Appendix E
Grabner Mini Method Instrument Application Study

Vapor Pressure Testing of Viscous Samples

1. Objective

Objective of this study was to determine the viscosity limits and vapor pressure limits for the measurement of high viscous, low VP samples with the VP Vision or the VPL Vision in its current configuration. The study shows what is possible and what works and what doesn´t work when testing high viscous samples.

Four viscous samples, including **three lubricant additives and one sample of fuel oil #6** were delivered from two different sources in the US.

For the lubricant additives, the request was to determine the vapor pressure in a manner comparable to **ASTM D2879 Isoteniscope method.** Lubricant additives are high molecular weight and high viscosity substances and are products of synthesis from lighter chemicals. As chemical reactions are always incomplete, small low molecular weight impurities in the substances are expected in the samples that contribute to higher VP. Due to safety requirements, these more volatile impurities are the most important. A potential problem could be in separation of the effect of these "volatile" substances from the dissolved gases that exist in the sample. If the sample is degassed too vigorously (as e.g. required by ASTM D2879 Isoteniscope method), then these "volatile" admixtures can escape and thus influence the measurement result. One of the tasks was to determine whether there is a quantifiable vapor pressure at an elevated temperature and if there was, then reduce the sample measuring cell temperature in steps in order to collect vapor pressure versus temperature data for each material across the greatest practical temperature range.

For the No. 6 Fuel oil (NIST 1620c), the request was to verify, if testers can reliably produce vapor pressure measurements for viscous heavy refinery liquids. The viscosity of fuel oil #6 varies greatly. It is typically measured at 100°C and its viscosity is between 15-50 mm^2/s as per ASTM D396 specifications. At 50°C, the viscosity of most residual marine fuels is between 180-700 mm^2/s and at 20°C the viscosity is expected to be between 300-3000 mm^2/s. The consistency of the sample at room temperature is similar to that of peanut butter.

2. Viscosity pretests

Pretests were performed to evaluate the maximum viscosity of samples for filling. Two viscosity standards (S60 and S600) have been used.

T [°C]	ν	η	ρ
°C	mm²/s	mPa s	g/mL
20	158,1	135,9	0,8597
25	117,5	100,7	0,8566
37,78	60,11	51,01	0,8486
40	54,13	45,86	0,8472
50	35,1	29,52	0,8411
60	24,02	20,05	0,8349
80	12,83	10,56	0,8227
98,89	8,014	6,499	0,811
100	7,817	6,334	0,8103

Table 1: ISO 17025 / ISO Guide 34 Certified Reference Standard; Standard Type: S60

T [°C]	ν	η	ρ
°C	mm²/s	mPa s	g/mL
20	2150	1882	0,8752
25	1460	1273	0,9722
37,78	603,8	522,2	0,8648
40	524,8	453,2	0,8635
50	293,3	251,6	0,8577
60	175,1	149,2	0,8519
80	74,11	62,27	0,8402
98,89	38,81	32,18	0,8292
100	37,52	31,09	0,8286

Table 2: ISO 17025 / ISO Guide 34 Certified Reference Standard; Standard Type: S600

The temperature of the measurement cell was kept constantly at a temperature of 20°C. The environmental temperature was in the range between 22.5 °C and 24.5 °C.

For all experiments and theoretical investigations only homogeneous material have been taken into account. In addition, used viscosity standards have an extremely low vapor pressure (‹ 0.5 kPa) within the temperature range from 20°C to 30°C, but vapor pressure testing was not purpose of the pretests.

All observed results show that:

- The flow for high viscosity materials is laminar at highest velocities (320 motor turns per minute) down to a kinematic viscosity of 0.2 mm²/s;

- The necessary/observed pressure difference is proportional to the velocity;
- The necessary/observed pressure difference is consequently also proportional to the viscosity of the material;
- The relation between pressure difference, viscosity and volume flow for the current VP-Vision emptying channel (length of internal tube = 170 mm) is given by:

$$\Delta p_V \sim 1.57\ \nu\ \rho\ l_{rel}\ \dot{V}$$

Filling

For filling, the maximum achievable volume flow is of importance; the volume flow as a function of dynamic viscosity and some potential possible pressure differences is shown in the following diagram:

