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## **A COMPARISON BETWEEN THE DIFFERENT METHODS FOR THE MEASUREMENT OF AN EXCESS ADSORPTION OF PURE GASES ON POROUS ADSORBENTS AT HIGH PRESSURE**

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### **ABSTRACT**

*The topic of this work is to compare several experimental methods such as volumetric and volumetric-gravimetric methods for measuring the equilibrium states of pure gases being adsorbed on the surface of solid materials. The investigation of different type methods and their advantages and disadvantages are discussed. The installations used for measuring the adsorption equilibrium by these methods are discussed in details. The installation for measuring the helium density of materials, i.e. volumetric density of solid adsorbents is also presented.*

*Keywords: measurement of excess adsorption, porous adsorbent, pure gases, high pressure.*

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### **INTRODUCTION**

The physical adsorption of high-pressure fluids onto micro-porous solids is very important both in science and engineering. The interest on this phenomena has reflected in a growing number of chemical, petrochemical and biochemical processes including adsorption based separation processes, purification of gases [1], solid-phase extraction, adsorbent regeneration using supercritical fluids [2], etc. There are also important industrial applications in storage of fuel gases [3], in catalysis and chromatography [4]. Most of these processes today are still driven by the respective adsorption equilibrium. As the gas adsorption equilibrium data

up to now can not be calculated accurately by theoretical or analytical simulation based models, it is necessary to measure them, i.e. to determine them by reliable and accurately performed experiments. Gas adsorption equilibrium can be measured by several basically different methods. In all cases the procedure must be adapted to the range of measure (temperatures and pressures) and the state of the gas adsorbed at these conditions. Also differences the temperature and the pressure, the properties of the solid adsorbent (chemical reactivity, state of aggregation, etc.) are very important for the measurements.

The standard method for the measure of pure gas adsorption equilibria is the volumetric or mano-

metric method [5]. Basically it is the mass balance of a certain amount of gas partly adsorbed on the sorbent material.

More accurate and reliable measurements can be performed by weighing the sorbent mass exerted to the gas atmosphere using a very sensitive microbalance. This is the gravimetric method [6-9].

Volumetric/manometric measurements and gravimetric measurements can be performed simultaneously on the same gas adsorption system in a single instrument [3,10-12]. This technique of measurement is known as a volumetric-gravimetric method.

The aim of this study is to compare several techniques for measuring of the adsorption equilibrium.

### THEORY

According to the classical definition of adsorption [13], the all molecules which are within the field the atoms or molecules forces on the surface of a solid sorbent represented the absolute quantity adsorbed. By integration of the density  $\rho(x)$  at any position  $x$  with respect to the whole volume ( $V$ ) of the adsorption space of a given system the distribution of density in the system can be obtained:

$$m_a = \int_V \rho(x) dV \quad (1)$$

In order to estimate the amount adsorbed the fundamental difficulty is the choice of the volume  $V$  used in the integration of Eq.(1). The volume  $\bar{V} = V(y)$ , where  $V(y)$  is the volume filled by the set ( $y$ ) of all molecules of the adsorbate, i.e. all molecules of the sorptive fluid influenced by or exerted to the surface forces of the sorbent material. This is an energetic criterion determining whether a molecule from the fluid is adsorbed on the surface of the solid material or not. If the energy of the molecules ( $E$ ) is:

$$E = E_{kin} + E_p^f + E_p^s \quad (2)$$

where  $E_{kin}$  is the kinetic energy of the translation,  $E_p^f$  is the potential energy of interaction of the molecules with other molecules from the fluid phase (f), and  $E_p^s$  is the potential energy of interaction of the molecules with the molecules of the solid.

If  $|E_p^s| \gg E_{kin}$  and  $|E_p^s| \gg E_p^f$  it is considered that the molecules are adsorbed even not in direct contact with the solid surface. Otherwise the molecule is considered to be not adsorbed. Consequently, molecules from the fluid phase may change their status of being adsorbed or desorbed between two molecular collisions and the "boundary" between adsorbed and not adsorbed molecules from the fluid phase naturally will become fuzzy. The adsorption density distribution  $\rho(x)$  exhibits a gradual change from the solid surface to the bulk, and its approach to the bulk density at a distance away from the surface is usually in the form of an exponential decay:

$$\rho^f = \lim_{x \rightarrow \infty} \rho(x) \quad (3)$$

For small pores, where the potential fields of the two opposite walls overlap, the density distribution everywhere will be greater than the bulk density. In such case one can choose the volume of the adsorbed phase as the pore volume and to calculate the absolute amount:

$$m_a = \int_{V_{pore}} \rho(x) dV \quad (4)$$

Here  $V_{pore}$  is the pores volume. Thus the adsorbed phase volume is pore-specific. So, the Gibbs excess mass can be define as:

$$m_{GE} = \int_V \rho(x) dV - \rho^f V = \int_V (\rho(x) - \rho^f) dV \quad (5)$$

