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Implementation of flow-based moisture desorption method using volumetric analyzer pV/T Master™ and external temperature-controlled chamber

By Jan Malczyk

A very practical and useful method for determination of mass loss of water and prediction of water content beyond the used temperature range is proposed. Using RH probe ensures selectivity towards water vapor as in gravimetric measurements where a balance is used, the high temperature programmable desorption determines only the total amount of gas/vapors loss. In addition to determining the mass of water loss, using either dry or humidified gas at various temperatures, the extracted volatiles can be delivered to other analytical devices.

The capabilities of the pV/T Master can be be substantially increased by providing a temperature controlled zone for the sample chamber. An external temperature controlled chamber can feature much larger temperature range then it is available in some pycnometers. Such a chamber can consist of a single temperature zone or multiple zones depending on particular purpose and can contain auxiliary hardware. The simplified diagram below presents the design of the dual and independently controlled temperature zones.

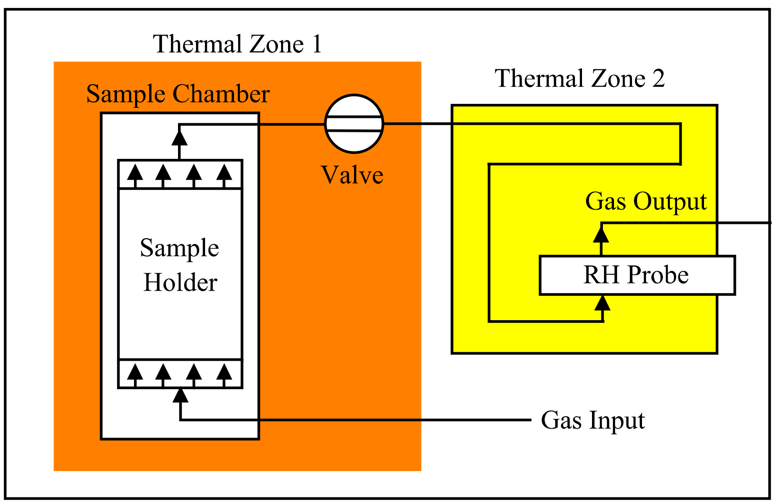
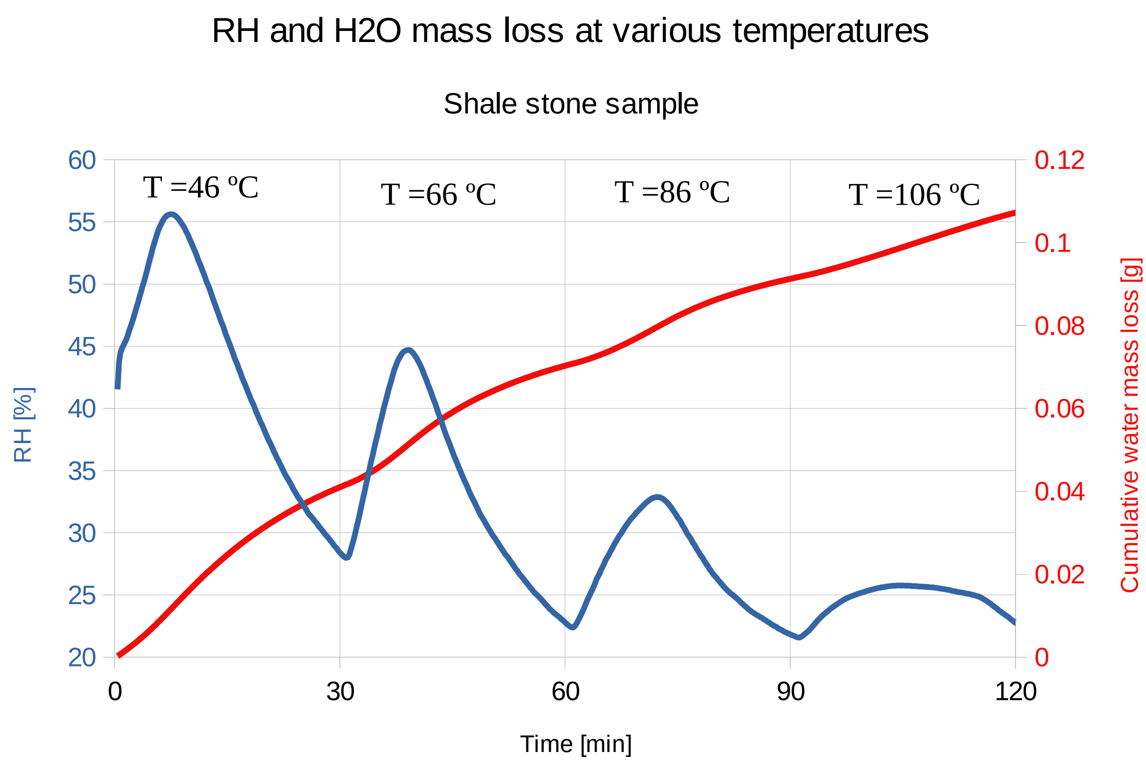


