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Testing of compressible materials and their thermal degradation using time-domain mode of the volumetric analyzer pV/T Master™ and external temperature-controlled chamber

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Addition of thermally controlled chamber to the pV/T Master volumetric analyzer allows for enhanced characterization of materials in the temperature range from above zero ºC to over 100 ºC. This technical note presents a new instrumental and methodological approach for studying materials that can change their properties versus temperature and pressure, e.g. foams. The previous application notes provide background information about the main instrument and approach:
1. Time-domain pycnometry and addition of dynamic mode of operation to gas expansion pycnometer.
2. Differential density concept and a new analyzer for studying of volume changes of compressible materials versus pressure intervals.

The temperature-controlled (TC) chamber is a standalone unit that was designed to provide additional capabilities for the volumetric analyzer. It can have two independent temperature controlled compartments, each with independent cooling and heating, one for the sample chamber (cell) and the second for housing other hardware, like sensors (e.g. RH probe). For safety reasons, 12 V DC is used for heating/cooling of the TC chamber systems in the standard version. The temperature controllers can be operated manually or automatically under software control.

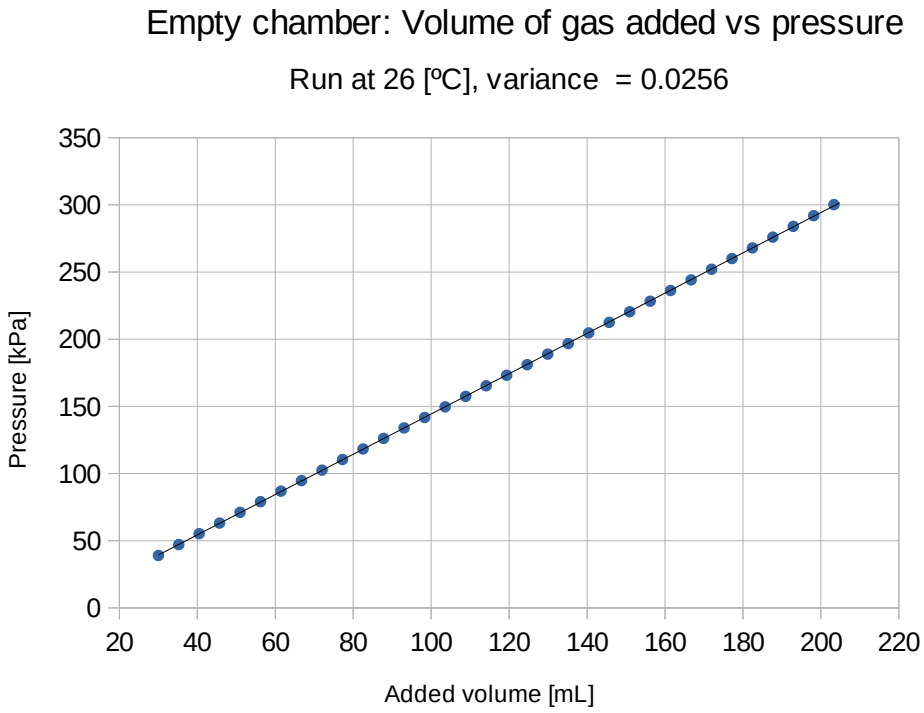
The design of sample cell in the TC chamber is similar to the one in the pV/T Master but this one has the cooling and heating capabilities. The output from the sample cell can be connected via a toggle valve to the second independently temperature controlled system that can be built-in in the TC chamber. When the toggle valve is closed and the TC chamber is connected to the main instrument, the pV/T Master can be considered as a two-temperature volumetric analyzer, the reference chamber being at room temperature and the external sample chamber at any other within the operational range of the TC chamber.

In the dynamic mode, the sample cell is filled with gas using a constant flow rate from initial to final pressure values. Typically the initial pressure value is a selected vacuum level that is generated by the built-in miniature vacuum pump (software controlled), about 7-10 kPa (absolute) as the minimum. The maximum final pressure value should be about 50 kPa less then the set pressure value by the precision low pressure regulator. The set pressure should never exceed the nominal upper limit of the absolute pressure transducer (about 340 kPa). In this experimental work, the flow rate of 200 mL/min was used and the range of pressures 10 to 200 kPa (absolute) was selected.

