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The gravimetric tank method to evaluate CO_2 adsorption in MOFs

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Academic year : 2019-2020
Thesis presented in partial fulfillment of the requirements for the degree of Master in bioengineering: chemistry and bioindustries

Table of contents

Acknowledgements

This master thesis could not be what it is without the many people who helped along the way. Mere words cannot fully express the value of their involvement in this work, but I will try my best to show my gratitude in this section.

Firstly, I would like to warmly thank my promoters. Prof. Yann Garcia, who trusted me despite my delay in the procedure when no one else would, and placed me in good hands with Prof. Yaroslav Filinchuk. And of course Prof. Yaroslav Filinchuk himself, who guided most of my work, providing me with the equipment and knowledge necessary to it, and addressing questions and issues always in an encouraging way.

My sincere gratitude goes to Xiao Li, who gave a lot of his time teaching me the good practices in the lab, as well as explaining me concepts where I had trouble, reviewing my results, and thinking with me to practical improvements when it was needed. And similarly, to Timothy Steenhaut, who provided me with more than just the MOFs as he took the time to teach me what they are and how to read their analyses, and from whom I also learned a lot about the life in the lab through casual chatting.

I would also like to thank in advance my readers, Prof. Sophie Hermans and Dr. Koen Robeyns, to whom I wish a pleasant reading, and from whom I am sure I will receive a pertinent and fair evaluation.

Finally, I thank my family and friends for their daily support, in particular my roommates, who contributed to maintaining work-proof living conditions in our home, and my friend Renaud, whose persistent disbelief in my ability to finish this thesis on time has only pushed me forward in my writing.

Abstract

Adsorption is at the heart of a lot of research in today's background of environmental challenges, as it can be applied for gas storage and separations. However, it is not a trivial phenomenon, and the methods and models to evaluate it are complicated, often prone to errors and controversies, and extremely time-consuming. In 2018, *Iakunkov et al.* proposed a new method : *the gravimetric tank method*. It uses a model based on simpler variables, focusing more on the practical aspect of gas storage, as opposed to the precise material characterization. In this thesis, we push their idea further by setting up a modified version of their method, which allows for a continuous monitoring of the adsorption through the filling and emptying of the test tank, while reducing greatly the time needed for a measurement, restoring the possibility to make full adsorption isotherms in a reasonable time. The method was tested by applying it to CO_2 adsorption on MOFs and comparing the results with a reference volumetric method, and the MOFs were characterized through BET, TGA, and other analyses to try and explain the observations more deeply. Encouraging results were obtained, even though their precision does not allow the method, at this stage of development, to be used on its own. Many sources of error were identified, as well as the next steps to be taken in the development of the method to make it competitive and complementary with the other ones available.

Abbreviations

- BET : *Brunauer-Emmet-Teller*
- BJH : *Barrett-Joyner-Halenda*
- FTIR : Fourier Transform Infra Red spectrometry
- GDS : Gibb's dividing surface
- GT : Gravimetric Tank
- MOF : Metal-Organic Framework
- PEEK : Polyether Ether Ketone
- PXRD : Powder X-Ray Diffractometry
- SBU : Secondary building unit
- SSA : Specific Surface Area
- TGA : Thermogravimetric Analysis
- TSD : Total Storage density
- WGT : Wired Gravimetric Tank

Symbols

- c : Concentration
- K : Equilibrium constant of the Langmuir equation
- n : number of moles
- P : Pressure
- R : Gas constant
- T : Temperature
- U : Uptake capacity
- V : Volume
- W : Weight
- Z : Compressibility factor

Introduction

Adsorption

The term adsorption is used to describe the phenomenon occurring at the interface between two phases, where the surface of one of the phases has a force of attraction to some species from the other, making them reach higher densities in the proximity of that surface than in the bulk of the phases. This phenomenon applies to some extent to many, not to say all types of interfaces and species, with varying strength. And while its microscopic effects remain mostly unnoticed in the everyday life, it can gain macroscopic importance in the case of high surface area materials, yielding a wide range of applications as much at the industrial scale as in the laboratory. Some of these applications use its separation capacity for gases or solutes in liquids, for extracting products or purifying wastes as polluted air or water, desiccation, respiratory protection. It can also be used as a method of gas storage, solid surface analysis and plays a role in controlled drug delivery. It is also the first step of all surface chemical reactions, giving it utmost importance in the field of heterogeneous catalysis. [1,2]

History of development

Adsorption has been present in the scene of science since the beginning of History. The Egyptians, Greeks and other ancient peoples already made use of natural adsorbent materials such as charcoal and clay for diverse medicinal purposes as well as purification of water, odors removal and in metallurgy [1,2].

The first reported scientific studies were carried out independently by Scheele and Fontana in the years 1773 and 1777 respectively, where they started to quantify uptake of gases by charcoal and clays. [3,4] The study of adsorption from liquid solutions began shortly after that, when Lowitz investigated in 1785 the decolorizing properties of charcoal. [5]

In 1814, de Saussure started more systematic work, finding out that all types of gases are taken up by all kind of porous materials to some extent. He was also the first to point out the exothermic nature of adsorption. [6] After that, it was subsequently discovered that the gases prone to condensation were adsorbed to the highest extent ; that the amount of gas taken up by a certain volume of adsorbent suggested that the adsorbate would be in the liquid state ; and that the heat of adsorption was larger than the heat of liquefaction. [7,8]

Kaiser introduced the term *adsorption* for the first time in 1881, and started the study of isothermal curves, relating the evolution of adsorption as a function of pressure under constant temperature. [9,10] It was then put into perspective with absorption, a slower process of gas uptake related to the bulk of a material as opposed to its surface, by McBain in 1909. [11] He also proposed to use instead the general word *sorption* to include both phenomena when the distinguishment cannot be made.

An important historical event happened in 1903 with the discovery by Tswett of selective adsorption, thanks to different components in a mixture having a different affinity for the adsorbent, which is the basis for most practical applications of adsorption. [12] He was able to isolate the different pigments from a plant mixture by selective adsorption on silica gel, inventing chromatography, one of the most powerful analytical technique up to this day.

The first attempt to a mathematical fit for the adsorption isotherms is known as the Freundlich equation, which is purely empirical. [13] It was used up to 1918, when Langmuir introduced his famous theoretical model of adsorption. [14] This model is based on the hypothesis that the adsorbent surface contains a finite number of adsorption sites, all equivalent and not influencing each other. The plateau observed in the isothermal curves would then be associated with the formation of a monolayer of adsorbate molecules on the surface of the adsorbent. While being far from enough for describing all real adsorption systems, the Langmuir model yields good results in the simple cases of adsorption, and was the starting point for the development of more accurate models. [15]

The next famous developed model was the BET theory, named after its inventors Brunauer, Emmett and Teller. [16] It generalizes in a way the Langmuir model by applying its monolayer equation to multilayers adding up on top of each other, enlarging its validity over higher pressures. Despite some remaining flaws, such as the need to stay below the critical temperature of the gas and the bad results in the region of capillary condensation for materials having a heterogeneous pore structure, it has become the reference for adsorption studies, and its application to low-temperature nitrogen adsorption is still used today as the standard procedure for the determination of the specific surface area of porous materials. [17]

Basic principles

As stated earlier, adsorption occurs at all kind of interfaces and is mostly studied and used on solid surfaces, from gas phase and liquid solutions. Even though the concepts and equations for describing both cases are quite similar, we will only further discuss the case of gas adsorption on solid surfaces, as it will be the subject of the later part of this work.

Adsorption is the result of attractive interactions existing between the gas and solid molecules. Those interactions can either be weak and driven by physical laws (e.g. Van der Waals forces), or strong and driven by chemical reactions. We speak respectively in terms of physisorption and chemisorption. While the interactions responsible for physisorption have a lower specificity, meaning they can apply to more types of adsorptive, they can extend past a single layer of adsorbed molecules to form a multilayer, i.e. an adsorption space with a thickness of several molecules. Chemisorption on the other hand forms chemical bonds with molecules in direct contact with the solid's surface and can therefore only form a monolayer at the maximum. It is also more specific, as it will only occur between solid and gas molecule that can react chemically together. In contrary to physisorption, chemisorption can have the structure of the adsorbed molecule altered and then be irreversible. [18] In some cases, an adsorbed molecule can penetrate into the solid's bulk. The adsorption equilibrium then cannot be reached, and the final total uptake does not relate to the solid's surface area but to its volume. This phenomenon is referred to as *absorption*.