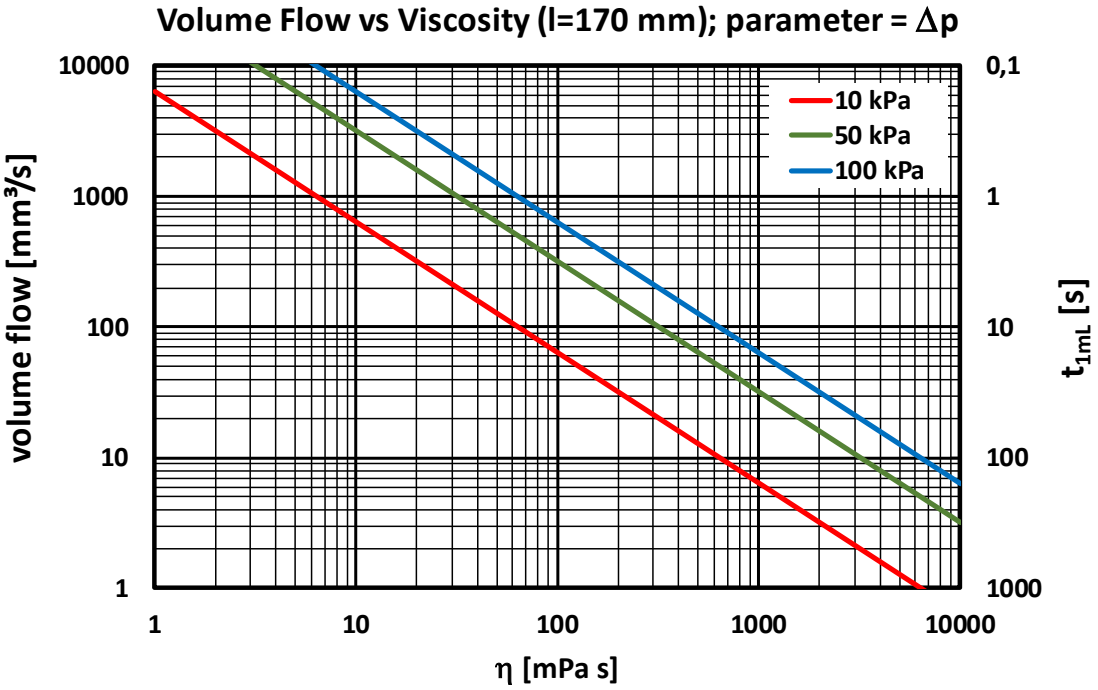


Table 3: Volume Flow vs. Viscosity (Filling)

The right side vertical scale shows the minimum filling time for 1 mL of viscous material with a standard tube length of 170 mm.

Emptying

For the emptying process usually the maximum pressure difference is limited (e.g. for the 1.5 bar sensor in VPL-Vision); therefore the next diagram shows the maximum speed (rotation speed of stepper motor left, step frequency at the right side) as a function of viscosity for three maximum pressure differences:

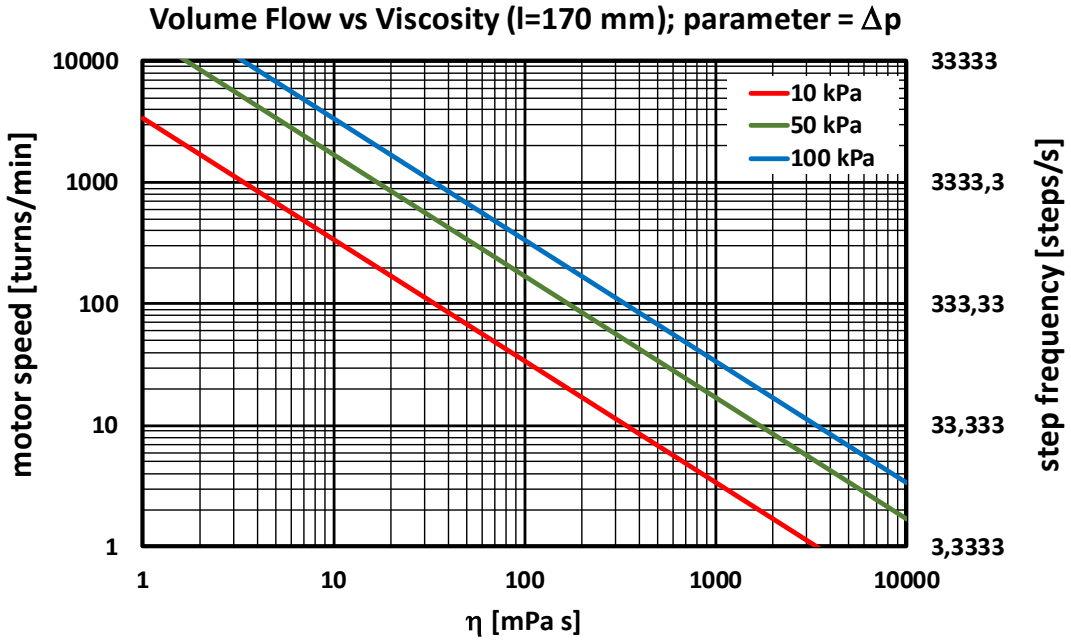


Table 4: Volume Flow vs. Viscosity (Emptying)

3. Findings of the viscosity pretests

Sample viscosity, the diameter of the filling tubing, the filling speed and the vapor pressure of the sample itself are limiting factors for analyzer filling. As the maximum filling viscosity is depending on these parameters, no single figure can be given. However, the diagrams derived in the pretests can be used to suggest the optimum piston velocity (motor speed) for a given viscosity or vice versa.

As an example the following holds true for the VPL Vision tester (0-150 kPa):

- At a motor speed of **80 turns/min** (standard filling speed of the Grabner VOC method)
- And at a maximum **vapor pressure** (pressure difference) of the sample of **50 kPa**
- The maximum filling viscosity of the **VPL Vision** analyzer is **limited to 210 mPas**

This limit is valid for filling without external tubes, e.g. filling from a syringe.

4. Test Design

a. **Analyzer:**
   Sample viscosity is critical not only during filling a piston based analyzer, but also during rinsing and sample discharge, as a considerable pressure will build inside the measuring cell during sample discharge. To protect the pressure sensor inside the instrument, Grabner vapor pressure testers are equipped with an overpressure safety feature.

For preliminary filling and measurement tests, a MINIVAP VP Vision (0-2000 kPa pressure range) was used, to allow a high pressure build up during sample discharge. If these tests proved successful, tests would be repeated with the low volatile version MINIVAP VPL Vision (0-150 kPa).

b. Filling:

As mentioned earlier, sample viscosity, tubing, the filling speed and the vapor pressure of the sample itself are limits for analyzer filling**.** If the vapor pressure is too high, the sample will start outgassing (boiling) during filling. Using the MINIVAP VP Vision slow filling mode **(VOC method)**, samples that do not have a considerable vapor pressure and a **viscosity up to 210 mPas at room temperature can be filled in the VPL Vision from an attached syringe.**

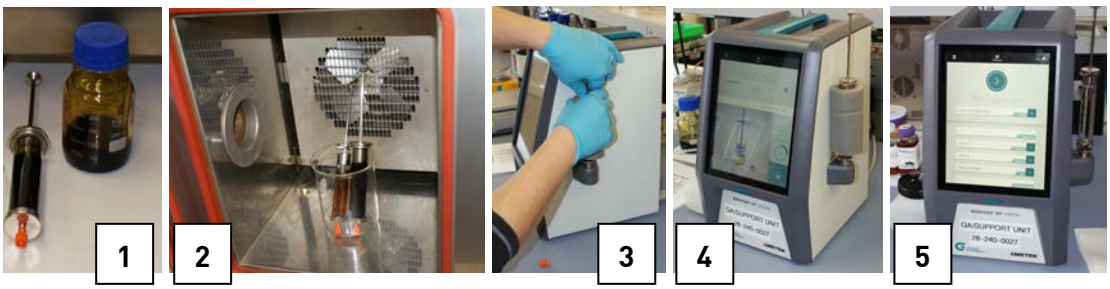
In this study the viscosity of the samples was far higher than 210 mPas at room temperature, so filling at 20°C failed. The vapor pressure of the samples was considered negligible, as lubricant additives and fuel oil #6 in general should not contain a significant amount of light components.

