‘Under Pressure’ - Automated Adjustment and Measurement of Volatile Substances

Relevant for: Petroleum industry, chemical industry – Testing labs, refineries, …

Anton Paar’s SVM 2001 / 3001 with Xsample 530 and Pressurized Measurement Unit (PMU) has for some time now enabled simple and reliable viscosity measurement of samples with elevated vapor pressure and/or low boiling point at elevated temperatures. What is new now: the SVM 2001 / 3001 can also be adjusted under pressure with the aid of the sample changer.

1 Introduction

In-service oils, solvents or low viscosity samples with a boiling point close to the measuring temperature often contain volatile components. For this reason, special measuring conditions under pressure are required. Performing a measurement under pressure helps with retaining all components in the sample and gives reliable and repeatable results. The automatic sample changer Xsample 530, equipped with a Pressurized Measurement Unit (PMU), enables filling the measuring system under pressure and successfully measures samples with trapped volatile components under sealed conditions.

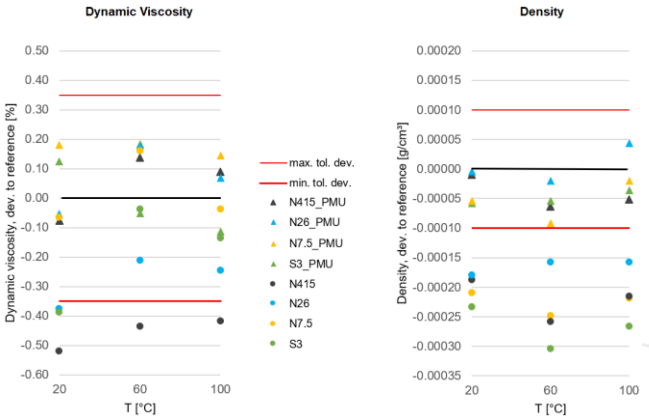
But, measurements under pressure influence the result. Deviations in viscosity and density can reach up to 1 % per 1 bar, depending on sample and temperature. To reduce such deviations, now also a Full Range Adjustment of SVM under pressure can be performed (available from software version 2.98-425).

2 Full Range Adjustment (FRA) under pressure

After adjusting (under pressure) SVM 2001/SVM 3001 combined with an Xsample 530 and PMU (= pressure-adjusted SVM), the viscosity reference standards used for the Full Range Adjustment were measured on the same instruments. Once with and once without PMU to determine how much the pressure in the system influences the measurement result. Comparing these results shows a difference between results obtained with and without PMU of approx. 0.5 % to 0.8 % over 3 measuring systems due to the applied pressure.

Not for all measuring situations a Full Range Adjustment is needed: If various samples over a wide temperature range are measured, the FRA under pressure is highly recommended. If only few sample types, e.g. solvents in a narrow temperature range, need to be measured under pressure, calibration corrections using the PMU may be sufficient. See also section 4.2.

Graph 1 compares results of reference standards tested on the pressure-adjusted system obtained from measurements under pressure and measurements without pressure. Some viscosity results (left side of the graph) but nearly all of the density results (right side of graph) were out of limits without PMU due to gassing.



Graph 1: Adjustment standards – deviations between results obtained with PMU vs. without PMU

3 Samples tested for this report

This report shows results of viscosity reference standards, a low-boiling alkane and typical in-service oil samples obtained with a pressure-adjusted SVM. All samples were measured with and without PMU.

Samples	Information
AP S3, AP N7.5, AP N26, AP N415	Viscosity and density reference standards used for FRA under pressure and for validation of the adjustment.
AP N75	Viscosity and density reference standard used as check oil (not used for FRA)
n-Pentane	Highly volatile alkane
In-service engine oils	Oil from a diesel engine with water and fuel contents and Oil from a petrol engine with engine failure
In-service compressor oils	Two oils with contents of system gas from a cooling compressor

4 Measurement

4.1 Instrument setup

To install the equipment, follow the instructions in the related documentation.