Except for energetic considerations, the main tool for adsorption study is the *isotherm*, i.e. the locus of the equilibrium states on a plot of the gas uptake versus the pressure of the gas phase, at constant temperature. As physisorption is a reversible process, these equilibrium states can be reached after an increase of pressure with the gas uptake going upwards, or with a decrease of pressure. The distinction is made by speaking respectively in terms of *adsorption* or *desorption* isotherms. Hysteresis can occur in some cases, meaning that the adsorption and desorption curves do not coincide. This phenomenon happens with solids that have pores of particular size and shape, and is caused mainly by the different curvatures of the interface between the gas phase and the adsorbed space when filling or emptying the pores, resulting in different saturation pressures. [19]

Strictly speaking, the *amount adsorbed* is the quantity of gas present in the adsorption space, a thin volume separating the two bulk phases, solid and gas. As the volume of the

adsorption space (V^a) is often unknown, the amount adsorbed can be replaced by another value : the surface excess amount (n^σ), which is the quantity of gas attributed to a hypothetical surface (Gibb's dividing surface, GDS) delimiting the 2 bulk phases : it is the difference between the total quantity of absorptive injected and the quantity of gas calculated by application of the gas laws to the volume accessible to the gas phase. If the GDS considered is close enough to the actual adsorbent surface, the amount adsorbed and surface excess amount can be considered identical at low pressures (up to 1 bar). However, as the thickness of the adsorbed layer grows when pressure increases, the difference cannot be ignored at higher pressures. In this case, the amount adsorbed is :

$$n^a = n^\sigma + V^a * c^g$$

with c^g being the concentration of the bulk gas phase. [20]

Adsorption quantification

The determination of adsorption isotherms is usually carried out using methods that can be divided in two groups. Volumetric methods imply the quantification of the amount of gas removed from the gas phase by the adsorption process, and gravimetric methods directly measure the increase in mass of the adsorbent. In this section we will give detail on the most common way these methods are put into practice, on their associated errors and why and when irreproducibility can occur.

For any adsorption determination, the adsorbent has to be primarily activated. Activation consists in removing all adsorbed molecules from the surfaces, as some molecules such as water will always already be adsorbed on a sample coming from ambient atmosphere and temperature. This is done by keeping the adsorbent for several hours under vacuum and high temperature. The exact required conditions depend on each adsorbent and have to be determined experimentally. [21]

Volumetric method

The volumetric method consists of two connected chambers of known volume, enclosed in a thermostat. The first chamber, here named storage vessel (V_{SV}), serves for admission of a known quantity of adsorptive gas. The second one, the adsorption chamber (V_{AC}), contains the adsorbent (see Fig. 1). At the beginning of the experiment, the adsorbent

is activated and the activation chamber is under vacuum. The storage vessel is filled with a certain quantity of gas, determined by knowledge of the pressure, temperature and volume. The expansion valve can then be opened so the gas flows to the adsorption chamber and starts adsorbing. The pressure in the system decreases until it reaches an equilibrium, which relates to the amount of gas remaining in the gas phase by application of the gas laws. In the case of an adsorption isotherm determination, the successive points at increasing (or decreasing) pressures are reached by stepwise increase of the pressure in the storage vessel. The activation is only necessary at the beginning and does not need to be repeated between each point.

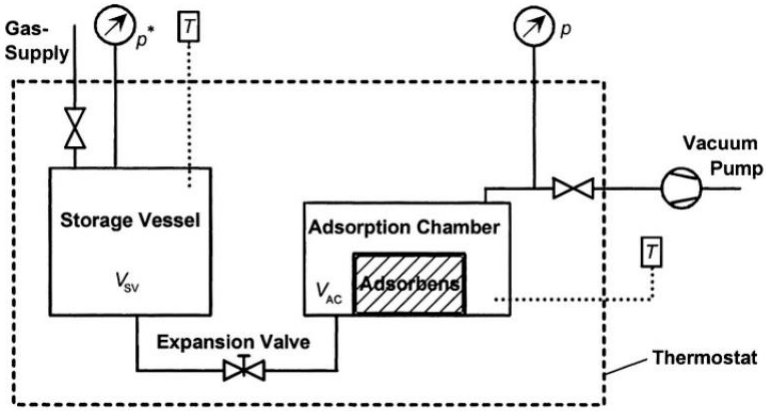

Figure 1 : Scheme of the experimental setup for the volumetric method. [21]

The calculation of the amount of gas remaining requires knowledge of the exact volume of the gas phase. Here this volume (V_f) is given by :

$$V_f = V_{SV} + V_{AC} - V_{as}$$

where V_{as} is the volume of the adsorbent (plus the potentially already present adsorbate phase). As this quantity is unknown, a value has to be attributed. The value commonly attributed is the skeletal volume, which is determined in the same system by doing the experiment with helium, which does not adsorb. Of course, the volume of the adsorbed phase is not at all considered. That's why instead of *amount adsorbed*, the result is given out in terms of *surface excess amount*, as explained above. To characterize a material's adsorption capacity, the absolute surface excess amount must be divided by the sample's mass. This result is called excess weight percent (wt%) and is calculated by : [21,22]

$$wt\% = 100\% * \frac{m_{excess}}{m_{sample}}$$

Gravimetric method

The gravimetric setup is composed of an adsorption vessel, containing a microbalance on which the adsorbent is put. The vessel is hermetic and connected to a vacuum pump and gas supply, and equipped with a thermometer and manometer. A thermostat is also needed around the adsorbent. Mounting as presented on Fig. 2 allows to keep the microbalance from the high temperature needed for activation of the sample. A different mounting can be used with corrosive gases, to keep them from the balance. In this case, the balance is outside of the adsorption vessel and weighs the sorbent vessel through magnetic suspension.

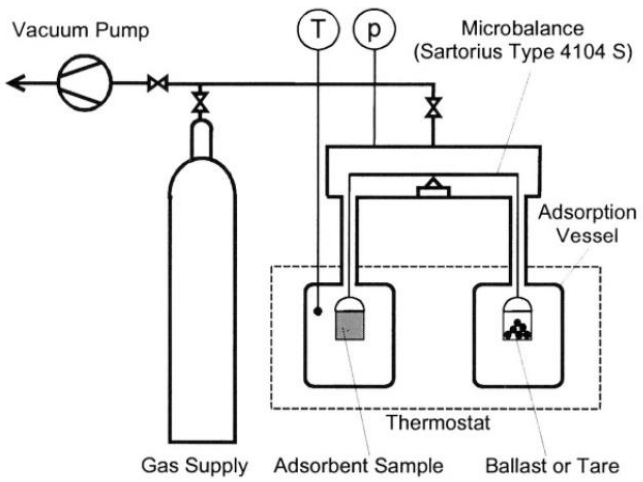

Figure 2 : Scheme of the experimental setup for the gravimetric method. [21]

Once the sample is activated, the adsorptive gas can be introduced at desired pressure and the adsorption process can be monitored on the balance. Stepwise increase can also be carried out for the determination of isotherms. The adsorption results in uptake of mass of the adsorbent, but the buoyancy effect of the gas surrounding the sample has to be taken into account, which involves once again the skeletal density of the adsorbent. The volume of the adsorbate phase remaining unknown, the gravimetric method also gives out the result as surface excess amount, which is converted to wt% in the same way as above. [21,22]

CO_2 Adsorption

In today's background of climate change, the challenge of separating CO_2 from other gases is of utmost importance. Effective ways to achieve industrially such a separation are

absorption in liquids, which exploits the good solubility of CO_2 and its affinity with some basic solutes, and adsorption on porous solids.

Thanks to its high boiling point (195K), quadrupole moment and molecular weight, CO_2 can make strong molecular interactions with other molecules. In addition to that, its small kinetic diameter gives it an advantage for diffusion through pores, and thus for adsorption kinetics. These characteristics often make it the most adsorbed molecule in a gas mixture. [23]

Separation of CO_2 by adsorption has some advantages over absorption in liquids, it is less subject to corrosion, and less energy consuming (considering the desorption process which includes elevation of temperature, and that water has a higher heat capacity than the porous materials used for adsorption). Porous materials can be functionalized by amines to enhance the binding strength and selectivity. However, separation by adsorption has to deal with the competition of H_2O, which has a higher boiling point and polarity, giving it an advantage in adsorbing on polar functional groups, and an even lower kinetic diameter. Moreover, water will sometimes destroy the porosity of non-covalent porous materials. This is a major drawback for this method, considering that water is often produced alongside with CO_2. [23]

Porous materials

As it is a surface phenomenon, in order for the adsorption to be noticeable and useful, the adsorbent surface must be high in regard to the total volume. This is why adsorbents must be porous materials, as they have a great specific surface area (SSA : The area of the surface of the solid per unit of mass, in m^2/g). In addition to the SSA and the strength of the adsorption bonding, the sizes and shapes of the pores and their distribution, affect greatly the shape of the adsorption isotherm. This is why adsorption can be very useful for the characterization of surfaces. [24] Notably, the presence and shape of the hysteresis loop, the presence and number of plateaus, of knees, all give important information about the solid's surface.