To allow proper filling, three filling parameters were changed:

- First, the filling speed was reduced to an experimental low speed (26 motor turns / min.)
- Second, samples were put into a syringe and heated to 60 or to 80°C.
- Third, the analyzer filling temperature was increased to 60 or 80°C, to reduce the risk of sample cooling and clogging.

Filling from syringe was selected, because it allows easy filling and can be attached directly to the analyzer – without additional tubing. An unheated tubing is prone to sample clogging, if the sample has to "wait" in the tube and cools before the measurement starts.

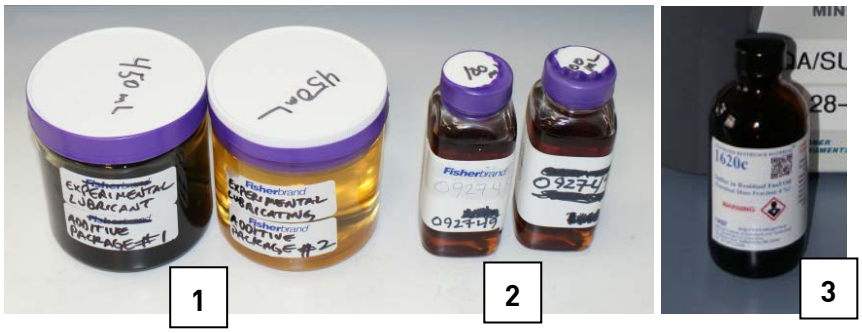
After the syringe was filled, a cap was put on the syringe outlet and the syringe was put into a heater and heated to the specified temperature.



Sample preparation:
Syringe filled (1); syringe heated in the oven (2) and attached to the analyzer (3/4); rinsing after the test (5)

5. Measurements

Three lubricant additives and one fuel oil #6 were tested. The lubricant additive samples were two very viscous experimental samples and one less viscous sample (#092749).



Samples: 2x 450 mL experminental lubricant additives (1); 2x 100 mL additive #092749 (2); Fuel Oil #6 (3)

a) Automated measurement of lubricant additive #092749

- Viscosity: estimated to be ~400-500 mPas @ 20°C
- Syringe + Filling temperature: 60°C
- Filling speed: Experimental low (26 motor turns / min.)
- Measuring method: VOC (static method, results comparable to D2879 Isoteniscope method); V/L ratio = 4/1; shaker turned on for rapid equilibrium
- Measuring points: multipoint at 60, 80, 100, 120°C
- Cleaning after measurement:
  - 5 rinses with petroleum spirit (exert pressure on the syringe)
  - Bake-out at 50°C (no sample)
  - 2 checks w/ n-Pentane
  - Bake-out at 50°C w/ vacuum pump attached to remove residuals
  - 5 rinses w/ air and vacuum pump attached to remove residuals

Result: Automated filling successful

Low volatile samples are extremely vulnerable to cross contamination. To prevent sample cross contamination, it is **recommended to dismiss the first measurement result.** With the first test dismissed, the sample could be measured repeatable:

Lubricant Additive #092749

Run	Temp [°C]	Pabs [kPa]	MV [kPa]	St.dev [kPa]	Pgas [kPa]
1	60	3.41	3.44	0.04	1.55
2		3.47			1.72
1	80	8.69	9.05	0.51	3.00
2		9.41			2.61
1	100	17.08	17.37	0.41	5.77
2		17.66			5.32
1	120	28.14	28.18	0.06	11.16
2		28.22			10.98

