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Time-domain pycnometry and addition of dynamic mode of operation to gas expansion pycnometer

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Combining dynamic (flow type) and static (gas expansion) modes in one instrument resulted in a highly capable and novel gas (helium) pycnometer. This technical note presents overview of a new instrumental and methodological approach for materials characterization as well as other possible applications of this volumetric analyzer.

Let us assume that a closed chamber of volume **Vc** contains $\mathbf{n_1}$ moles of ideal gas, and that we know the pressure $\mathbf{p_1}$ and temperature **T** in this chamber. If we are able to add somehow a volume $\mathbf{V_1}$ of gas to this chamber at the same temperature, then the pressure in this chamber will increase to $\mathbf{p_2}$ value. Using the ideal gas law, the mass balance equation can be written as

$$\frac{p_1 \cdot \mathrm{Vc}}{\mathrm{RT}} + \frac{V_1}{V_M} = \frac{p_2 \cdot \mathrm{Vc}}{\mathrm{RT}} \qquad \text{(eq. 1)}$$

where the V_M is the molar volume of gas, and R is the ideal gas constant.

It is trivial to deduce, that if the volume $\mathbf{V_1}$ and pressures $\mathbf{p_1}$ and $\mathbf{p_2}$ are known, then the chamber volume **Vc** can be easily found. If the volume $\mathbf{V_1}$ was added from a separate chamber (often called added or reference volume) by means of a valve, then the principle of gas expansion pycnometer would be discussed. Since this type of gas pycnometer is covered in details in other literature, it will be omitted here. If the volume $\mathbf{V_1}$ was added at a known constant flow rate over time $\mathbf{t_1}$, like from a precision mass flow controller (**MFC**), then knowing the flow rate **F** and the time $\mathbf{t_1}$, the volume $\mathbf{V_1}$ can be simply written as

$$\mathbf{V_1} = \mathbf{F} \cdot \mathbf{t_1} \quad \text{(eqn. 2)}$$

Substituting $\mathbf{V_1}$ from eq. 2 into eq. 1, it is clear that the chamber volume **Vc** can be calculated by measuring the time alone. If a sample of volume **Vs** is introduced into the **Vc** chamber, then the available volume is reduced to **Vc - Vs,** and the time **t2** needed to fill the chamber to the same final pressure should be shorter.

$$\frac{p_1 \cdot (\mathrm{Vc}\text{-}\mathrm{Vs})}{\mathrm{RT}} + \frac{F \cdot t_2}{V_M} = \frac{p_2 \cdot (\mathrm{Vc}\text{-}\mathrm{Vs})}{\mathrm{RT}} \qquad \text{(eq. 3)}$$

After simple manipulations of eq. 1, 2, and 3, the sought sample volume Vs can be easily calculated:

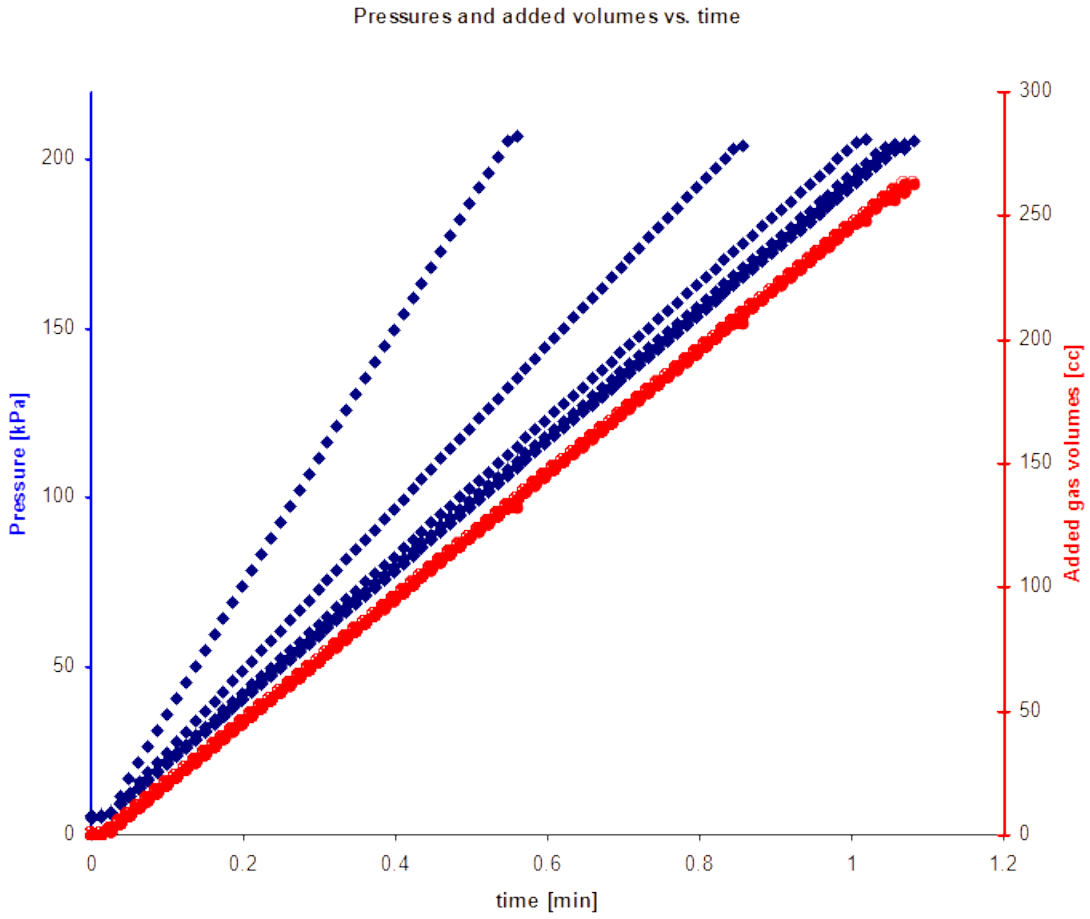
$$\mathrm{Vs} = \frac{F \cdot R \cdot T \cdot (t_1 - t_2)}{V_M \cdot (p_2 - p_1)} \qquad \text{(eq. 4)}$$