Equipment	Info
SVM 3001	Master instrument Viscosity according to ASTM D7042, density according to ASTM D4052 Alternatively: SVM 2001, if density according to ASTM D4052 is not required
Xsample 530	Automatic sample changer 35 pos. magazine with 40 mL vials*
Pressurized Measurement Unit (PMU)	Required to perform measurements with overpressure of 2 bar.
Pressure delimiter 2 bar (29 psi)	Supplied with Xsample 530. Required to reduce the air pressure safely to 2 bar. Required incoming air supply: 3.5 bar to 8.0 bar (50.8 psi to 116 psi) relative

*** Please note:** For the FRA under pressure, 40 mL vials are required. For sample measurements also 20 mL vials can be used.

4.2 Calibration

Use only a calibrated instrument. The calibration shall be performed periodically using certified reference standards. For a pressure-adjusted SVM, perform also the calibrations using a pressurized system. If you use an SVM without pressure adjustment, perform at least the calibration (correction) under pressure.

To perform the calibration and to apply the correction, refer to the SVM X001 Reference Guide.

Please note: Calibration (corrections) applied under pressure are valid only for measurements under pressure!

4.3 Sample Preparation

If the sample is not freshly drawn from a production line or other reservoir, homogenizing the test specimen may improve the measurement repeatability.

Transfer volatile samples always quickly into the vial. Immediately close the vial tightly with the screw cap.

Some samples may benefit from pre-cooling before pouring them into the vial.

Protect volatile samples from temperature stress. Store them under stable conditions (e.g. tempered storage, fridge) before drawing the test specimen.

As long as the samples are stored in sealed vials, it is no problem to prepare a batch and to start a sample list. Due to the fact that counter-pressure is applied during the complete procedure of filling and measuring, it is not necessary to cool the magazine during the waiting time.

When measuring in-service oils, remove ferromagnetic particles prior to pouring the sample into the vial.

Please note: Xsample 530 with PMU cannot be operated together with the Magnetic Particle Trap.

For more information on sample preparation refer to the SVM X001 Reference Guide.

4.4 Filling

Prior to performing measurements, ensure that the entire system of measuring cells, hoses, connectors and Xsample 530 with PMU is leak tight, clean and dry.

For measurements with PMU, the filling procedure is performed by compressed air pressure. The entire system is kept under 2 bar pressure during the entire measuring procedure. The sample is filled and re-filled with a pressure difference, which can be adjusted depending on sample viscosity and measuring temperature.

For more information on filling with PMU refer to the Pressurized Measurement Unit Instruction Manual.

Find suggestions for measurement settings with PMU in section 4.5. For measurements without PMU the filling settings were adapted depending on the sample.

4.5 Settings for SVM 3001 and Xsample 530

Measurement settings	SVM 3001
Set precision class	Ultraprecise (for the reference standards) Precise (for the tested samples)
RDV limit [%]	0.10
RDD limit [g/cm³]	Default: Ultraprecise 0.0001 Precise: 0.0002
Temperatures [°C]	20, 40, 60, 100 depending on samples
Measurement mode	Repeated Mode
Number of repetitions (max.)	5
Automatic prewetting	Yes

Filling settings	Xsample 530 with PMU
Air supply	High (compressed air supply)
Auto air check before filling	Deactivated (usually not required for SVM)
Auto self-test before filling	Activated
Filling mode	Pressure Mode – High Volatile Sensor Controlled
Overfill mode / Overfill	Not available with PMU
Fill for repetition [s]*	5 to 50*
PMU parameters [mbar]*	20 to 1000*

* Fill time for refills and different pressure values depend on vial size, cell temperature and sample viscosity. E.g. S3 at 100 °C: 25 mbar / 7 s; N415 at 20 °C; 1000 mbar / 50 s.

Cleaning settings	Xsample 530 with PMU
Solvents*: For the reference standards: only petroleum benzine (100/140) For the in-service oils: only ternary mixture of toluene, petroleum benzine and IPA (40:30:30) for all cleaning rows	
Draining mode: Up to approx. 15 mm²/s: No draining Approx. 15 mm² and higher: With compressed air to waste	

* Connect the solvents to the selected rinse connectors and adapt the settings accordingly.
For cleaning the system after *n*-Pentane measurements, no solvent was used, the cells were dried only.