This surface mass excess represents the difference between the absolute amount adsorbed in a volume  $V$  and the amount of volume that could be occupied by molecules with the same density as that of the bulk. Thus the surface mass excess is positive if the adsorption density in the volume  $V$  is greater than the bulk density (see Fig. 1).

It is negative when the adsorption density is less than the bulk density everywhere throughout the volume  $V$ . According to [14] for the absolute amount adsorbed:

$$m_a = m_{GE} + \rho_{bulk} V_{ADS} \quad (6)$$

were  $V_{ADS}$  is the volume of the adsorbed phase.

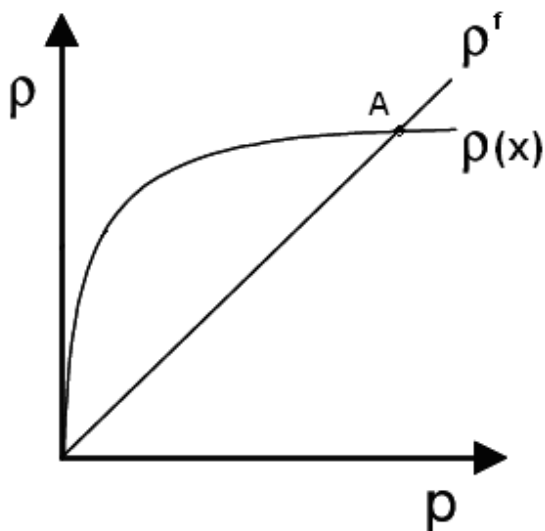


Fig. 1. Bulk end surface density.

It is the volume whose boundary is such that the density at the boundary  $\rho^*$  is equal to the bulk density.

All sorbent materials may change their adsorption properties over the years due to internal physico-chemical processes, but also due to uptake of gases and vapours (humidity) from the ambient air. Especially for carbon based sorbent materials this should be taken into account. The very important aspect of the equilibrium investigation is the activation or the preparation procedure of the sorbent material prior to adsorption of gases on it, i.e. degasification procedure, vacuum treatment, heating procedure. In this work the follow procedure for regeneration and secondary degasification of adsorbent are used:

- The adsorbent is put in a vessel, to be treated at a vacuum and to be heating up to 350°C during 24 h. The procedure is finished when the pressure is stabilized at  $10^{-6}$  Pa. Thus the adsorbent is regenerated completely.

- The adsorbent is refrigerated at room temperature. Then the vessel is filled with helium at one atmosphere. The helium penetrates into micropores of the solid adsorbent and blocks them for other molecules.

- The adsorbent is transferred from the vessel to the cell of adsorption. It has to be done helium quickly because the air from the surrounding will be adsorbed on the adsorbent.

- The cell is heated at temperature up to 350°C and treated with vacuum. The process is finished when the pressure is stabilized at  $10^{-6}$  Pa. The helium is adsorbed slightly, thus the secondary degasification is easy.

## VOLUMETRIC MEASUREMENT TO THE VOLUMETRIC MASS OF MATERIAL

A very important aspect for the investigation of the adsorption equilibrium is to knowledge of the type and the structure of the solid adsorbents. There are many approaches to determine them [15]. In this work is used the volumetric helium measurement for the determination of the volumetric mass of the solid adsorbents. This information is very important to calculate the amount adsorbed. On Fig. 2 is shown the installation used for the volumetric measurement of helium density of material and on Fig. 3 the cell of adsorption. The adsorption of helium on the sorbent at temperature 400°C is very slow and it can be neglected it. Thus the volumetric mass of materials can be determined by mass balance of the system when the volume of the reservoir, the volume of the adsorption cell and the absolute mass of the adsorbent are preliminary known.