Porous materials come in various types, some natural, other synthesized. They can be classified according to their composition. Inorganic porous materials include naturally occurring minerals, zeolites, which can also be synthesized to design useful characteristics, along with activated carbons, and many others. Organic porous materials are polymers whose units are designed to self-assemble into porous structure. Finally, the type we will use in this

study are metal-organic frameworks (MOFs). They are synthesized compounds formed of connected organic and inorganic units, some of which comprise a permanently porous structure.

MOFs are crystalline networks of metal-containing units, joined with organic linkers. These organic linkers are ditopic or polytopic negatively charged molecules such as carboxylates. They link together the metal-containing-units, called secondary building units (SBUs), in such a way that forms an open porous structure. On top of that, their structure in some cases stays constant with upsizing of the organic linkers or the SBUs, and with chemical functionalization. [25] This property gives them a large potential in many fields of chemistry, for example catalysis, separation, and gas storage, which will be our main concern in this study. Their interest for gas storage relies on the fact that they develop such a large surface area, that the amount of gas in the pores and adsorbed on the surfaces, in a tank full of the material, can be greater than the amount of gas that would be contained in this empty tank at a given pressure. In the case of carbon dioxide, MOFs make a reversible adsorption, and some have an uptake capacity greater than any other known material. In particular, some MOFs' have been found to have an extremely high affinity for CO_2, so that their uptake capacity and selectivity would make them suitable for separation of CO_2 from mixtures of gases. [27,28]

Aim of our project

In a paper from 2018, Iakunkov et al. [26] put a strong criticism on the current most common methods to quantify gas sorption on porous materials. They notably put light on controversies regarding overestimations in the case of hydrogen sorption, due to the difficulty to acquire reproducible results with these methods. To address this problem, they proposed a new simpler method for such quantification, *The gravimetric tank (GT) method*. This method gives results under the form of a whole new parameter, *Gain*, which is independent from other variables often prone to error, like buoyancy, skeletal volume, etc. This *Gain* parameter, which will be further explained later, is presented to be the simplest one to carry the relevant information in the study of sorption for applications of gas storage. However, in the effort to make it as simple as possible for this application, this method is mainly intended for single point determination of sorption at one given pressure. Multipoint determination of sorption isotherms on the other hand would take an unreasonable amount of time compared to the

other methods, and isotherm determination in the quasi-equilibrium continuous mode is not possible.

In this thesis, we aim to go further in their direction. We will present our own version, quite modified, of the *Gravimetric tank method*. In particular, we investigate the feasibility of our method and the quality of the results obtained, in the case of carbon dioxide adsorption on metal organic framework materials (MOFs).

The gravimetric tank method

The gravimetric tank method as proposed by Iakunkov et al. differs from the presented traditional gravimetric method in the fact that the whole pressurized adsorption space is weighed on a balance outside of this space, instead of weight measurement being done inside the pressurized atmosphere. Doing this removes the need of calculating the buoyancy, and thus the dependency on the skeletal density of the sample, and the ambiguity between the surface excess amount, which is a theoretical quantity based on a 2-phase model where the adsorbed molecules are attributed to a 2-dimensionnal surface ; and the adsorbed amount, which is the real quantity relevant for adsorption, but mostly inaccessible due to the lack of accurate model describing the adsorption volume on the adsorbent surface.

In this method, the adsorbent is held directly in a tank that can be pressurized and disconnected (see Fig. 3). After activation, the tank is disconnected and weighed a first time, then reconnected to supply the adsorptive at the desired pressure. When pressure and temperature equilibrium is reached, the tank is disconnected and weighed again. The difference between the 2 masses is the important value here. It comprises the mass of the adsorbed gas, and the free gas in the dead volume, volume of the tank unoccupied by the sample.

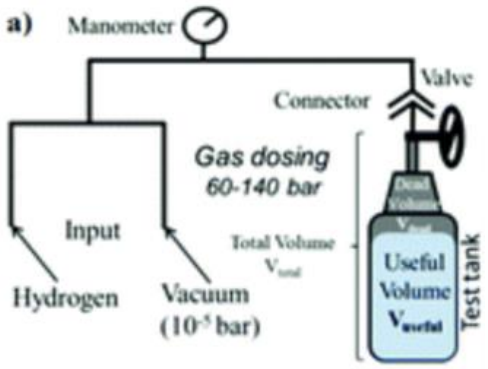

Figure 3 : Scheme of the experimental setup of the gravimetric tank method. [26]

The point of this method is not to precisely characterize an adsorption phenomenon occurring on a specific material. Rather than that, the focus is put on the gas storage capacity of that material, or even of the tank itself. In other words, the quantity of interest here is how much gas can be stored in a tank full of this material. In consequence to this, the relevant volume of the adsorbent for calculation of the dead space is not the skeletal volume but the much more easily accessible bulk volume, which simply describes the quantity of material that can be stored in a tank of a certain size. Therefore, the question of the adsorption space volume is also not relevant.

New values had to be introduced to render this new way of quantifying adsorption. The total storage density (TSD) is the total amount of gas that can be stored in a volume completely filled with porous adsorbent at a certain pressure. Thus, it comprises the adsorbed amount, plus the gas phase inside the pores and between the grains, in the unavoidable dead space. Another value was introduced: the gain. It is, in percent, the ratio between the TSD of the material, and the TSD of the vacuum. It describes how much the presence of the adsorbent improves the gas storage capacity of the tank, relative to an empty tank. In practice, a tank containing an adsorbent with a gain of 10%, will be able to hold 10% more gas than the same tank with only gas inside, at the same pressure. The gain can therefore have a negative value when adsorption is weak or porosity is too low.

For comparisons to be made, the gain and TSD can of course be converted into the surface excess amount and weight percent values of the previous methods, but doing so reintroduces the possible errors linked to the determination of the skeletal volume.

Modifications

In this thesis, we propose another analogous gravimetric method, the *wired gravimetric tank (WGT) method*, and investigate its potentialities and flaws. The focus on gas storage capacity remains, as well as the weight measurement done outside of the adsorption space, thus weighing the whole adsorption tank. In consequence, this method can also give results independently from the skeletal volume.

The difference of our method to the *gravimetric tank* lies in the fact that our tank will remain connected to the gas supply at all times through a thin tube, including during weight measurements. The challenge in doing so is to minimize the influence of the tube on the

results. More precisely, the weight of the tube itself will inevitably influence the absolute weight on the balance, but the aim is to get relevant reproductible results on the weight difference before/after adsorption. If this can be achieved, the manipulations and equilibration times between experiments could be drastically reduced, allowing the fast determination of sorption isotherms, and the possibility to operate in the continuous mode could be restored.

In the next section, the experimental setup that we put in place will be described with more details.

Materials and methods

Wired gravimetric tank (WGT) method: experimental setup

The adsorption chamber in our setup is composed of a small steel tank, connected in continuity with a flexible polyether ether ketone (PEEK) tube of 0.75 mm internal diameter to a control board with manual valves that operate the system. These valves are connected to each other by steel tubes, and allow the adsorption space to be connected to the pressure and temperature probe, and either to the vacuum pump, the gas supply or the atmosphere, for evacuation of the excess gas during desorption. The tank is laid on an analytical balance (Steinberg SBS-LB-300A), which gives a readability of 0.001 g. The pressure probe gives a readability of 1 mbar, but with a constant noise of about ±2 mbar. It also gives a small variable bias, displaying between -30 mbar and 5 mbar when under vacuum. In regard to the high pressures handled in the experiments, these small defects will be considered negligible. The CO_2 bottle gives a maximum pressure of around 60 bar. This setup is depicted on Fig. 4.

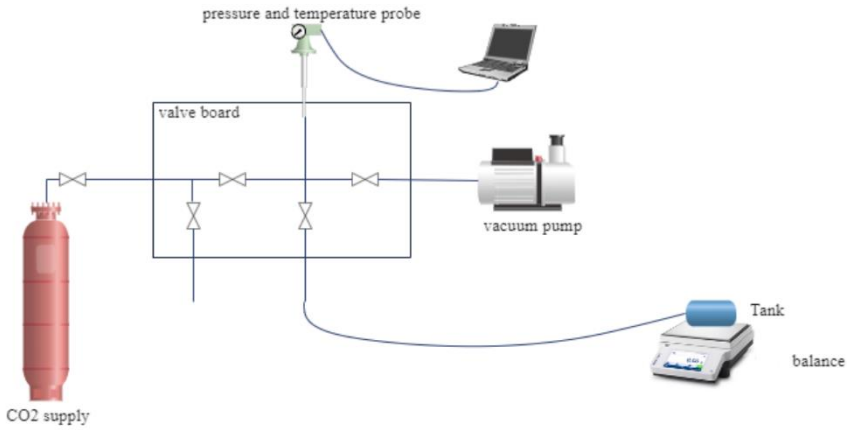

Figure 4 : Scheme of the setup put in place for the WGT method.