Cleaning settings		
No. of cycles	Dry Time [s]	Cleaning mode
2	0	High volume
3	5	Turbulent
2	150	High Volume

Expert settings				
Pressure source clean	Dunk times	Soak Times [s]	Pressure source dry	Drain
High	4	30	High	Activated
High	0	0	High	Activated
High	2	20	High	Activated

Tip: *Cleaning settings depend on temperature and sample viscosity. The given settings work for a large variety of the tested samples. For low viscosity samples, less intensive cleaning, for solvents only drying may be sufficient. Adapt the cleaning settings accordingly.*

5 Results

The most challenging step is to obtain stable and repeatable results from volatile or gassing samples. Measuring results were performed according to ASTM D7042 and show average values out of n=5 measurements for the reference standards and some typical samples. Only from the in-service compressor oils fewer measurements were performed as only a very small sample volume was available.

The measurement series covered a viscosity range from approx. 0.32 mm²/s to 1360 mm²/s. The results were well repeatable and some of the samples only were measurable with the pressurized system.

Table 1 compares results of in-service oil samples and *n*-Pentane obtained from measurements with and without PMU.

SVM 3001 with Xsample 530 and PMU, 35 pos./40 mL magazine

Table 1: Results of some typical samples, displaying the average value and statistics

		With PMU				Without PMU				
Sample	Temp. [°C]	Kin. Visc. mm²/s	Repeat-abilty %	No. of deter-minations	Achieved precision class	Kin. Visc. mm²/s	Repeat-ability %	No. of deter-minations	Achieved precision class	Problems
***n*-Pentane**	20	0.3994	0.09	2 to 3	Viscosity and density: Ultraprecise	0.3997	1.31	5	Viscosity and density: Ultraprecise	Stability criteria of UP achieved, but poor repeatability
***n*-Pentane**	40	0.3188	0.24	5	Viscosity and density: Ultraprecise	no results	-	5	Viscosity and density: Ultrafast to Ultraprecise	Sample is already boiling (boiling point: 36.1 °C), Timeout error, RDV/RDD exceeded
***n*-Pentane**	50	0.2865	2.04	5	Viscosity and density: Ultraprecise	no results	-	-	not measurable	Sample is boiling
In-service engine oil with fuel and water content	100	7.169	0.21	2 to 3	Viscosity and density: precise	7.976	20.57	5	Viscosity: precise, Density: varies between ultrafast, fast and precise	Filling warning, Timeout error. Main problem: bubble formation in the density cell.
In-service engine oil, petrol engine, engine damage	100	7.869	0.09	2 to 3	Viscosity and density: precise	8.225	11.34	5	Viscosity: precise, Density: varies between fast and precise	Filling warning, Timeout error. Main problem: bubble formation in the density cell.
In-service cooling compressor oil with system gas content; 1 *	40	32.05	-	3	Viscosity and density: Precise	no results	-	-	not measurable	Severe gassing
In-service cooling compressor oil with system gas content; 2 *	40	84.22	-	3	Viscosity and density: Precise	no results	-	-	not measurable	Severe gassing

*not enough sample volume available for statistics determination

6 Conclusion

Most accurate results can now also be obtained with the aid of Xsample 530 equipped with a PMU after performing an automatic Full Range Adjustment respectively calibrations under pressure.

Therefore, measurement differences, that occur when adjustment and measurement are not performed under the same conditions can be eliminated.

No additional cooling of the magazine is needed; samples filled into the tightly sealed vials (20 mL or 40 mL) and measured under compressed air pressure do not lose volatile components.

7 Literature

J. W. P. Schmelzer, "Pressure dependence of viscosity", The Journal of Chemical Physics, vol. Volume 122, no. Issue 7, 11 February 2005.

Anton Paar, „Characterize crude oils by determining their viscosity, density and API degrees“, online, Graz, accessed 01-2022

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