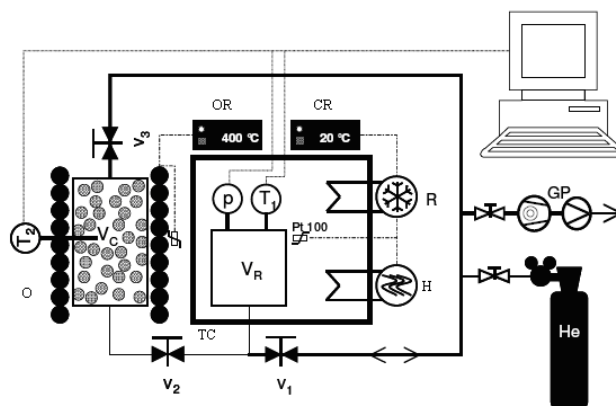


Fig. 2 O, Oven; TC, Thermostatic cage;  $V_R$ , Reservoir; HR, Oven regulation; CR, Cage regulation; H, Heating; R, Refrigeration; GP, Group of pumps;  $V_1$ ,  $V_2$  end  $V_3$ , Valves.

The adsorbent is regenerated following the procedure described above. The temperature and the pressure measured both in the thermostatic cage and in the reservoir. The procedure can be divided to the following steps.

1. The cage and the reservoir is calibrated with xenon (99.9996 %);

2. The adsorbent is regenerated at high temperature;
3. The system of heating of the adsorption cell is switched on and the process of heating is regulated at rate of increasing 2°C/min up to 100°C;
4. During the secondary degasification the temperature increases to 400°C;
5. The adsorption cell is cooling at ambient temperature;
6. The valve is closed and the pump is stopped;
7. The mass of the activated material is determined;
8. The system is connected to the reservoir;
9. Points 3-4 are repeated;
10. Helium is injected to the reservoir;



Fig. 3. Cell of adsorption for measure to the mass volumetric of material.

The volumetric mass of the material is determined by the following equation:

$$V_{Ads} = \frac{\rho_2(T_2, p_2)V_C(T_2) - V_R(T_1)[\rho_0(T_2, p_1) - \rho_1(T_1, p_2)]}{\rho_2(T_2, p_2)} \quad (7)$$

where  $\rho_0$  is the density of helium in the reservoir before the connection to the cell of adsorption,  $\rho_1$  is the density of helium in the reservoir after the connection to the cell of adsorption,  $\rho_2$  is the density of helium in the cell of adsorption,  $V_R$  is the volume of reservoir,  $V_C$  is the volume of the cell of adsorption,  $T_1$  is the reservoir and  $T_2$  is the temperature of the adsorption cell.

### VOLUMETRIC MEASUREMENT OF PURE GAS ADSORPTION EQUILIBRIUM

The standard method for the measurement of the pure gas adsorption equilibrium is the volumetric or manometric method [5]. Basically it is the mass balance of a certain amount of gas partly adsorbed on the sorbent material. Complemented by a gas analyzer (chromatograph, mass spectrometer) this method also can be used for the measurement multicomponent adsorption

equilibrium. The volumetric gas adsorption experiments consist in: a given amount of sorptive gas is expanded into a vessel which includes a sorbent sample and which initially has been evacuated. Upon expansion the sorptive gas is partly adsorbed on the (external and internal) surface of the sorbent material, partly remaining as gas phase around the sorbent. By a mass balance, the amount of gas being adsorbed can be calculated if the void volume of the sorbent, i. e. the volume which can not be penetrated by the sorptive gas molecules is known – at least approximately. On Fig. 4 the installation for measurement of adsorption equilibrium by volumetric method is represented.

An instrument for volumetric measurements of pure gas adsorption basically consists of a gas storage

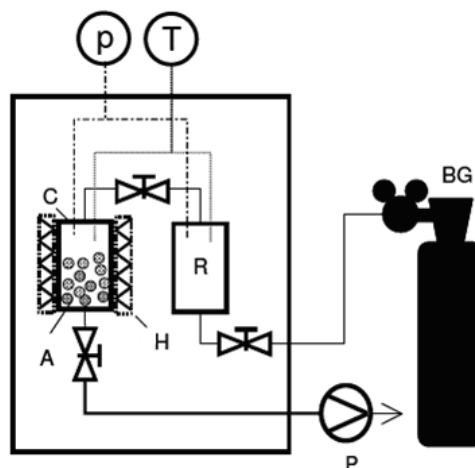


Fig. 4. p, Manometer; T, Thermometer; R, Reservoir; H, Heating; C, Cage; A, Adsorbent; R, Refrigeration; P, Pump; BG Gas bottle.