Fig. 1. Simplified diagram of temperature controlled chamber

Such chamber is a standalone instrument and can be used for any suitable purpose but if is combined with the pV/T Master, then the chamber control and gas input are provided from the main instrument. The incoming gas is equilibrated with the Zone 1 temperature and passes through the sample holder. The proprietary design of the sample holder ensures equal distribution of the flow into and out of the sample holder. If the valve is closed, then the chamber can be used for volume (density) determination, compressibility, gas evolution, etc. versus the user selectable temperatures. The temperature controllers can be set manually or they can be automatically operated by the software. The temperature range can vary depending on particular design, but typically it is from just above 0 to 105 ºC if Peltier modules are used for cooling. The low voltage 12 V DC power is used for all heating and cooling to ensure safety of the operation.

In case of single temperature zone design, if the valve is opened, the flow can be delivered to any other analytical setup or just exhausted to atmosphere. In case of having dual thermal zones, various sensors can be housed in the Zone 2. The flow from the Zone 1 passes through the Zone 2 before it is available for other uses. In the above design, the RH probe can be used to monitor the humidity of the incoming stream and the temperature of the Zone 2. From the data of relative humidity (RH) and temperature, the corresponding dew point and partial pressure of water can be calculated. Knowing the flow rate, the mass of water versus time can be also calculated. Since various temperatures can be used, the loss of mass of water for each temperature can be determined. Thus the detailed information of water loss versus temperature can be obtained. In principle, the setup allows water loss measurements without the need of any laboratory balance. However, either for verification purposes or if other volatile substances are removed at elevated temperatures, the user may weigh the sample before and after the experiment.

As an example of the method application, the following results are presented below. Several shale stones of gray color were washed and kept at room temperature at relative humidity (RH) around 50 % for several days. They were crushed to small pieces with substantial amount being as small flat flakes and in powdered form. Sample amount of 60.0411 g was placed in the sample holder and flow rate of 200 mL/min was used. The 30 minutes maximum time was declared for each of the temperatures: 45, 65, 85, and 105 ºC for the sample chamber while the RH probe zone was maintained at ambient temperature as the relative humidity values were within the range that did not require any automatic adjustment of the RH probe housing temperature.