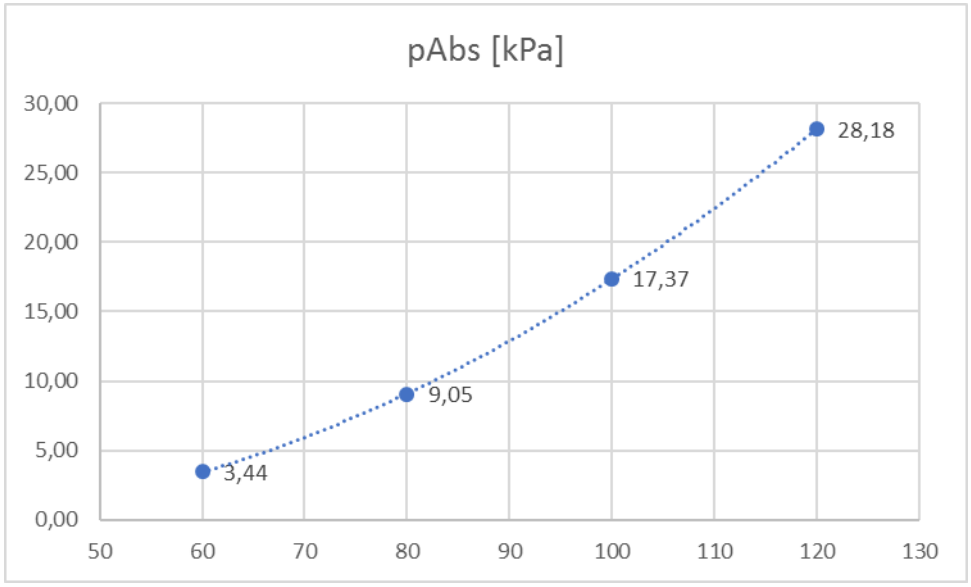


Table 5: Vapor Pressure of lubricant additive #092749

It should be noted that this sample does contain a significant amount of volatiles, resulting in a significant increase in vapor pressure with temperature. In addition, the sample produced **a pressure of about 1.7 bar,** when it was **discharged** from the measuring cell. This is comfortably within analyzer pressure specifications (0-20 bar).

b) Measurement of two extremely viscous experimental lubricant additives

Automated measurement (filling from syringe, without pressure)

- Viscosity: estimated to be above ›500 mPas @ 20°C
- Syringe temperature: 80°C
- Filling temperature: 80°C
- Rinsing cycles: 3
- Filling speed: Experimental low (26 motor turns / min.)
- Measuring method: VOC (static method, results comparable to D2879 Isoteniscope method); V/L ratio = 4/1; shaker turned on for rapid equilibrium

Result: Automatied filling not successful

Although the temperature of the syringe and the analyzer were set to the analyzer maximum (80°C), the samples could not be filled with automatic filling. When the samples were discharged during rinsing, **a pressure increase to more than 25 bar** was measured inside the heated cell, which led to termination of the measurement, to protect the pressure sensor. It was thus considered the sample was still too viscous to allow proper sample measurement and discharge. For cleaning of the analyzer, multiple runs with petroleum spirit were required.

Manual measurement (filling from syringe, adding pressure)

A different approach was taken than with manual filling:

1. **Analyzer preparation**

Before testing, the analyzer was prepared with multiple **rinsings** with **petroleum spirit.** To remove volatiles and to prevent cross contamination, the **"Bake out"** function was started after rinsing, with the **vacuum pump** attached. The Bake out function increases the heat in the analyzer, opens the valves and rinses with air, to remove residual sample from the measuring cell. After Bake out was finished, **rinsings with air** were started, with the vacuum pump attached. During rinsing, valves are alternating between open and closed state, and evacuation made sure no volatiles remained in the cell.

2. **Measuring procedure**
   - **Filter removed**
   - Syringe temperature: 80°C
   - Filling temperature: 80°C
   - Rinsing cycles: 3
   - Filling speed: Experimental low (26 motor turns / min.)
   - Measuring method: VOC (static method, results comparable to D2879 Isoteniscope method); V/L ratio = 4/1; shaker turned on for rapid equilibrium
   - Multipoint measurement at 20, 40, 50, 60, 80, 100, 120°C
   - **Rinsing and filling:**
     - During rinsing pressure was exerted onto the syringe
     - No pressure was exerted onto the syringe, when filling cycle started (during pressure check).
     - Pressure was exerted when cell expansion during filling started and kept until a pressure ›101.3 kPa was reached.

NOTE:
Before filling the sample, the analyzer checks the pressure. DO NOT exert pressure during this pressure check. Once the analyzer expands it is safe to exert pressure on the syringe to support the filling procedure.

   - Cleaning after measurement:
     - Start Bake-out, inject petroleum spirit (exert pressure on the syringe). During Bake-out, all valves are open and the measuring cell is heated. Petroleum spirit can be pushed through the measuring cell.
     - 5 rinses with petroleum spirit
     - 2 checks w/ n-Pentane
     - Bake-out at 50°C w/ vacuum pump attached to remove residuals
     - 5 rinses w/ air and vacuum pump attached to remove residuals

Result: Manual filling partly successful

Measurements with **Additive Package #2** were successful and are listed below. Again it is recommended to dismiss the first result.

