement of the vapor pressure. Using the triple expansion method, sources of error - such as operator bias - are eliminated, yielding highly precise results. Figure 2 shows typical sample behaviour, when testing according to ASTM D5191 against measurements according to ASTM D6378 by MINIVAP ONLINE.

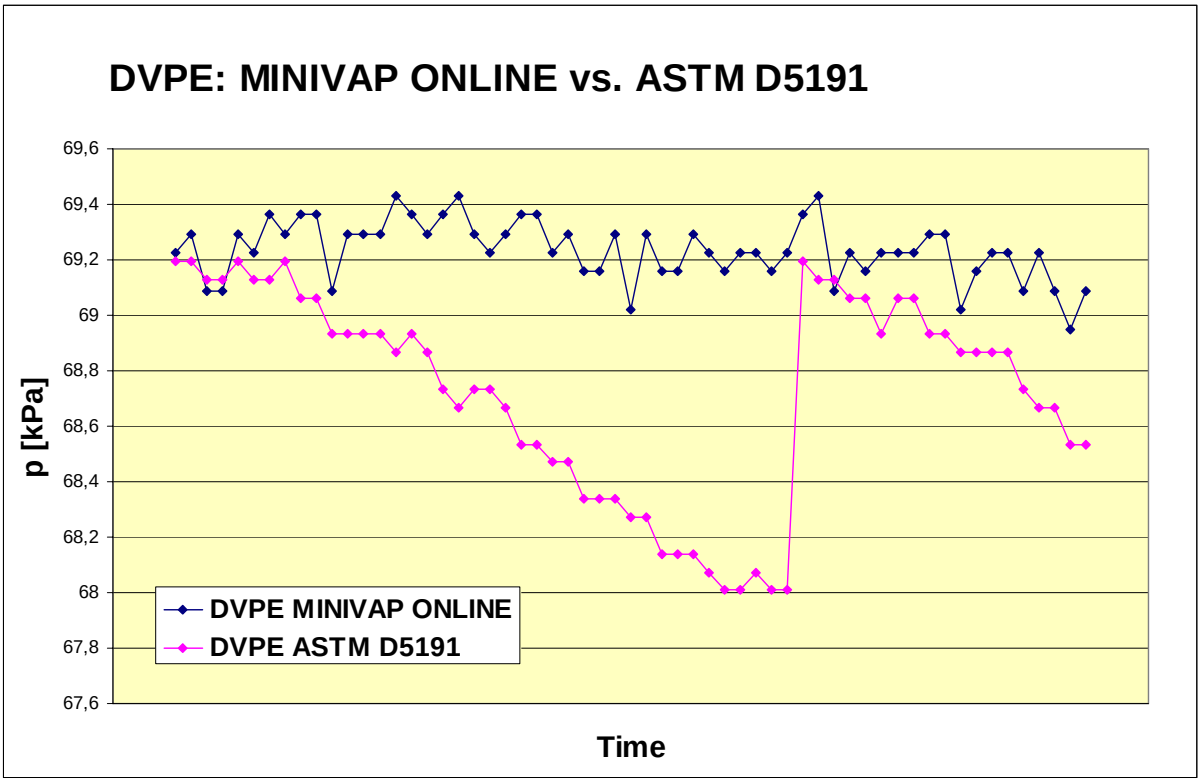

Figure 2: DVPE of gasoline - MINIVAP ONLINE vs. ASTM D5191. Jump in the D5191 line indicates that chilling and air saturation of the sample has been performed as per standard requirements.

Performance comparison (liquids): MINIVAP ONLINE vs. Lab Analyzer

Whereas most Vapor Pressure Process Analyzers correlate to a specific standard, MINIVAP ONLINE provides direct vapor pressure testing, without unreliable, read-adjustable and unproven correlations to standard methods. Table 1 and 2 are showing the high accuracy of MINIVAP-ONLINE measurements compared to lab analyzer measurements.

Sample	Pabs - Lab Analyzer [kPa]	Pabs – Process analyzer [kPa]	Delta [kpa]
neo-HEX	68.2	68.6	-0.4
neo-HEX	68.3	68.6	-0.3
neo-HEX	68.3	68.6	-0.3
Cyclopentane	68.4	68.8	-0.4
Cyclopentane	68.2	68.8	-0.6
Cyclopentane	68.4	68.8	-0.4
91 octane	84.8	84.5	0.3
91 octane	84.9	85	-0.1
91 octane	84.8	84.9	-0.1
95 octane	86.6	86.4	0.2
95 octane	87.1	87.2	-0.1
95 octane	86.8	87	-0.2
Average	77,1	77,3	-0,2
Min	68,2	68,6	
Max	87,1	87,2	