The eq. 4 is the basic equation of an ideal time-domain pycnometer. It allows determining sample volume by carrying out two runs and measurements of two times alone, one when filling out empty chamber and another one when filling the chamber with sample in it, assuming that all other parameters remain the same

in both runs. Unlike in the gas expansion models where two chambers are needed, this type of pycnometer uses only one chamber.

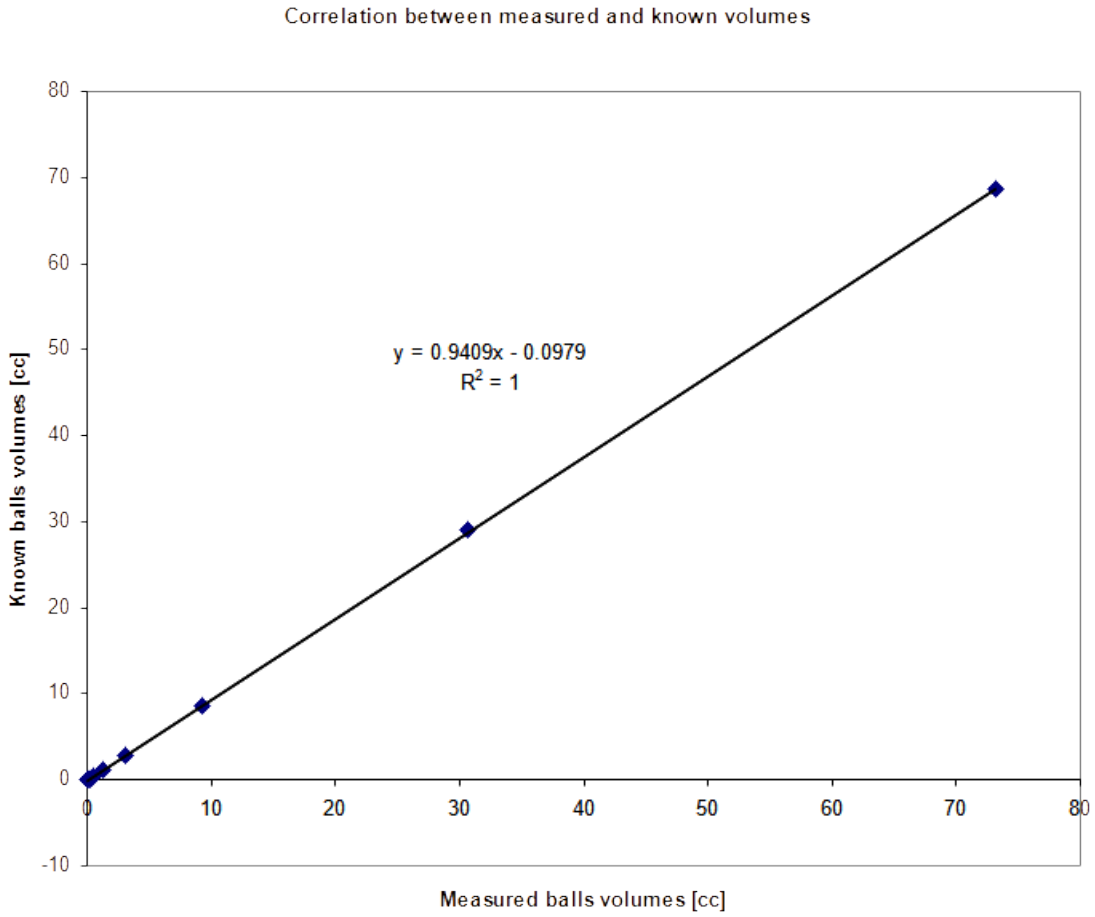
The commonly used automatic gas pycnometer use the gas expansion principle which can be considered as a static method in a sense that the gas after reaching pressurization and depressurization state gets equilibrated for some time according to applied criteria of pressure stability. The time-domain pycnometer can be considered as a dynamic type as no particular equilibrium states are needed and the time measurements are involved.

