InstruQuest Inc.

Providing Complete Solutions

Technical Note
May 2017

By Jan Malczyk and Teresa Malczyk

Temperature programmed desorption of water vapor in controlled way using new design of Helium pycnometer and auxiliary hardware.

The purpose of this note is to present the hardware concept and one of many analytical techniques that can be implemented by using the new approach to gas (helium) pycnometer design and in particular, the enhanced version of the IQIPyc series of gas pycnometers. The IQIPyc as a pycnometer only is a scalable design and can be offered for different volume ranges. The new approach of "Pycnometer to the sample" allows for attaching external components to the sample and reference chambers, as well as using the hardware and software resources of the pycnometer for other usage. Therefore, combining simple modules into an as needed setup and carrying out experiments in automated way using the provided software can materialize variety of analytical capabilities. Instead of using the pycnometer occasionally for density measurements, it becomes the core of more complex setups, which can replace many other expensive instruments and be operated with high flexibility and at minimal expense.

The commonly available borosilicate glass tests tubes, 16 mm OD x 150 mm length, were selected as the external sample chambers to allow universal usage without the cost associated with custom made glassware. In addition to borosilicate glass or quartz, test tube can made of other materials, like ceramic, metal, etc. In order to use the test tube effectively and conveniently, a special housing assembly with multiple ports was designed. Using vacuum, pressure, or flow-through is easy to accomplish. To ensure safety, one port is dedicated for installation of adjustable check valve (e.g. 3 to 50 psig), which opens to ambient if undesired level of pressure develops above the set threshold. The bottom port serves for attaching the test tube. The upper port can be utilized for introduction of specific hardware, like volume reducing adapters, rigid borescopes or sensors into the test tube. Additional ports serve for connection with the pycnometer or with any other external equipment.

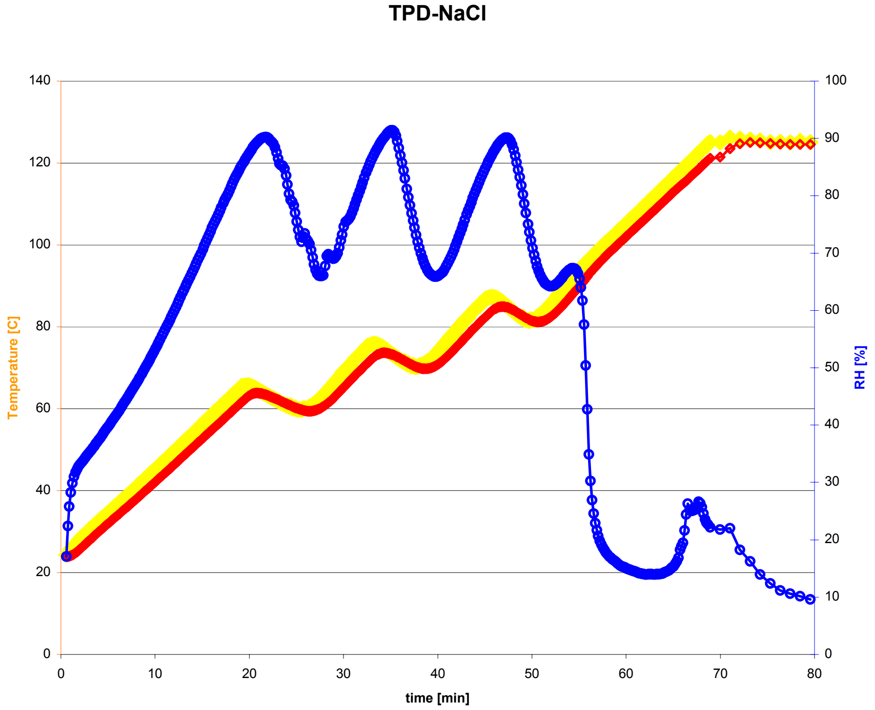
Although the assembly consisting of the test tube and the housing (holder) can be utilized as is, it is far more convenient to attach it to a specially designed stand. Two vertical rods are attached to the base and the horizontal shelf can slide up and down the rods to any level and be maintained at a given position by tightening thumbnuts. In addition to the test tube assembly that is normally mounted on this shelf, other components can be attached to the shelf to allow implementation of various configurations. Of course, safety is paramount importance, and since glass can disintegrate without any warning at any time, shields of various constructions can be attached to the rods and positioned as needed. The user is still obligated to wear proper eye and face protection while in the lab.