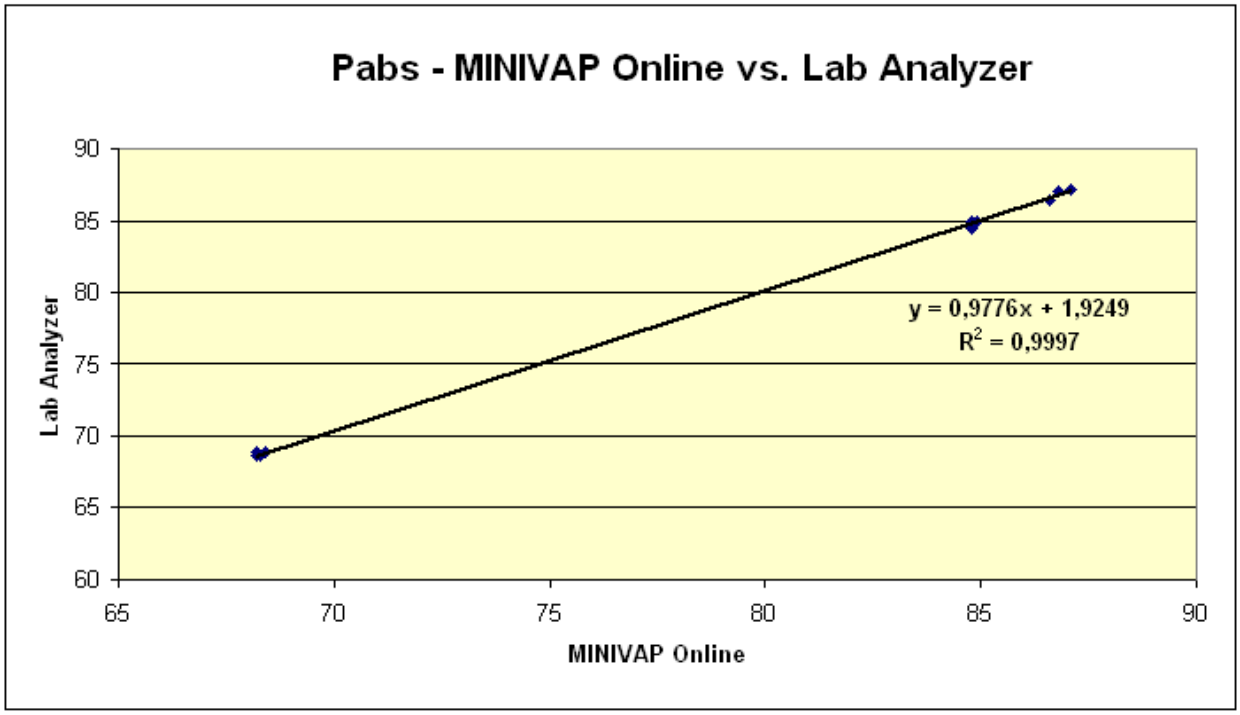

Table 1 / Figure 3: Pabs of MINIVAP ONLINE vs. Lab Analyzer, various samples, method: ASTM D6378

Performance comparison (LPG/NPG): MINIVAP ONLINE vs. Lab Analyzer

In addition to Gasoline and Crude Oil VP-determination, MINIVAP ONLINE is capable of testing LPG and NPG, too. Table 1 and 2 are showing typical LPG measurements according to the standard ASTM D1267, compared to MINIVAP ONLINE (ASTM D6897):

Measurement	VP-ASTM D-1267 psig	MINIVAP ONLINE psig	DELTA psi
1	195,5	195,4	-0,1
2	195,5	195,5	0,0
3	195,5	195,4	-0,1
4	195,0	194,8	-0,2
5	195,0	195,0	0,0
6	195,0	194,9	-0,1
7	195,5	195,8	0,3
8	198,0	197,9	-0,1
9	198,0	198,1	0,1
10	198,0	198,1	0,1
11	197,5	197,7	0,2
12	197,5	197,9	0,4
13	197,5	197,7	0,2
14	197,0	197,1	0,1
15	197,0	197,5	0,5
16	196,5	196,4	-0,1
17	196,5	196,7	0,2
18	196,5	196,7	0,2
Average	196,6	196,7	0,1
Min	195,0	194,8	-0,2
Max	198,0	198,1	0,5