Experimental Additive Package #2

Temp [°C]	Pabs [kPa]	Pgas [kPa]
20	0.17	0.46
40	0.33	0.54
50	0.45	0.59
60	0.60	0.69
80	1.11	0.85
100	2.05	1.19
120	3.84	1.97

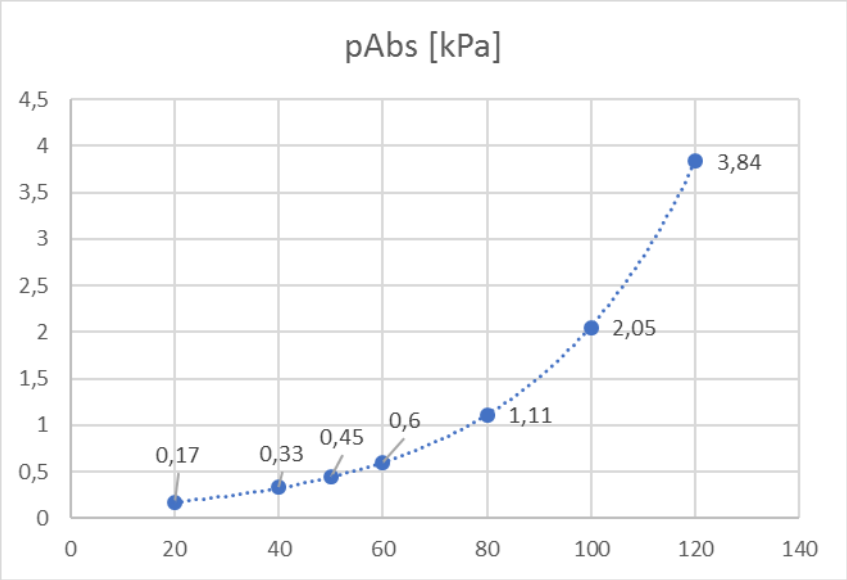


Table 6: Vapor Pressure of experimental additive package #2

Viscosity of **Additive Package #1** was even higher and the stickiness proved to be problematic. When measuring Additive Package #1, pressure errors were encountered during rinsing. Still there was **sample in the emptying tube**, so rinsing obviously worked. To prevent a pressure error during measurement, **rinsing cycles were set to 0** and the outlet tube to the **waste container was removed**, before another filling started.

Every time during filling, the analyzer performed an empyting cylce. During this emptying cycle, residual sample was spit out of the outlet and collected with a tissue. No pressure error observed and a measurement could be performed.

Still, after the test, sample could not be discharged due to a pressure error and no measurement result was displayed. We employed a workaround and read out the instrument data log (through the service page). Thus we were able to retrieve the measured vapor pressure data:

Experimental Additive Package #1

Temp [°C]	Pabs [kPa]	Pgas [kPa]
80	0.08	1.15
100	0.13	1.44
120	0.37	1.87

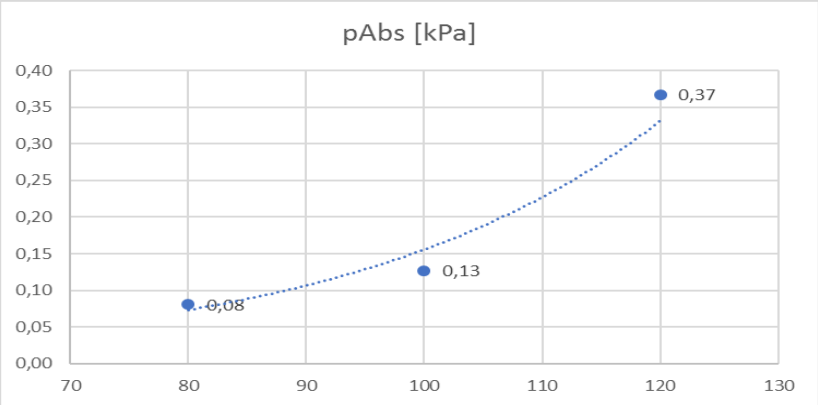


Table 7: Vapor Pressure of experimental additive package #1

c) Measurement of No. 6 fuel oil

Viscosity: Sample NIST 1620c is specified with a viscosity of

- 7131 mm2/s at 40°C
- 2982 mm2/s at 50°C
- 151 mm2/s at 100°C

Automated measurement (filling from syringe, without pressure)