Technically, the setup described so far can be utilized as a general-purpose sample chamber for various experiments. When interfaced with the IQIPyc, it forms a remotely positioned sample chamber for true volume (density) and other measurements. The distributed design allows for placing the stand away from the pycnometer, e.g. in the hood or other containment place if nature of the sample dictates that. Since a temperature sensor can be installed inside the test tube, the temperature of the sample can be measured. Basically, this design forms a dual temperature pycnometer. Placing the test tube in a temperature-controlled device increases the capabilities of such measuring system. The 24-bit resolution of the data acquisition employed in the IQIPyc and ability to control external temperature source, provides the user with highly capable and flexible volumetric analyzer.

One of the solutions for uniform and accurate heating of test tubes is the specifically design Test Tube Heater for this purpose. It has temperature range from ambient to 300 ºC and it operated using 12 VDC. Thanks to low mass and proprietary design, less then 40W is used for operation. Standard test tubes up to 20 mm OD can be placed inside the uniform heating zone. Specific reducing adapters can be utilized for using test tubes of smaller diameters. Although manual control of temperature can be used, the remote control of temperature using the pycnometer hardware and software is most useful in automatic operations. The picture below presents the IQIPyc housing the stand with the Test Tube Heater.

In one of the possible hardware arrangements for the flow-through techniques in general, , the gas output from the sample chamber of the pycnometer can be connected to the rotameter input. Precision pressure regulator ensures very good stability of pressure at the input to the rotameter and the metering valve allows setting of various flow rates. The flow from the rotameter is directed to the test tube and is allowed to leave the test tube via different port after sweeping the headspace over the sample. Different gas flow designs, like through the sample is also possible for appropriate design of hardware inside the test tube. Once the gas leaves the test tube, it can pass through specific sensors, like a RH probe for measurements of amount of water vapor released by the sample. Additional option is installation in series a CO2 probe for simultaneous measurements of CO2 or instead of the RH probe, if only CO2 concentrations are of interest. The output stream can be interfaced with other analytical equipment. For example, it can be passed through a sample loop or concentrators and delivered to a GC or GC/MS for analysis of specific chemicals. Instead of a rotameter, a mass flow controller can be utilized. The flow rate of the gas exiting the RH probe can be measured more precisely with a suitable flow meter as this value is important in determining the total mass loss by the sample during desorption.

Out of many possibilities of experimental setup design, only the RH probe is being used in this example. Once the sample is weighed and placed in the test tube, and the test tube attached, the experiment can be started. From the software procedure for the Flow-Through setup, the user can use either a linear ramp or a set of discrete temperature values (steps). The linear ramp can consists of up to four segments with individual temperature increase rates. Each segment can be followed by a period of programmable duration after the end temperature of the segment was reached. The chart below shows water vapor desorption results from NaCl sample of 2.4029 g mass which was exposed previously to close to 100 % RH. Linear temperature ramp from 25 to 125 °C with 2 °C /min rate and 10 minutes of dwell time were used.