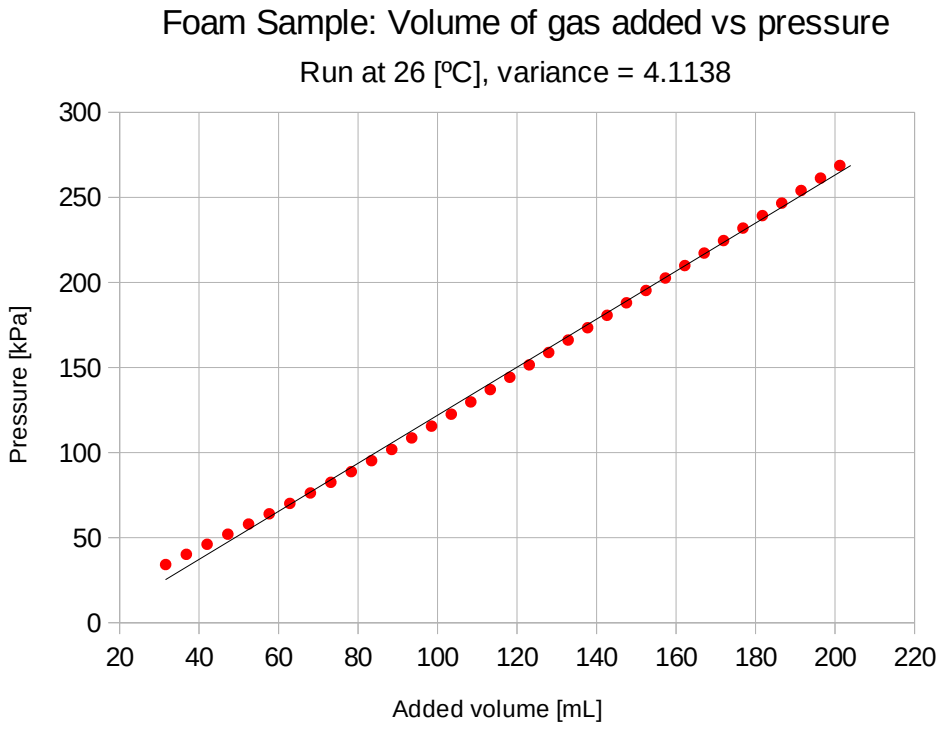
It is intuitively expected that in a closed system, the pressure should increase linearly versus the volume of gas added. The main assumption is that such a closed system is rigid and thermally stable. Even if parts of such systems are kept at different temperatures, the gas can quickly equilibrate thermally and its flow rate is sufficiently low that it will not affect to any significant degree the thermally controlled components.

The graph below presents the results of pressure increase versus gas volume added in the empty sample chamber. The variance is the sum of squares of differences between the best fit straight line and the

experimental data (dots) divided by the number of data point minus one. When the sample chamber does not contain any sample, the linear relationship is obtained and the value of the variance is small.



However, when a compressible sample, like a piece of foam is introduced into the sample chamber, the variance increases substantially. Such results are depicted on the following graph.



The values of the variances (or standard deviations) can serve as a measure of compressibility of sample versus pressure. Such evaluation can be done much faster then carrying out volume (density) measurements at various pressures or pressure intervals. Carrying out measurements at various temperatures allows not only to evaluate compressibility versus temperature but also to study the temperature effect on the specimen stability. The table below present results of runs at five different temperatures with no sample and the same runs with a foam sample inside the sample chamber and repeated three times.

	No sample		Foam sample Run 1		Foam sample Run 2		Foam sample Run 3	
Run temperature [°C]	Variance	Vcell [mL]	Variance	Vcell [mL]	Variance	Vcell [mL]	Variance	Vcell [mL]
26	0.0256	165.62	4.1138	153.95	0.6928	159.63	0.2185	161.72
37	0.0222	160.62	2.8045	150.12	0.5424	155.06	0.1530	156.97
47	0.0229	156.45	2.2611	147.43	0.4117	151.35	0.1464	153.01
57	0.0201	152.31	1.4209	145.06	0.3672	147.90	0.1641	149.25
67	0.0207	148.83	0.7251	143.27	0.2733	145.10	0.0879	146.17

Table 1. Change of foam properties under temperature and pressure

The variances for the runs without sample are small and remain fairly the same. For the runs with the foam sample, the values of variances are much larger and decrease with temperature. They also decrease with consecutive runs. After the three repetitions, the foam sample degraded substantially. Its thickness decreased from 25 mm to about 15 mm and the initial straight cutout resulted in an irregular shape. In addition to the shape change, the foam sample changed mechanically resulting in a more compacted sponge, easily deformable, and the "springiness" was substantially decreased.

The data Vcell [mL] showed in the neighboring columns to the variances represent the volume of the sample chamber obtained from the dynamic mode of the pycnometer operation. After each repetition of the multi-temperature run with the sample, the Vcell [mL] data show increasing trend for the same temperature. The decrease of the initial sample volume can be easily deduced for each consecutive run.

The foam sample was cut out from a commercially available kneeling pad. At about room temperatures, the foam material seemed to be unaffected by using pressure or vacuum and retained its properties over time. However, increasing the temperature causes degradation of the material and irreversible changes in its properties. Since the standard methods for measurements of properties of many materials are carried out mostly at about room temperatures, such specifications are of limited value.

Evaluation of many materials properties would far more valuable if other temperatures were used. Information about thermal degradation of plastic materials is important from the application point of view. That would allow for better selection of specific materials for a given application. Having such analytical equipment at hand would allow the formulation chemists to thoroughly research the final products in a quick and easy way and evaluate applicability of such products for usage at extended range of temperatures. Evaluation of existing plastic products for usage at various temperature can be easily accomplished using the equipment. Other analytical techniques, like controlled water vapor desorption, headspace extraction, can be materialized by addition of auxiliary hardware.

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