vessel (volume  $V_{sv}$ ) and an adsorption chamber ( $V_{ac}$ ) being connected by a tube bearing a valve. Both vessels should be placed completely within a thermostat and provided with tubes for gas supply and evacuation as well as with thermometers and manometers for measurement of the temperature (T) and pressure (p) inside the vessels. The adsorption chamber includes a sample of sorbent material with mass ( $m^s$ ) which prior to measurement have been “activated” at higher temperature under vacuum for 24 hours to reduce the amount of pre-adsorbed molecules. Standard procedures for activation have been described above. To measure adsorp-

tion a certain amount of gas with mass ( $m^*$ ) is prepared in the storage vessel and the adsorption chamber is evacuated. When opening the expansion valve, the gas expands to the adsorption chamber where it is partly adsorbed on the (external and internal) surface of the sorbent material. After thermodynamic equilibrium, (constancy of pressure ( $p$ ) and temperature ( $T$ ) inside the vessels), has been realized, these data can be taken as a basis to calculate the mass of the gas adsorbed on the sorbent ( $m^*$ ). From the mass balance of the sorptive gas we have:

$$m_{GE} = V_{SV} [\rho_0(p_0, T_0) - \rho_{Bulk}(p_1, T_1)] - (V_{AC} - V_{Ads}) \rho_{Bulk}(p_1, T_1) \quad (8)$$

were  $\rho_0$  is the density of gas initially prepared in the storage vessel,  $\rho_{Bulk}$  is the density of the sorptive gas in the adsorption equilibrium state considered.

In the case of microporous adsorbents according to [14], we can consider that  $V_{Ads} = V_{pore}$ . Thus  $V_{pore}$  can be obtained by experimental measurements of helium density of the adsorbent.

### VOLUMETRIC - GRAVIMETRIC MEASUREMENT OF PURE GAS ADSORPTION EQUILIBRIUM

Volumetric/manometric measurements and gravimetric measurements can be performed simultaneously on the same gas adsorption system in a single instrument. The experimental measurements are based on the gravimetric-volumetric method [3,10-12]. In Fig.5 the schematic setup used is shown.

The mass of the gas present in the system is dynamically measured. Moreover, after each state of equilibrium, the gas is re-injected to the system. As illustrated in Fig. 5, the system is weighed directly and the gas is injected by a capillary tube. To avoid the systematic errors due to the gas mass, the pressure vessel must be symmetrical and the axis should remain vertical. The vertical alignment of the system is obtained with a counterweight. This one compensates both due to the weight of the capillary tube. A precision adjustment is possible starting from the micrometric table (Fig. 6). At the left end of the capillary, the balance is connected and on the right-the micrometric table. The axial deviation ( $y$ ) of the balance is slightly influenced by elasticity ( $E$ ) of the capillary tube. We used a capillary tube (stainless 316L,

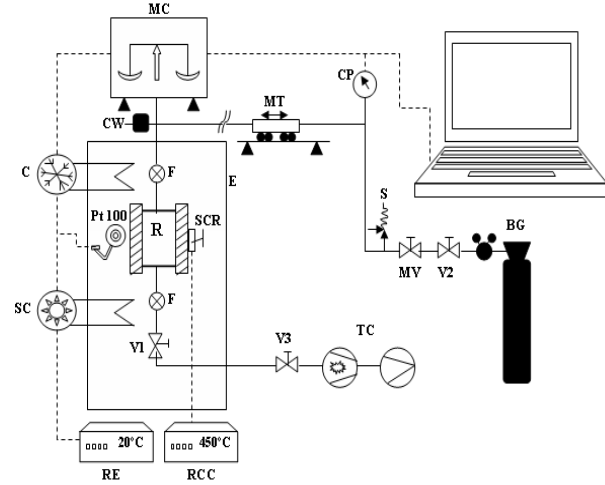


Fig. 5. MC, Mass Comparator (Mettler Toledo, PR2004); E, Climatic Chamber (S.P.A.M.E.); C, Unichiller (Huber, 7006A-H); SC, Heating System; Pt 100, Platinum temperature sensor; R, Pressure Vessel; SCR, Heating system of the pressure vessel; F, Micro filters; v, Valves (Autoclave); RE, Climatic chamber regulation (Eurotherm 2404), RCC; Regulation of the SCR (Watlow Série 93); TM, Micrometric table (Micro Controle); CP, Pressure gauge of reference (DH Budenberg DPM1); S, Security valve (Air Liquide); VM, Micrometric valve (Autoclave); BG Gas bottle; TC, Turbo pump (Pfeiffer Vacuum TSH 071); CW, counterweight.