In practical implementation of the dynamic gas pycnometer, the eq. 4 is a bit more complex as generally the initial pressure $\mathbf{p}_1$ and the final pressure $\mathbf{p}_2$ are somewhat different from run to run. The volume of gas added is calculated as the sum of current values and time elapsed between the readings. The calibration can be easily achieved by measuring metal ball of known volume and applying correction factor or correlation function in the volume measurements for the runs with actual sample(s).



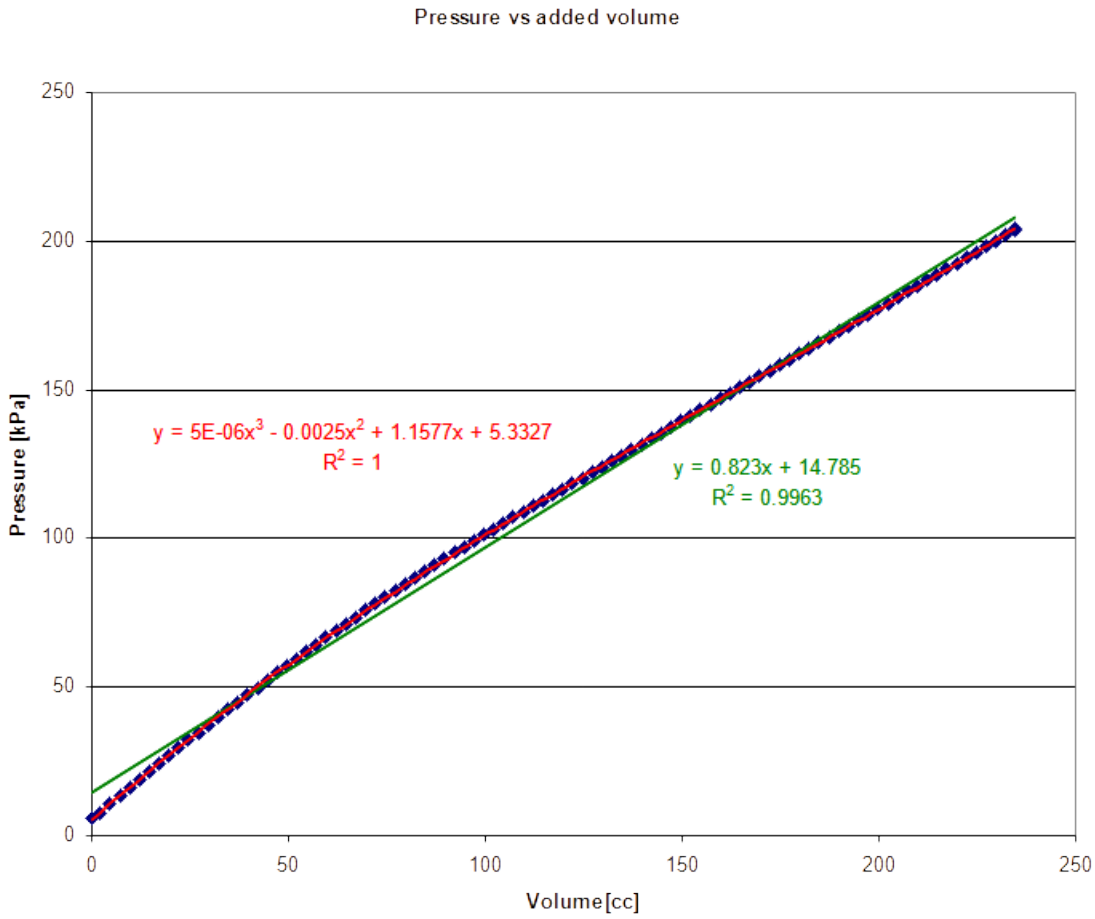
The above chart shows pressure profiles for empty sample chamber and various metal balls inserted into the chamber. Except the very start of pressure buildup and the very end when reaches its supply pressure limit, the linearity of pressure increase is very good. In the same time interval as the pressure lines for various balls, the added volume of gas (red circles) is plotted with the values referenced on the secondary y-axis. In this graph several lines of the added volumes obtained for the various balls are superimposed to show the linearity of the added volume versus time and the stability of the same flow rate of the MFC. For actual calculations, the start of any pressure interval and its end can be selected by the user in the software.