- Syringe temperature: 80°
- Filling temperature: 80°C
- Rinsing cycles: 3
- Filling speed: Experimental low (26 motor turns / min.)
- Measuring method: VOC (static method, results comparable to D2879 Isoteniscope method); V/L ratio = 4/1; shaker turned on for rapid equilibrium
- Measuring points: multipoint at 20, 40, 50, 60, 80, 100, 120°C

Result: Automated filling not successful

Viscosity at 80°C was too high to fill the measuring cell properly. When studying the MSDS of the sample, it was noted that the sample is by far exceeded the ASTM D396 viscosity specifications for #6 Fuel Oil, which limits the viscosity to 15-50 mm2/s at 100°C. It was also observed that the sample produced a considerable vapor pressure during heating, as the syringe piston was extended after heating. It is thus likely that the sample contained a significant amount of volatiles. To prevent outgassing of the sample, filling e.g. from a heated floating piston cylinder is recommended.

Manual measurement (filling from syringe, adding pressure)

1. Analyzer preparation

Before testing, the analyzer was prepared with multiple **rinsings** with **petroleum spirit.** To remove volatiles and to prevent cross contamination, the **"Bake out"** function was started after rinsing, with the **vacuum pump** attached. The Bake out function increases the heat in the analyzer, opens the valves and rinses with air, to remove residual sample from the measuring cell. After Bake out was finished, **rinsings with air** were started, with the vacuum pump attached. During rinsing, valves are alternating between open and closed state, and evacuation made sure no volatiles remained in the cell.

2. Measuring procedure

- **Filter removed**
- **Outlet tube and waste container removed**
- Syringe temperature: 80°C
- Filling temperature: 80°C
- Rinsing cycles: 1-3
- Filling speed: VOC method (80 motor turns / min.)
- Measuring method: VOC (static method, results comparable to D2879 Isoteniscope method); V/L ratio = 4/1; shaker turned on for rapid equilibrium
- Multipoint measurement at 20, 40, 50, 60, 80, 100, 120°C
- **Rinsing and filling:**
  - During rinsing pressure was exerted onto the syringe
  - No pressure was exerted onto the syringe, when filling cycle started (during pressure check).
  - Pressure was exerted when cell expansion during filling started and kept until a pressure ›101.3 kPa was reached.

NOTE:
Before filling the sample, the analyzer checks the pressure. DO NOT exert pressure during this pressure check. Once the analyzer expands it is safe to exert pressure on the syringe to support the filling procedure.

- Cleaning after measurement:
  - Start Bake-out, inject petroleum spirit (exert pressure on the syringe). During Bake-out, all valves are open and the measuring cell is heated. Petroleum spirit can be pushed through the measuring cell.
  - 5 rinses with petroleum spirit
  - 2 checks w/ n-Pentane
  - Bake-out at 50°C w/ vacuum pump attached to remove residuals
  - 5 rinses w/ air and vacuum pump attached to remove residuals

Result: Manual filling successful

No overpressure errors were seen, when the outlet tube was removed. Three tests were performed on Fuel Oil #6 with only one rinsing in between the tests. To keep the measuring procedure consistent, the first result was again removed from the evaluation. Measurement produced very repeatable results:

Fuel Oil #6, NIST 1620c

Run	Temp [°C]	Pabs [kPa]	MV [kPa]	St.dev [kPa]	Pgas [kPa]
1	20	0.25	0.21	0.06	2.01
2		0.17			0.96
1	40	0.29	0.35	0.08	2.36
2		0.40			1.18
1	50	0.47	0.49	0.03	2.59
2		0.51			1.49
1	60	0.6	0.61	0.01	2.97
2		0.62			1.86
1	80	1.06	1.10	0.05	3.65
2		1.13			2.49
1	100	1.88	1.89	0.01	5.14
2		1.89			4.02
1	120	4.06	4.04	0.04	6.42
2		4.01			5.41