It must be noted that the exact volume of the adsorption space is unknown in this setup, as it comprises the inside of the tank, the flexible tube and the steel tubes between the valves. However, this value is irrelevant, as it is not the volume of gas that will effectively be weighed on the balance. This *weighed volume* will then have to be determined by calibration.

For the weight measurements to be meaningful, they must not be influenced by any other mean than the inflow of gas. For this reason, the path of the flexible tube must be as straight as possible, and not in contact with the table, the walls of the balance or anything else. Also, the tank must stand stably on the plate of the balance, i.e. on a flat edge (the tank here is not cylindrical but with a hexagonal section), as is depicted on Fig. 5. And finally, the valve board must be stable and on the same table as the balance. Those precisions are important to consider to avoid movement of the system that could result from the differences of pressure or the manipulation of the valves.

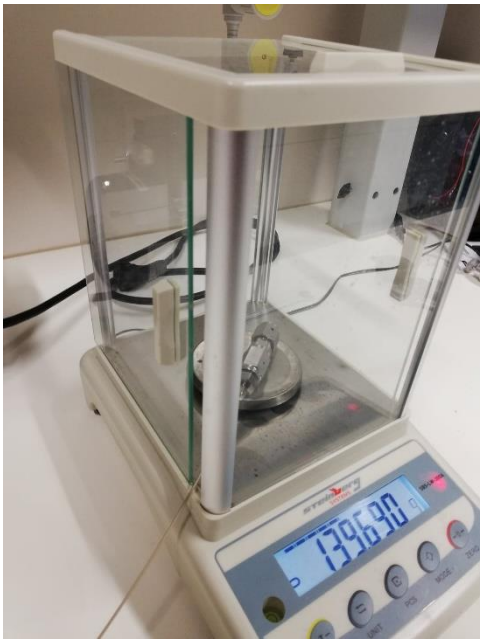

Figure 5 : Picture showing how the tube and tank must be placed to avoid interferences in the measurements.

Samples

The determination of adsorption isotherms was carried out using CO_2 as adsorbent on 6 different MOF samples :

- MIL-100(Fe)
- MIL-100(Fe,Ni)
- MIL-100(Fe,Mg)
- MIL-100(Fe,Zn)
- MIL-100(Fe,Co)
- HKUST-1

The former 5 were under the form of a fine powder, while HKUST-1 was made of bigger crystals with a diameter between 0.1 and 0.5 mm. These MOFs were synthesized in our lab using a green method described by *Steenhaut et al.* [29,41].

MIL-100(Fe) is an iron(III) carboxylate. It is composed of trimers of iron octahedra (iron atoms at the center of oxygen octahedra) with one common vertex, and these trimers are bound together by benzene-1,3,5-tricarboxylate. This system assembles into supertetrahedra, that form at the larger scale a zeolitic architecture as is depicted on Fig. 6. This structure

contains 2 types of small mesopores of 25 and 29 Å, accessible via apertures of about 5.5 and 8.6 Å respectively [30]. The other 5 MIL-100(Fe,M) only differ by the introduction of the doping metal alongside iron. These metals replace a fraction of the iron atoms in their atomic sites, without changing the overall structure. HKUST-1 is composed of copper "paddlewheel" units, linked together by benzene-1,3,5-tricarboxylate and assembling in a structure containing channels of square micropores with a size of 10 Å [31].

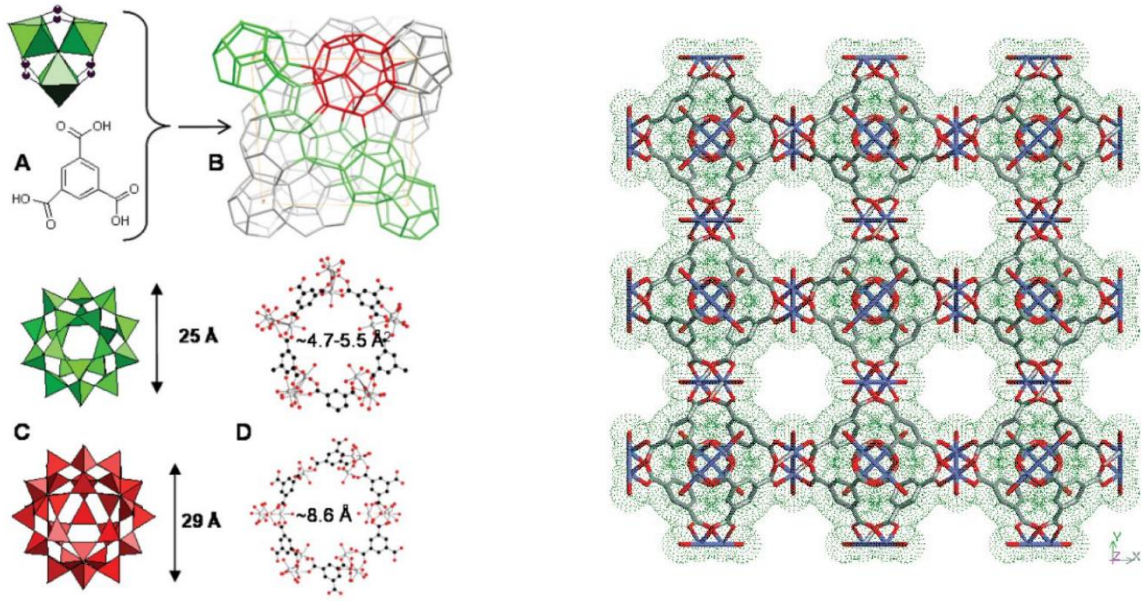

Figure 6 : Left : Schematic structure showing the architecture of MIL-100 at successive scales [30]
Right : Schematic structure of HKUST-1 [31]

In an attempt to get significant results with our new gravimetric method, implemented for practical reasons with a relatively low precision balance (readability of 0.001 g, i.e. 10 times less precise than the balance of the attempt from *Iakunkov et al.* [26]), the weights of adsorption needed to be maximized, in order to minimize the relative error. This is why we chose CO_2 as the adsorbent, given its high molar mass and good adsorption properties, as well as the MOFs MIL-100 and HKUST-1, which have been reported to yield a high uptake of CO_2 under pressure [28,32], on top of their high porosity and surface area. The particular instances of MIL-100 that we used, were taken for their abundance in our lab.

Characterization

After synthesis, the samples were characterized by various methods to verify their nature, crystallinity, surface area and porosity.

- **BET**

The Brunauer-Emmett-Teller method was carried out on the *Micromeritics ASAP 2020* system. A small quantity of each adsorbent was introduced into the system (between 0,035 and 0.1 g), and activated at 200°C under vacuum for 10h (only 150°C for HKUST-1 because of its lower temperature resistance). After cooling, the adsorption and desorption isotherms were then determined using N_2 at its boiling point (77.35 K), with all the range of pressure between vacuum and the N_2 saturation pressure (i.e. 1 atm). The system then analyses the results automatically to give the surface area of the sample, according to the BET theory. The system also gives an estimation of the pore size distribution by the BJH method.

- **TGA**

A thermogravimetric analysis of the samples was done on a *Mettler Toledo TGA/DSC 3+ STARe system*. The samples were not activated before this analysis. The program kept them at 25°C for 15 minutes, then increased the temperature by 10°C/min, under atmospheric pressure and a flow of dry air of 100 mL/min, while recording the evolution of the mass. This analysis permits to verify the temperature of desorption of the synthesis solvents and atmospheric water, and the temperature of combustion of the sample.

Another thermogravimetric experiment was done using the same equipment, to check for the adsorption of CO_2. The samples were first activated by heating them to 200°C for 2.5 hours under a flow a helium, and let to cool down to 25°C. Upon equilibration of the weight, the flow of helium was switched for CO_2, and the uptake recorded. The flow was switched back and forth between helium and CO_2 until 3 adsorptions were recorded, each cycle during 5 hours.

- **Supplementary quality checks**

The materials were characterized by FTIR and PXRD analyses, to verify their nature and crystallinity. These analyses were performed respectively by a Bruker Alpha II Platinum ATR, and a Stoe Stadi P, CuK(alpha1) radiation of 1.5405 A.

Calibration

As explained above, the total volume of the adsorption space is unknown. However, as the weight measured on the balance relates to a certain quantity of gas, a reference volume

is needed to calculate how much of this gas is actually adsorbed, and how much is still in the gas phase. A first estimation of that volume was done by filling the tank with ethanol and weighing it. However, it was quickly noted that this method did not account for the volume of the tank's lid. Finally, the volume was determined by calibration, i.e. by recording the increase in weight at increasing pressures of CO_2 in the empty tank.

The tank was put under vacuum and tared on the balance. The pressure was increased by steps of 5 bar up to 60 bar, and back to atmospheric pressure. This procedure was repeated twice, and the volume was then calculated by application of the gas law.