To compare the balls volumes obtained from measurements by this time-domain pycnometer with their actual volumes, the measured volumes (x-axis) and the known volumes (y-axis) were plotted to obtain the correlation relationship. The results are presented in the graph below.



Initial experimental results for testing repeatability yield standard deviation of 0.1476 for the empty sample chamber of 145.62 cc using 10 repetitions.

The high level of linearity of pressure increase versus added volume can be effectively utilized in additional methods of characterization of materials. For example, to quickly verify level of expansion/ compressibility of sample from vacuum to pressures well above atmospheric. When the user-selected flow rate is declared and the sample chamber closed, then the pressure increases. The current flow rate is read and the total volume added to the chamber can be calculated. Graphing the current pressure values against the cumulative volume added a straight line is obtained in case of sample chamber without sample or with incompressible sample like a metal ball. Calculation of residual errors between the experimental line and fitted straight line yields a very small number. However, when a foam sample is added, the pressure versus added volume is rather a curve then a straight line. Calculating residual errors between fitted straight line and the curve results in a much larger number. Such a number can be an indicator of volume changes versus pressure. The experimental results of using a compressible material, like a foam sample, are illustrated in the chart below.



In the graph above the blue color diamonds are the experimental results of pressure increases versus linear supply of volume. The green line is the best fit straight line and it is used to calculate the residual errors, as the sum of squared differences between the experimental results and the fitted line divided by the number N-2 of experimental data. For expandable/compressible materials, such residual errors are much larger then for incompressible materials. In this particular foam material, a 3-rd degree polynomial can be fitted as the minimum order to ensures good correlation. Any simple formulas based on linear relationships, like isothermal compressibility coefficient, can be questionable to apply.

In the dynamic mode, the analysis time can be quite short, usually under one minute, although it can depend on selected flow rate and size of the chamber. Since only one chamber is required, then it is well suited to be an in-situ process analyzer as it is relatively easy to connect it to external chambers. Carrying out quick runs and comparing the curves of P = P(V) after some chemical/thermal treatment or repeated runs every so often can yield information about the material behavior.

A separate application note entitled *"Volume changes of compressible materials versus pressure intervals and foam characterization by a density profile instead of a single value using pV/T Master, a versatile volumetric analyzer"* describes ability to measure foam densities in user selected pressure intervals from vacuum to the maximum value allowed. The main consequence of this approach is realization that **density in case of compressible materials is not a single number but rather a complex profile with some range of values.** The dynamic mode of this enhanced pycnometer can be utilized for quick test of sample expansion/compression properties.

The combination of the time-domain and gas expansion techniques in one instrument offers new capabilities in characterization of materials that are not available in other pycnometers designs. The combination of embedded and software controlled vacuum pump, the ability to built any pressures in a controlled way using MFC, and the unique software and hardware design forms a core of quite capable volumetric analyzer. Regular density measurements and compressibility evaluation s can be carried out using the basic instrument. The concept of open-architecture design with all resources available for external usage, this analyzer can be a handy tool in many volumetric applications.

Utilizing (optional) auxiliary hardware that can be either supplied or developed by the user and which can be easily attached to the instrument, several analytical techniques can be materialized. Various specific research/development ideas can be tested using such auxiliary hardware which can be obtained at a fraction of cost of a separate analyzer.

Some examples of possible implementations are:
- Bubble point technique,
- Liquid expulsion porometry
- Gas transfer rates through various barriers, like films, filters,
- Flow rates measurements through packed beds of powders
- Surface area analyzers, e.g. by flow through packed beds of powder – permeability.

If the user has ability to control the sample temperature, then gas sorption experiments can be potentially carried out. For example, by providing liquid nitrogen and appropriate LN2 container, the experiments of nitrogen sorption can be carried out using either dynamic or static mode. The typical surface area analyzers have pressure range from vacuum to just around atmospheric. The advantage of this pycnometer is that it can build pressures up to 2.4 bars above atmospheric using 50 psia transducer, and so the CO_2 sorption experiments can be carried out at around dry ice or other temperatures. Using permeability theory, the specific surface area of many powders (e.g. cement) can be easily found by measurements of flow rates through packed beds of powder. Our concept of using a quadratic equation instead of the linear one and proposal of new model is discussed in previous application notes. Ultimately, the surface areas obtained by different experimental techniques can be evaluated using the same instrument.

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