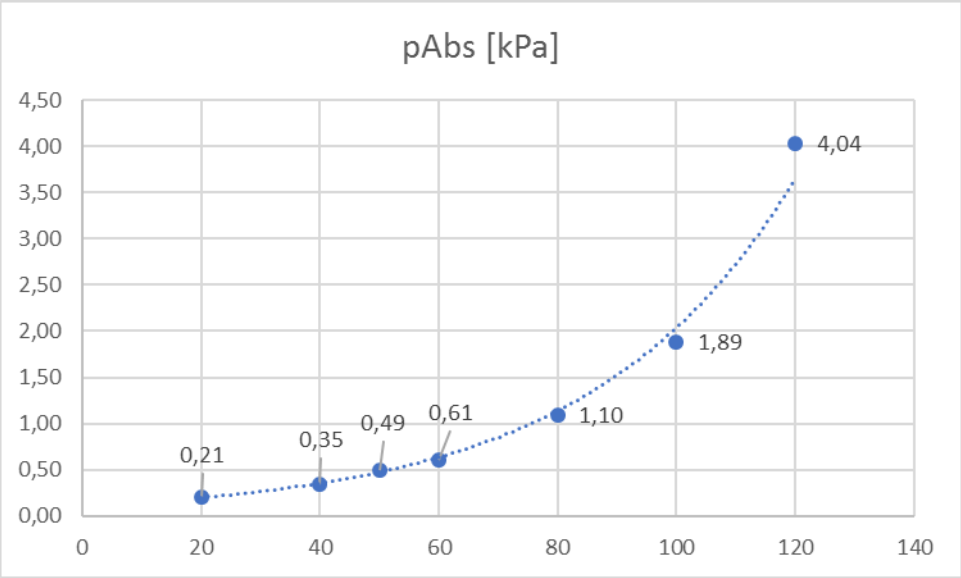


Table 8: Vapor Pressure of Fuel Oil #6 (NIST 1620c)

6. Findings (Procedure)

For filling very viscous and low volatile samples, the following procedure is suggested to achieve repeatable results:

- Prepare analyzer diligently (rinsing, bake-out and evacuation)
- Reduce filling speed or use VOC method (80 motor turns / min.)
- Remove inlet filter
- Remove outlet tubing
- Increase filling temperature to 80°C
- Use heated glass syringe (80°C)
- Do careful rinsing (adjust rinsing cycles to prevent overpressure)
- Do careful filling: Wait for pressure check before filling; once the piston is expanding, exert pressure until ›101.3 kPa is reached
- Do multiple measurements w/o rinsing or w/ only one rinsing in between
- Dismiss the first result

7. Summary

It could be shown that through adjustments in filling speed, an increase of the filling temperature and filling from a heated syringe extends the viscosity range of samples which can be automatically measured with the MINIVAP VP Vision. Especially for samples with only very little vapor pressure, the filling from a syringe provides an easy procedure to run vapor pressure tests. An almost gas tight **glass syringe** had to be used, because considerable pressure had to be used to fill the instrument from a syringe. A plastic syringe does not withstand pressure exerted during filling and will also facilitate outgassing, when the sample is being heated in it. As the analyzer is calibrated from 0 – 2000 kPa, it shall also be noted that a higher repeatability is to be expected for VP measurements below 2 kPa.

At the expense of usability, the use of a heated FPC, heated tubes and the application of a certain back pressure can add some improvement to feeding viscous samples into the analyzer. A heated FPC minimizes the risk of losing light components that can occur because of sample heating and consequent outgassing. In addition, the backpressure attached to the FPC can prevent the build up of a vapor lock during rinsing and filling.

Filling and rinsing speed is another important parameter for filling viscous samples: First, a sample needs time to be able to flow through the tubes and into the measuring chamber.

Second, when the sample is discharged, viscous samples build a high pressure inside the measuring chamber, which can easily provoke premature termination of the measurement. A slower filling and rinsing speed will help to reduce the risk of overpressures. During the above tests, a pressure build-up between 1.7 and 25 bar has been observed during sample discharge, even though the samples were filled at an experimental low filling and rinsing

speed at elevated temperatures. This leads to the conclusion that it is not recommended to test high viscosity samples (› 200 mPas) with the low volatility tester MINIVAP VPL Vision (0-150 kPa), as an overpressure error is likely to happen independent from the filling procedure. Instead, viscous samples should be tested with the more robust version MINIVAP VP Vision (0-2000 kPa).