Methodology

Each sample's adsorption isotherm was determined using 2 methods: the volumetric method performed by automated and calibrated equipment often used in our lab, to serve as a reference, and our WGT method

The volumetric method was carried out by an automated system (Hidenisochema IMI-HTP) working in the way explained in the introduction. It was loaded with a quantity between 0,1 and 0,15 g of each sample (only 0,05g for HKUST-1 due to lack of sample), and covered with quartz wool. The samples were activated in situ, kept at 200°C for 24h under vacuum. An additional isotherm was determined for MIL-100(Fe,Ni) with an activation at only 100°C, to evaluate the influence of the difference of activation temperature. After cooling down to room temperature, one measurement is made with introduction of helium. As helium does not adsorb at room temperature, this measurement allows the system to automatically calculate the volume of the adsorbent. Once the volume is known, and the sample re-equilibrated under vacuum, the determination of the isotherm begins. 14 measurements were made with stepwise increase of CO_2 pressure between 0 and 35 bar, each introduction of gas beginning only after the previous step has reached equilibrium. Desorption was measured too, with 9 steps back to vacuum, to check for the presence of hysteresis. Each isotherm was determined twice.

The volumetric system is equipped with a software that performs on its own all the calculations needed to arrive, from pressure and temperature measurements, to the uptake of gas in µmol, while taking into consideration the non-negligeable compressibility of CO_2 under such pressures, the volume of adsorbent and the volume of quartz wool. Simply dividing

this uptake value by the mass of introduced sample then gives the uptake capacity of the adsorbent in µmol/mg, which is plotted against the pressure to yield the isotherm.

For the WGT method, a quantity between 0.1 and 0.15 g of each sample was loaded into the tank, and covered with some quartz wool (about 0.06 g) to prevent outflow of sample during degassing. Activation was made in situ: the tank was closed and placed inside a tubular heating device (depicted on Fig. 7), electronically controlled and equipped with a thermometer, and was connected to the running vacuum pump. Activation was carried out for 24 hours, at a temperature of 100°C. Higher temperature would have been preferred to match that of the volumetric method and BET, but the PEEK tube in contact with the tank couldn't withstand such a temperature.

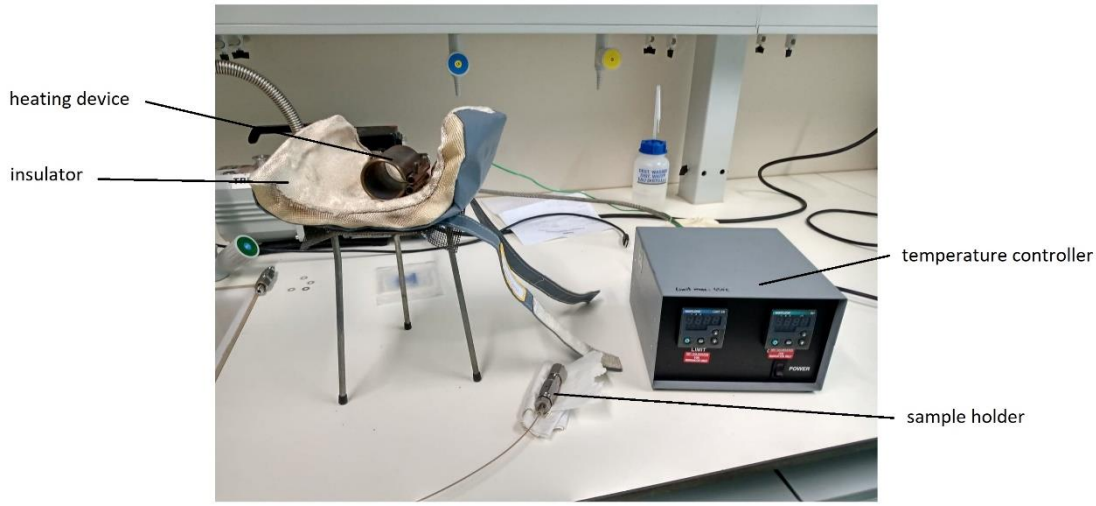

Figure 7 : Electronic heating device used for in situ activation in WGT method.

After the activation, the samples were let to cool down to room temperature. The vacuum pump was disconnected and the balance tared with the tank. Then, a step-wise increase in CO_2 pressure was performed, with steps of about 5 bars, up to 60 bars. Between each step, pressure was kept constant for about 5 minutes to let adsorption reach equilibrium, then the readout on the balance was recorded. After completion of the adsorption, the desorption isotherm was determined in the same way with a step-wise decrease in pressure. Each isotherm was determined twice. The sample wasn't reactivated before the second adsorption but was let to equilibrate under vacuum.

Calculations

- **Calibration**

The volume of the quantity of gas that was weighed was calculated using the ideal gas law corrected for compressibility:

$$PV = ZnRT$$

where n, the quantity of gas in moles, was directly derived from the measured weight by dividing it by the molar mass (i.e. 44 g/mol). The table of compressibility factor Z for CO_2 was taken from the software of the volumetric machine mentioned earlier.

- **Uptake capacities**

Firstly, the measured weight (W) was divided once again by the molar mass of CO_2 to give the total quantity of gas present in the tank in moles (n_{tot}). Then the volumes taken by the quartz wool (V_{wool}) and the material (V_{mat}) were calculated by dividing their mass by their density. For the materials, the skeletal density (ρ_{skel}) was used, which was calculated from the helium pycnometry measurement of the volumetric machine. The remaining volume available for the gas phase (V_{free}) was calculated by subtracting these volumes from the total volume of the tank determined earlier (V_{tot}).

The quantity (n_{free}) of gas in the volume V_{free} was determined by using the same gas law as previously, and finally, the quantity of adsorbed gas (n_{ads}) is the result of the subtraction of n_{free} from n_{tot}. The uptake capacity of the material (U_{mat}) is then simply given by the division of n_{ads} by the mass of material that was introduced (m_{mat}).

Here is a summary of the procedure in mathematical terms:

Initial data:

- Measured weight (W)
- Pressure (P)
- Temperature (T)
- Sample : mass (m_{mat}) and skeletal density (ρ_{skel})
- Quartz wool mass (m_{wool}) and density (ρ_{wool})
- CO_2 : molar mass (M_{CO2}) and compressibility (Z)

- Gas constant (*R*)
- Total tank volume (V_{tot})

Procedure:

$$n_{tot} = \frac{W}{M_{CO_2}}$$

$$V_{mat} = \frac{m_{mat}}{\rho_{skel}}$$

$$V_{wool} = \frac{m_{wool}}{\rho_{wool}}$$

$$V_{free} = V_{tot} - V_{mat} - V_{wool}$$

$$n_{free} = \frac{P * V_{free}}{Z * R * T}$$

$$n_{ads} = n_{tot} - n_{free}$$

$$U_{mat} = \frac{n_{ads}}{m_{mat}}$$

- **Fitting curves**

For all the adsorption isotherms (volumetric and gravimetric), the curves were drawn by fitting the Langmuir equation [14] to the data by the least squares method:

$$U = U_{max} * \frac{K * P}{1 + K * P}$$

where *K* (the equilibrium constant) and U_{max} (the theoretical plateau from Langmuir's model) are the 2 fitting variables.

Results and discussion

Characterization

- **BET**

The isotherms of N_2 adsorption at 77K are gathered in Fig. 8. As expected from their common structure, all MIL-100 isotherms are very similar, and they also share most of their characteristics with HKUST-1. According to the IUPAC classification system [20], they all show a mainly type I look, with a very steep increase at low partial pressures up to a plateau, but with a slight trait of type IV, by the inflexion point that they all present before the plateau. The sharp climb at the beginning of the curve indicates the presence of micropores (< 2 nm). Due to their size, these pores directly get filled by a liquid-like phase at very low pressure, rather than start in a monolayer-multilayer pattern. After that, the inflection point reveals the presence or mesopores, with a certain gap of pore diameter from the micropores. While the micropores are filling up at the beginning of the curve, the mesopores adsorb in a normal monolayer-multilayer manner. The initial decrease of the slope is due to the width of the range of micropore diameter as well as the covering of the mesopores surface. But its subsequent re-ascent corresponds to when these mesopores start filling up by pore condensation. Once they are filled (which again may be over a broader or narrower range of pressure depending on their size distribution), a plateau is reached : the external surface remaining for multilayer adsorption is quite insignificant compared to the quantities already adsorbed inside the material.

By this analysis, we see that all our samples are mainly composed of micropores, those of HKUST-1 being restricted to the smallest diameter while those of the MIL-100 series have some size distribution. The mesopores on the other hand, while being far less represented in both cases, seem to have a slightly wider size distribution in HKUST-1. We can also notice the presence of a small hysteresis loop in MIL-100(Fe, Mg and Zn), a type H4 loop, which is common among micro-mesoporous materials. [20]

These results are acceptable considering the structures presented in section 2, with the 10Å pores of HKUST-1, and the 25 and 29Å pores of MIL-100. These last ones are particular as they are at the boundary between the definitions of micro- and mesopores (respectively: <2nm and between 2 and 50nm of diameter), which may be the reason of such an apparent

mix of characteristics in the isotherms. The presence of wider mesopores could be the consequence of defects in the structure.