200 GPa) with a length of 1520 mm, where a load of 0.1 mg at the free end induces a deviation of the capillary tube equal to 0.02 mm. If the length of the tube is  $l$ , the axial deviation is given by:

$$y = \frac{F_G l^3}{3E \frac{\pi(D_e^4 - d_i^4)}{64}} \quad (10)$$

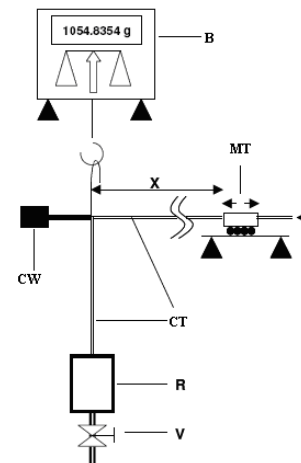


Fig. 6. B, Balance; MT, micrometric table; X, length of capillary; CW, counterweight; CT, capillary tube; R, Reactor; V- Valve.

Where  $D_e$  is the external diameter and  $d_i$  - the internal diameter of the capillary tube.

The procedure of measurement of the capacity of adsorption can be subdivided in several stages:

- The mass of the adsorption cell is obtained with an internal vacuum ;
- The volume of the cell is filled with the adsorbent (35 cm<sup>3</sup>) then it is sealed;
- The climatic chamber is set at 273.15 K to prevent the heating of the high pressure
  - valve;
- The system is connected gradually to the pumping installation (see Fig. 3) ;
- The heating system of the cell is regulated with 2 K/min until 373.15 K;
- There is a stage at 373.15 K to eliminate water in the adsorbent cell;
- When secondary vacuum is reached, the heating process (2 K/min) continues until the final temperature is reached (573 to 723 K depending on the decomposition temperature of the adsorbent);
- The heating process is finished at high temperature and secondary vacuum;
- The adsorption cell is cooled down to ambient temperature;
- The high pressure valve is closed and the vacuum pump is stopped;
- The procedure is repeated (3-8) after having determined the mass of activated material;
- The acquisition of the measurements starts;
- The pressure is preset via the mano-pressure reducer;
- The gas is injected by opening the micro-valve;
- At equilibrium, the procedure 12 starts again until the end of the measurement.

The adsorbed gas mass  $m_a$  is expressed in mole per gram. In this study the following equation was applied to the adsorption of pure gases. The adsorbed mass of these gases obtained by volumetric-gravimetric measurement is:

$$m_a = \frac{m_{Gas} - \rho_{Gas}(T_{Int}, P)[V_c(T_{Int}) - V_{Ads}(T_{Int})] - \rho_{Gas}(T_{Int}, P)V_{Cap}(T_{Ext})0.5}{m_{Ads}M_{Gas}} \quad (11)$$

where  $m_{Gas}$  is the total mass of gas,  $\rho_{Gas}$  - bulk the density of the gas,  $T_{Int}$  - the temperature inside the cli-

matic chamber,  $P$  - the gas pressure,  $V_c$  - volume of the pressure vessel,  $V_{Ads}$  - volume of the adsorbent,  $T_{Ext}$  - the external temperature,  $V_{Cap}$  - the volume of capillary tubes,  $m_{Ads}$  - masse of the adsorbent and  $M_{Gas}$  - is the molar mass of gas.

The bulk density of the gas is evaluated by the equation of state of Peng-Robinson. In order to determine precisely the volumes, the thermal dilation of all materials is taken into account.

## RESULTS AND DISCUSSION

On Fig. 7 the results (LIMHP) for adsorption of hydrogen on a zeolithe 13X obtained by volumetric-gravimetric method at three different temperatures and results of AIR LIQUIDE Co. for adsorption of hydrogen on the same adsorbent at same conditions obtained by volumetric method are compared. The maximum deviations are up to 2.5 % at 20°C, 3 % at 40°C and 3.5 % at 60°C. Thus there is very good correlation between the data. The isotherms of hydrogen in this range of pressure have a linear character. The deviations of the results obtained by the two methods increase with the increasing of temperature. It is due to the mode of calculation of adsorption results by volumetric method, i.e. the choice of equation of state for estimation of gas density.