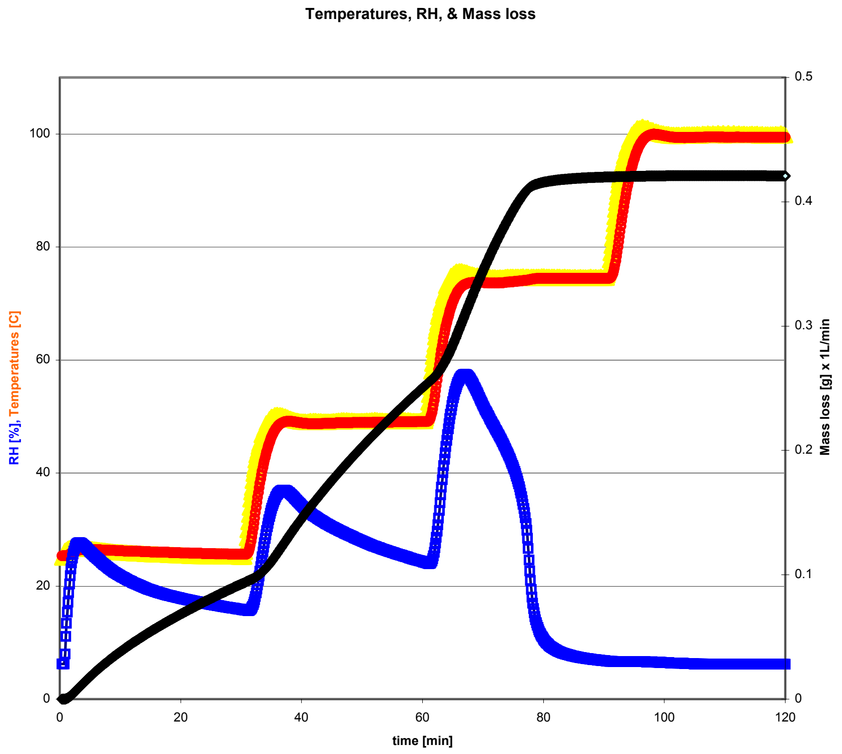


Linear temperature ramp with preset RH limit

The temperature indicated by the monitoring thermocouple of the Test Tube Heater is shown in yellow color. The red curve just beneath it is the temperature measured by external thermocouple with its tip placed centrally in inside the test tube in the middle of the sample. The RH measured by the RH probe is shown as the blue curve. The upper limit of RH can be set and the software decreases the temperature when this threshold is exceeded. The temperature ramp will not continue until RH drops below certain level. Depending on the water amount in the sample, several non-linear segments on the RH and temperatures curves can be present as shown in the above graph. By setting different RH limits, this setup has the ability to control release of water as per the user-selected conditions.

When using the other method of discrete temperature steps instead of the linear ramp, up to 1000 steps of different duration time can be programmed into a single experiment. During the course of the experiment, all data are recorded in text format for easy transfer to spreadsheets. From the relative humidity and temperature values provided by the RH probe, the partial pressures of H_2O can be calculated and the cumulative amount of water in grams assuming the flow rate of one Liter per minute can also be calculated. The user needs to determine the exact flow rate from the rotameter scale or independent measurements and multiply the results by the proper flow factor. For example, if the actual flow rate is 200 cc/min, which is 5 times smaller then the assumed 1L/min, then the total amount of water desorbed needs to be multiplied by 0.2 factor. The test tube with the sample or the sample itself can be reweighed and water loss can be compared with the RH probe results.

Another sample of the NaCl of 1.9343 g was subjected to discrete temperatures, 25, 50, 75, and 100 °C and duration time for each temperature was set to 30 minutes. After the experiment the sample mass was 0.0657 g lower then the initial amount. The actual flow rate measured by a precision flow meter was 161.4 cc/min. Semi-dry gas of dew point -13 °C was used. The results of this experiment are presented on the next graph.



Water vapor desorption using temperature steps

As in the previous graph, the yellow and red curves are the temperatures of the Test Tube Heater thermocouple and the external thermocouple inserted inside the test tube. The blue curve represents the RH probe humidity data. Since the RH probe is kept at ambient temperature which remains stable during the experiment course, the RH values for each temperature step are representative of the desorption kinetics at the given temperature. The RH probe plays a role like the microbalance in gravimetric instruments which records mass loss versus time at a set temperature. Since RH probe responds to water vapor only, it is a specific sensor rather then general mass loss which can be also have a contribution from other gaseous species then water vapors only. The accumulated mass of water vapor loss calculated from the RH probe data is represented by the black color curve. The final results are in excellent agreement with the mass loss obtained by weighing.

The above instrument has many unique advantages:

- Ability of modifications of the setup by the user, simplicity of operation;
- Low cost per sample (the test tube can be treated as a disposable sample chamber), and overall cost being much lower then microbalance-based systems;
- It is far more damage resistant then delicate and high-cost to repair gravimetric analyzers, practically no maintenance is needed;
- It can use more representative sample size and measure temperature inside the sample. The gas flow into the sample is far more efficient in removing moisture then in DVS analyzers, and time of analysis is short.