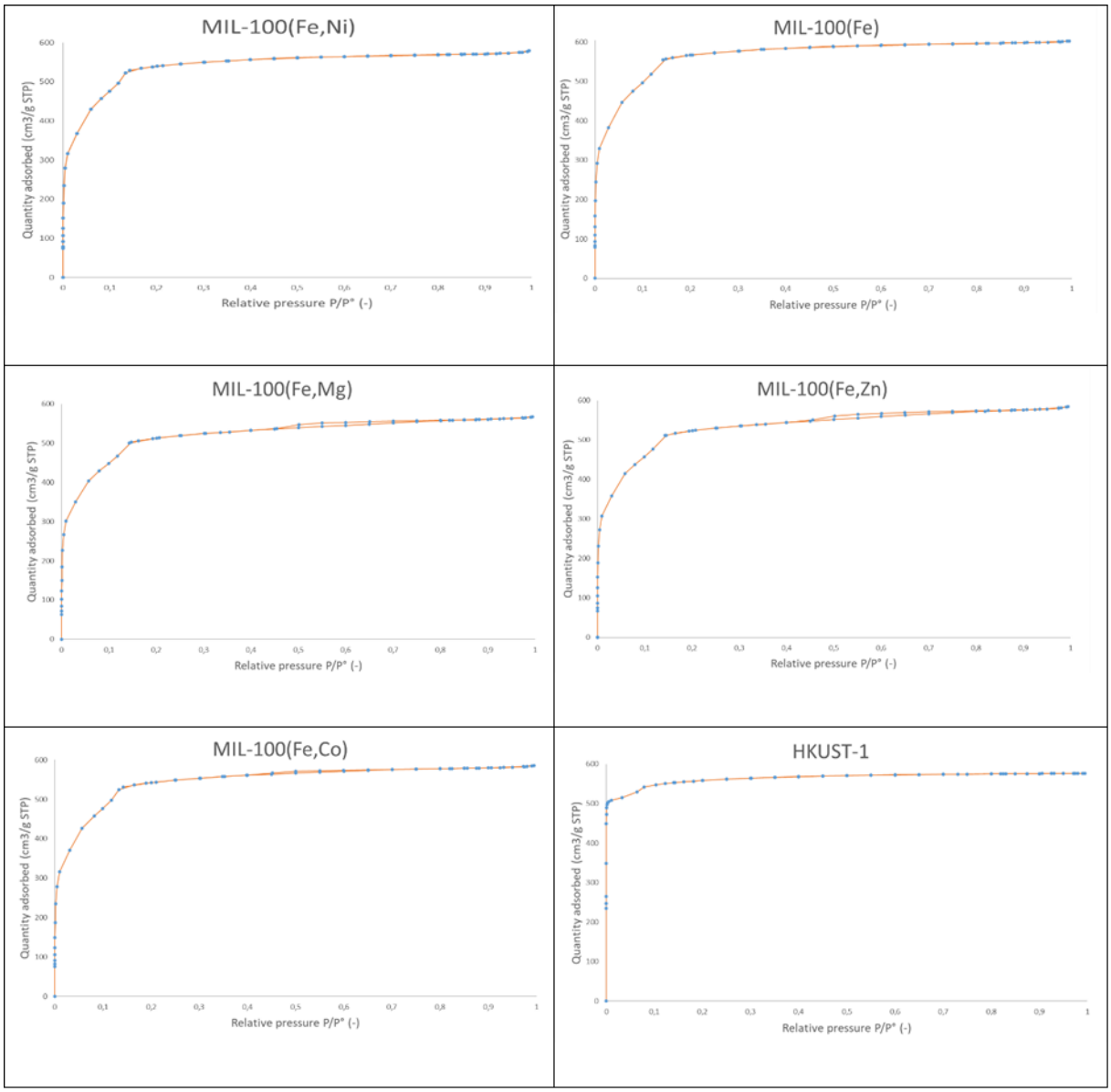

Figure 8 : BET adsorption isotherms (N_2 , 77K).

The BET surface areas calculated from those isotherms are presented in Table 1. All these results are exceptionally high compared to most data already available in the literature for these materials [30-38]. These great surfaces should provide a large adsorption capacity for CO_2, which will be discussed later.

Table 1 : Surface area results.

	BET surface area (m^2/g)
MIL-100(Fe,Ni)	1920
MIL-100(Fe)	2048
MIL-100(Fe,Mg)	1849
MIL-100(Fe,Zn)	1878
MIL-100(Fe,Co)	1940
HKUST-1	1881

- **TGA**

The TGA results (see Fig. 9) show that the combustion of all the samples starts after 300°C, which corresponds to the high peak in exothermicity accompanied with a steep weight loss. Below that temperature, slower weight losses seem to happen in at least 2 steps, as is shown by the changes in the slope of the weight curve. Unfortunately, due to the heating rate, none of those steps seem to have reached equilibrium, except for the second step in HKUST-1 which terminates in a plateau. As a consequence, we lack information about the real ranges of temperature over which each step happens.

The small vertical drop at the start corresponds to the first step already beginning during the initial 15 minutes of air flow without increase in temperature. This step goes on up to about 100°C, where the slope decreases. The presence of these 2 distinct steps is not surprising, as it could easily be explained by the consecutive desorption of ethanol and water, which were expected to remain in the materials after their use as solvent and washing liquid during the syntheses. A more intriguing aspect of the curves is the apparent small exothermicity rising between 150 and 200°C, well after the beginning of the second desorption step, as desorption is always endothermic. The calibration of the calorimetric device could be questioned since all graphs show a comparable exothermicity also on the right side where no weight loss is associated. But if we rule out the hypothesis of equipment failure, this could indicate some unwanted reactions happening, possibly inducing a deterioration of the porous structure.

As mentioned earlier, these graphs cannot allow us to draw much conclusions concerning the activation temperatures, apart from HKUST-1, which we know, can be completely activated at maximum 200°C. Concerning the solvent contents, the same problem holds. HKUST-1 had a solvent content of 37%, and the MIL-100 series had “at least” between 18% (for MIL-100(Fe,Ni)) and 33% (for MIL-100(Fe)).