Results of the equilibrium for nitrogen adsorption on a zeolithe 13X at three different temperatures are shown in the figure 8. There is the difference of 1.3 % at 20°C, 2.1 % at 40°C and 60°C in this case. The figure shows also that the isotherms are first type iso-

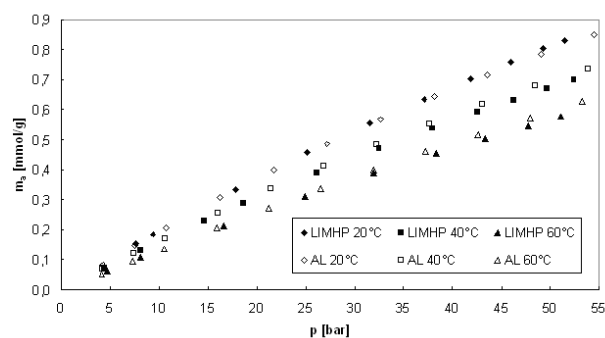


Fig. 7. Comparison of hydrogen measurements obtained by gravimetric-volumetric device (LIMHP) and volumetric device (AL) on the zeolite 13X.

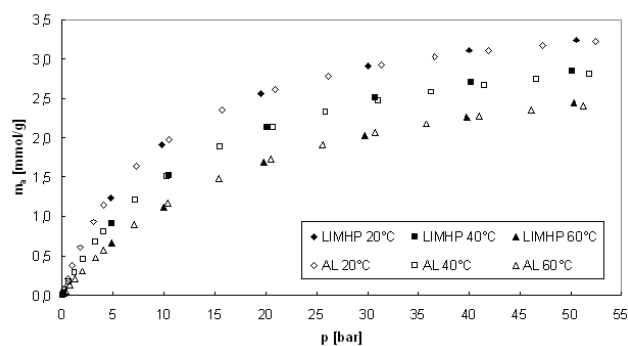


Fig. 8. Comparison of nitrogen measurements obtained by gravimetric-volumetric device (LIMHP) and volumetric device (AL) on the zeolite 13X.

therms. These data also show that the difference between the two methods increase with the increasing of the temperature.

## CONCLUSIONS

The installations for volumetric and gravimetric-volumetric measurements as well as the installation of volumetric helium measurement for determination of the volumetric mass of solid adsorbents are described in details. The comparison between the results of adsorption equilibrium using volumetric-gravimetric technique and result obtained by AIR LIQUIDE Co. using volumetric method is made.

The volumetric measurements of gas adsorption equilibrium are reduced, if the mass of the sorbent sample used is preliminary known, to the measurements only of pressures and temperatures in gas phases. On the other hand prior to adsorption experiments the sorbent sample should be activated by heating the adsorption chamber, degassing etc. During this procedure the mass of sorbent is changed by 1 % or more. This change normally can not be included in volumetric experiments but must be taken into account afterwards, at least approximately. Gas adsorption processes may last for seconds, hours or sometimes even days. Therefore we can never be sure whether thermodynamic equilibrium in a volumetric experiment has been realized. Hence the time which should elapse between opening the expansion valve and reading of instruments, especially thermometer and manometer has to be chosen according to the experience. Finally upon expansion from the storage vessel the sorptive gas may not only be adsorbed on the

surface of the sorbent material but also on the walls of the adsorption vessel and the tube connecting both vessels. This may cause additional uncertainties in measurement.

Basically, volumetric-gravimetric measurements (VGMs) combine all the advantages and the disadvantages which occur in either volumetric or gravimetric measurement procedures. Commercially available instruments for VGMs usually need several grams of sorbent material to perform reasonably accurate measurements. Operations technical of measurements are fairly simple and the procedure easily can be automated. Activation Procedure of the Sorbent Material is recommended to provide an electric heating system for the adsorption chamber of any instrument of VGMs. This will allow the activation of the sorbent material “on site” and thus avoid any pre-adsorption of for example ambient air’s components, especially humidity, if the sample is activated outside the instrument and then built in the adsorption chamber.

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