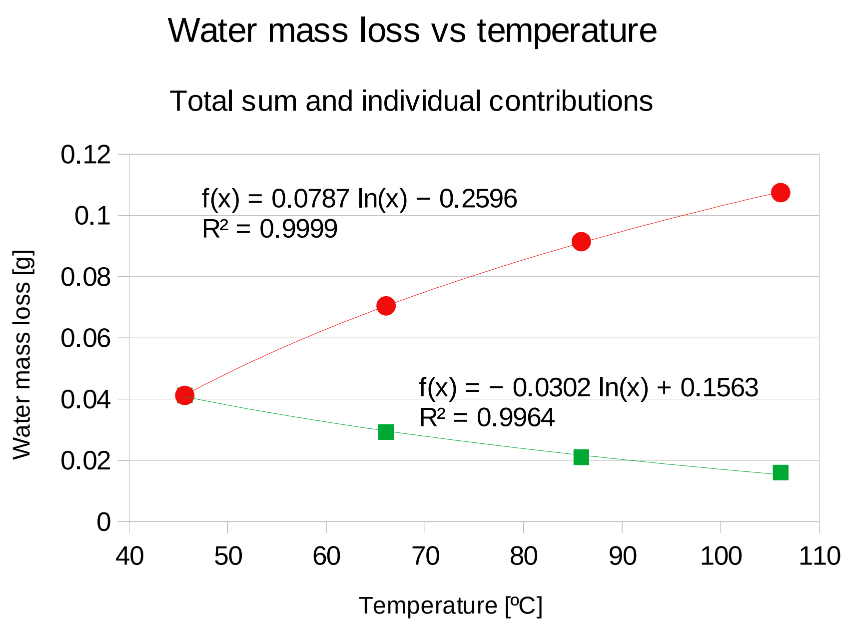


The RH profiles for each temperature segment are quickly falling down and the amount of water loss is small. It should be pointed out that the selected 30 minutes time for the test run is totally arbitrary and more complete RH profiles could be obtained at much longer time. Actually, a better criterion like a small RH change per unit of time could be used for completion of each temperature segment. Also the time of achieving the next temperature and thermal equilibration of the relatively large amount of sample can be different. Thus, the preliminary quick run can only provide some general idea about the rate of water loss and what experimental conditions should be selected for the subsequent experimental work and interpretation of the results.

After the experiment, the weighed mass was 59.9438 g, resulting in 0.1023 g water loss. The value obtained from RH and temperature readings at the 200 mL/min flow rate yielded 0.10739 g water loss. The small error of few percent can be contributed to some level of moisture in the carrier gas. Within the temperature range tested, the particular shale stones do not have any significant water content as only 0.17% of the initial mass was lost. The particular shale slate stones have very low water permeability and when used for placing around plants, they are supposed to decrease the rate of moisture evaporation from soil. However, their water carrying ability is negligible.

In addition to plotting the mass loss versus time as in the above chart, the mass loss can be plotted versus the temperatures used. The chart below shows data values of cumulative mass loss (red dots) and net contributions at each temperature (green squares) plotted against the step temperatures. The added logarithmic trend lines fit quite well to the data points. Therefore, it is tempting to extrapolate the water loss values beyond the temperature range used. Using the logarithmic equation f(x) =

-0.302 ln(x) + 0.1563 for the individual contributions at each temperature, complete removal of water is expected at about 177 ºC. Substituting this value into the second logarithmic equation, the total amount of water loss is projected to be around 0.14776 g. As mentioned before, improving the experimental parameters can result in different actual and predicted mass loss values and equations, but the main purpose is only to present the foundations of this methodology.



There are many moisture or loss on drying analyzers on the market today that use balances and fast heating to high temperature. The main marketing point is the speed of obtaining results, but their design, the way of heating of the sample, and the results can be questionable. Anyone with some experience with moisture sorption/desorption processes knows that these processes are not fast, especially if larger amount of sample is involved.

Using the above flow based technique, detailed information about the process of water loss is obtained. The user can access what temperatures are needed for fairly complete removal of moisture from samples. Additional applications of can be materialized like evolved gas analysis where gases evolved at various temperatures can be fed to other analytical devices. The standalone temperature-controlled chamber can also accept other sources of gas/vapors, like a humidified stream from a RH generator. Extraction of various substances like formaldehyde using water vapor can be used for finding of concentrations of such substances that are of environmental concerns. Feeding the evolved gaseous substances at various temperatures to concentrators and subsequently to other analytical equipment (e.g. GC-MS) creates a vast area of applications for this versatile system.