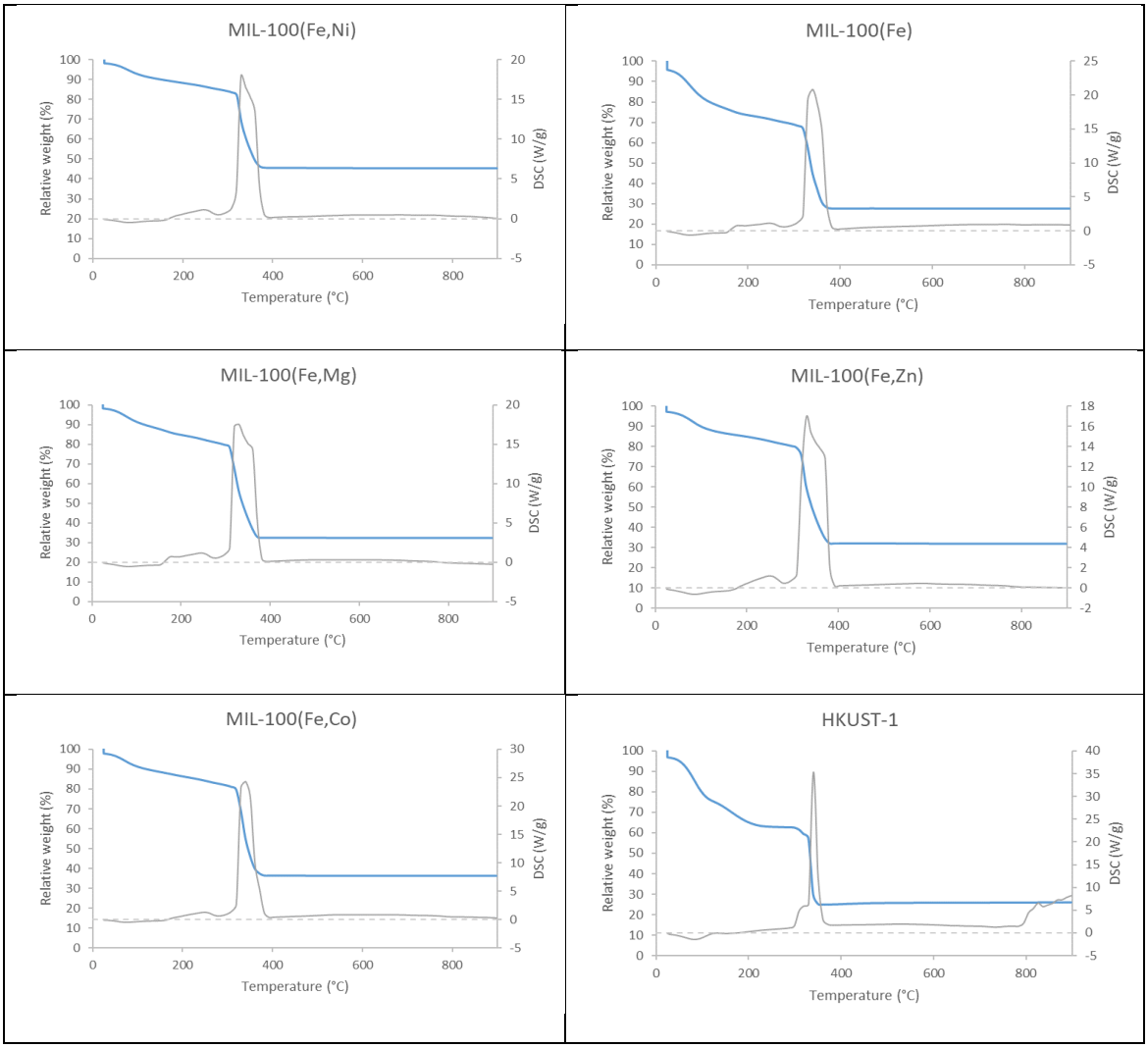

Figure 9 : TGA and DSC results.

The gravimetric experiment in presence of a CO_2 atmosphere will be discussed later to be put in perspective with the other gravimetric results.

- **Supplementary quality checks**

The graphs of the results of the FTIR and PXRD analyses are provided in the appendices 8 and 9. However, their detailed analyses is outside of the scope of this study.

Calibration

During the calibration by uptake of gas in the empty tank, the weight increase followed the expectations as it obeyed the gas law for a constant volume, at least between 30 and 60 bars. Here is a depiction of these results:

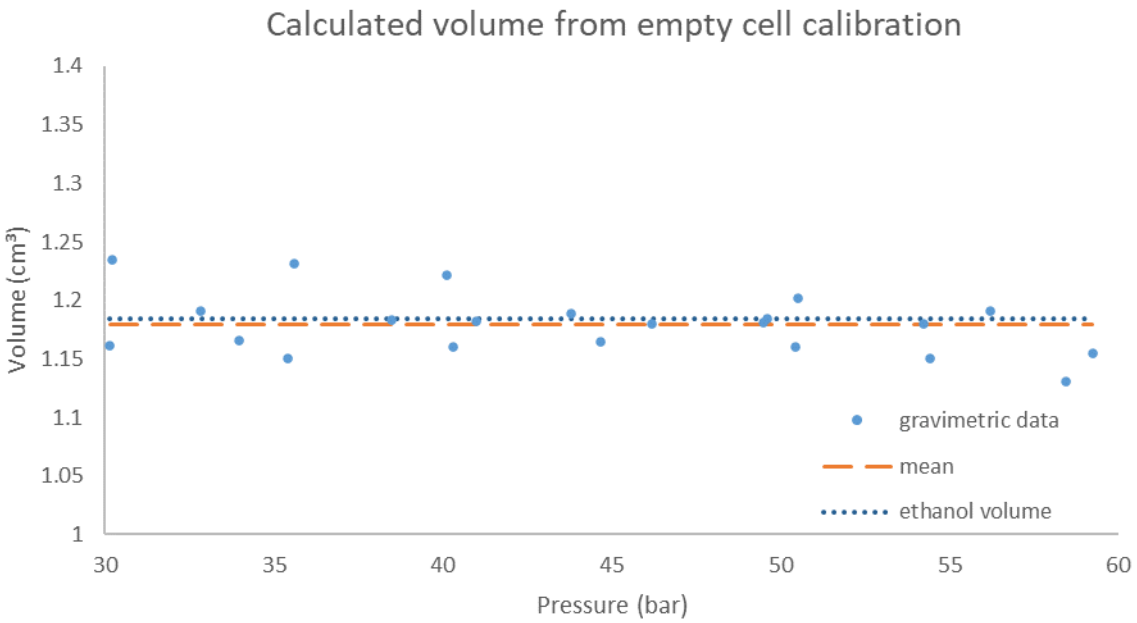

Figure 10 : Tank volume calibration results.

	Ethanol result	Calibration result
Tank volume :	1.184 cm^3	1.179 cm^3

The volume derived from the successive weight measurements in the considered range shows a standard deviation of 0,026 cm^3. This deviation corresponds to an experimental error in the weight measurement ranging from 0.002 g at 30 bar, to 0.005 g at 60 bar, i.e. between 2 and 5 graduations of the used balance.

The mean volume however is very close to the first approximation using the ethanol density. The difference observed is coherent considering that the lid of the tank was absent in the ethanol volume determination, and that the tube joint in the lid takes up a small space inside the tank.

The results of the measurements below 30 bar were not taken into consideration, as they showed a far more important deviation from the mean at higher pressure. Indeed, as the pressure lessens, the imprecision of the balance has a growing impact on the volume. These

results are reported in Appendix 1. In particular, the lower pressure points reveal a directionality in their deviation: the measured volume gets lower and lower, both while increasing and while decreasing the pressure. This could be the effect of a downward drift of the balance, a phenomenon which is caused by the buildup of static electric charges. [39] This kind of buildup is favored by friction in a dry environment with insulating material, and could well be caused in our case by the flow of CO_2 in the thin plastic tube.

This effect was considered negligible over 30 bar, as the calibration points are distributed more evenly across the mean. As the mean volume for this set of results was in good accordance with our first approximation, we took it as the reference adsorption space volume for the calculation of the gravimetric isotherms up next.

Adsorption isotherms

In order to evaluate the quality of the data obtained from the WGT method, we will directly compare the results with the analyses by the volumetric method.

Let's first take a look at the results for MIL-100(Fe,Ni) on Fig. 11. It was the only sample that was re-analyzed volumetrically after an activation at only 100°C.

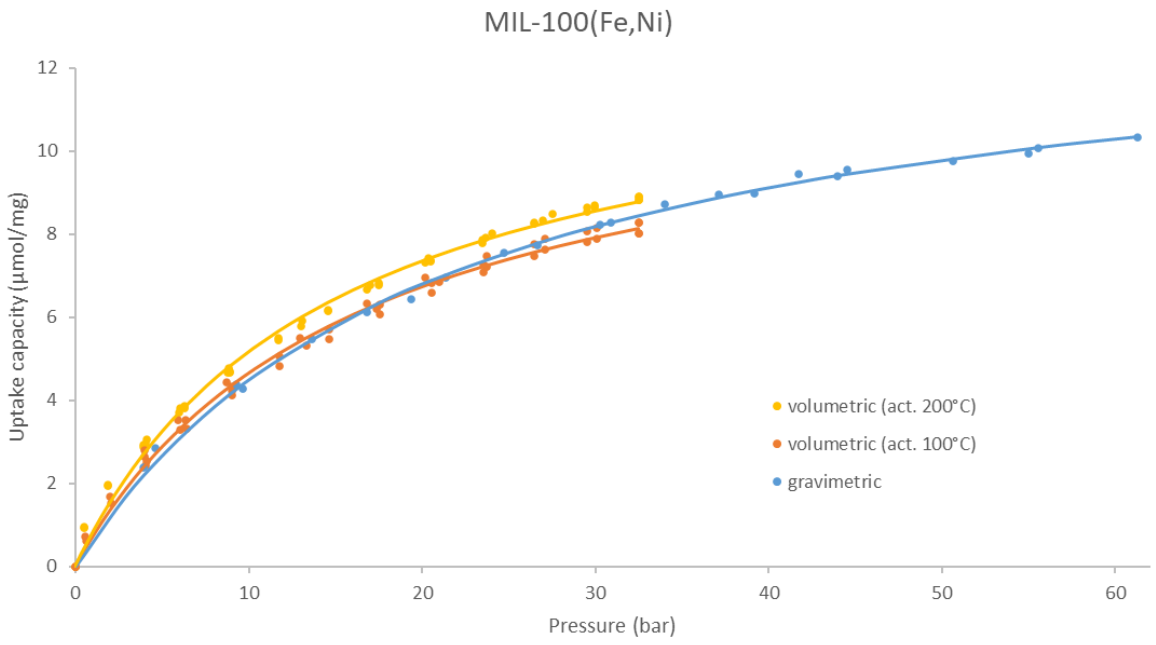

Figure 11 : MIL-100(Fe,Ni) CO_2 adsorption isotherms according to different methods.

As we can see here, the difference of activation temperature had an effect on the uptake capacity for CO_2 in the order of 10%. The gravimetric isotherm follows relatively

faithfully the volumetric one with activation at 100°C, and we see that the dispersion of the points around the fitting curve is comparable to that of the volumetric data, which proves a good precision in this case for the WGT method.