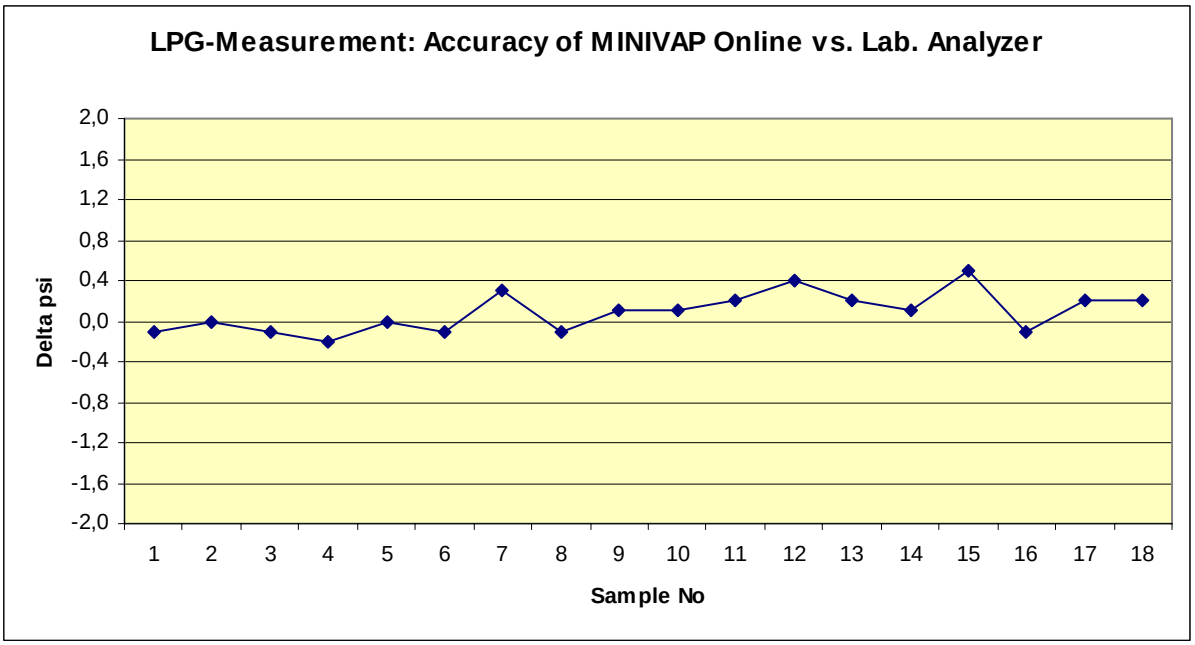

Table 2 / Figure 4: Psig of MINIVAP ONLINE vs. ASTM D1267, sample: LPG

d. Repeatability & Reproducibility

MINIVAP ONLINE r/R conform to the strictest vapor pressure standards. Even better measurements than required by the standards are possible, when testing pure substances. Thus precision with MINIVAP ONLINE is higher than precision of other Vapor Pressure Process Analyzers.

Instrument precision:

Repeatability r = 0.3 kPa (0.04 psi)
Reproducibility R = 0.7 kPa (0.10 psi)

Table 3 is depicting the repeatability for MINIVAP ONLINE, tested according to ASTM D6378.

Measurement	Pabs [psi]	Pabs [kPa]	Pgas [kPa]	P1	P2	P3
1	9.91	68.3	3.1	83.8	76.0	71.4
2	9.91	68.3	3.1	83.4	75.9	71.4
3	9.88	68.1	3.2	83.6	76.0	71.3
4	9.91	68.3	3.1	83.6	76.0	71.4
5	9.91	68.3	3.1	83.6	76.0	71.4
6	9.89	68.2	3.2	83.5	76.0	71.4
7	9.91	68.3	3.1	83.7	76.0	71.4
8	9.91	68.3	3.1	83.7	76.0	71.4
9	9.91	68.3	3.1	83.8	76.0	71.4
10	9.91	68.3	3.1	83.7	76.0	71.4
11	9.91	68.3	3.1	83.4	75.9	71.4
12	9.91	68.3	3.1	83.6	76.0	71.4
13	9.89	68.2	3.2	83.4	76.0	71.4
14	9.91	68.3	3.1	83.6	75.9	71.4
15	9.89	68.2	3.2	83.5	76.0	71.4
16	9.93	68.5	3.0	83.8	76.0	71.5
17	9.91	68.3	3.1	83.6	76.0	71.4
18	9.88	68.1	3.2	83.2	75.9	71.3
19	9.88	68.1	3.4	84.4	76.4	71.5
20	9.91	68.3	3.1	83.8	76.0	71.4
21	9.91	68.3	3.1	83.7	76.0	71.4
22	9.89	68.2	3.2	83.5	76.0	71.4
23	9.91	68.3	3.1	83.2	75.9	71.4
24	9.91	68.3	3.1	83.3	75.9	71.4
25	9.92	68.4	3.0	83.5	75.9	71.4
26	9.91	68.3	3.1	83.4	75.9	71.4
27	9.89	68.2	3.2	83.4	76.0	71.4
28	9.91	68.3	3.1	83.7	76.0	71.4
29	9.88	68.1	3.2	83.3	75.9	71.3
Average	9,90	68,27	3,13	83,58	75,98	71,40
Min	9,88	68,1	3,0	83,2	75,9	71,3
Max	9,93	68,5	3,4	84,4	76,4	71,5
Repeatability	**0,029**	**0,197**	0,167	0,521	0,204	**0,093**

Table 3: Repeatability of MINIVAP ONLINE, method: ASTM D6378

3. Summary / Conclusion

Due to governmental regulations the measurement of vapor pressure of gasoline is the most prominent application. However, based on its modular arrangement MINIVAP ONLINE can be used for all kinds of liquids produced by industries where the determination of vapor pressure is required for manufacturers´ safety data sheets or for quality control.

The unique expansion method make MINIVAP ONLINE an unrivalled analyzer for the determination of the vapor pressure of different kinds of liquids. MINIVAP ONLINE is the only vapor pressure process analyzer fully compliant with all relevant ASTM, EN and IP specifications, using the same method as the laboratory instruments, which are US EPA reference for highest precision. Fast and direct vapor pressure testing saves you time and money.

No matter for which application you use it - deciding for the MINIVAP ONLINE will pay off within a short time.