The other samples were not analyzed volumetrically with activation at 100°C, but we can expect a similar behavior at least in the MIL-100 series of samples. According to this approximation, the isotherm obtained for MIL-100(Fe) in Fig. 12 yields the same comments as the previous one: a good precision and accuracy.

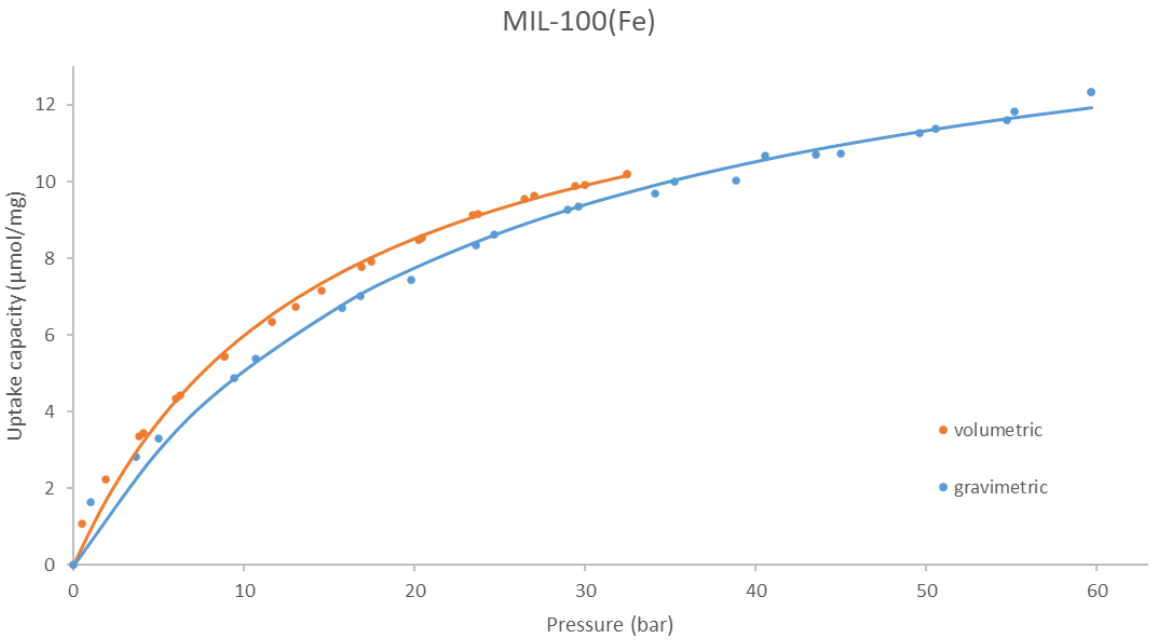

Figure 12 : MIL-100(Fe) CO_2 adsorption isotherms.

However, this behavior was not constant through all the samples. The following 2 samples on Fig. 13 do not retain this gap from activation temperature difference, the Zn gravimetric curve even overpassing the volumetric analysis. One must also notice that the precision of gravimetric measurement in the Mg sample is far from as good as the other ones.

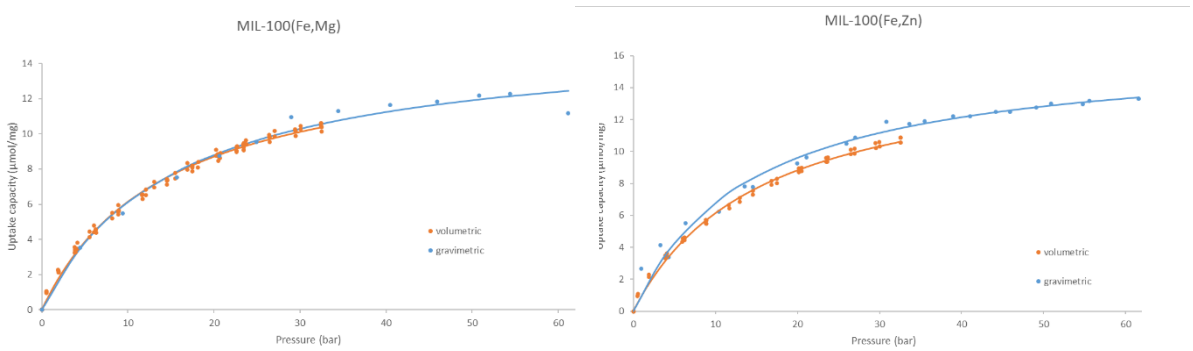

Figure 13 : CO_2 adsorption isotherms of MIL-100(Fe,Mg) (left) and MIL-100(Fe,Zn) (right).

Unfortunately, the TGA analysis does not give any hint on why the different of activation temperature does not have a noticeable effect here. If anything, it rather says the opposite of what we observe: MIL-100(Fe) has the steepest weight drop at low temperatures, meaning it should be the easiest one to activate, hence the one showing the least difference in adsorption between the 2 activation temperatures.

From the BET analysis, we see that Mg and Zn are the 2 samples showing a small hysteresis loop. If this means that they have on average bigger pores, the facilitated diffusion could begin to explain why the activation is more efficient at only 100°C than for the other samples. However, aside from these theoretical speculations, we will review in the next chapter the possible practical causes that could have given rise to this kind of bias, as well as the lack of precision in the Mg analysis.

The last 2 sample analyses both show more important flaws, as is shown on Fig. 14.

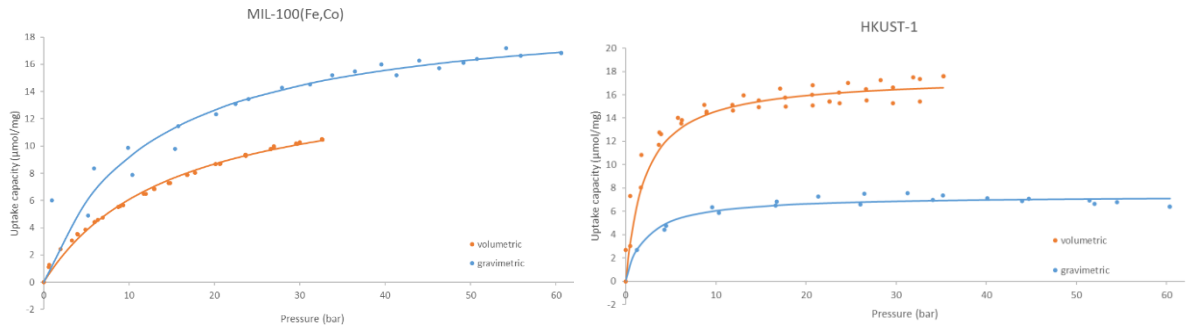

Figure 14 : CO_2 adsorption isotherms of MIL-100(Fe,Co) (left) and HKUST-1 (right).

In the case of HKUST-1, the failure of the WGT method is easily explained. As this MOF has a far better affinity for water than the MIL-100 series [40], the activation at 100°C was not at all effective enough. The water remaining in the pores thus prevented the adsorption of CO_2. Another noticeable flaw is the spreading of the data points at the higher pressure in the volumetric curve. This was caused by the quantity of sample in the analyzer being smaller than it had been for the other samples (46mg vs 100-150mg), giving away the increase of experimental error with increasing pressure, associated with this method of analysis.

The case of MIL-100(Fe,Co) is less trivial. One way to explain such an inferiority of the results of the volumetric analysis would be by a significant degradation of the porous structure at the higher temperature of 200°C. But this hypothesis is not coherent with the fact that its TGA and BET graphs do not differ much from those of the other MIL-100. Moreover, comparing the values of the adsorption, the volumetric curve is closer to the comparable

samples than the gravimetric one. We must then admit that the WGT method has overestimated by far the adsorption in this case. However, one interesting feature shown by the curve is the spreading of the data points at the lower pressures. As in the previous case, we lacked sample to match the quantity that was analyzed of the other samples (here 68mg vs 100-150mg). But with this method, the increase of experimental error is confined to the lower pressures rather than the higher. This could also explain the overestimation of the adsorption: other sources of error, such as the uncertainty of the tank volume or the temperature, could have been spread more widely to the result because of the smaller quantity of sample.

Discussion

In all the graphs presented before, the isotherms determined by the WGT method only include the points from the first determination of the isotherm out of 2. The values of the second measured isotherm were significantly lower than the first one for all samples. The graphs showing the differences are available in Appendices 2 to 7. We attribute 3 possible causes to this tendency, which all suggest that the first isotherm would be the most reliable one.

1) After the first isotherm determination by the WGT method, on MIL-100(Fe,Ni), while unloading the tank, we noticed that some sample had been blown out of the tank during its degassing (some sample was stuck in the quartz wool up to the top). Outflow of the sample between the first and second isotherm determination explains the lowered values for the adsorption. We then increased the quantity of quartz wool in the following experiments, to try and stop this outflow, and the presence of sample at the exit of the tank was not noticed again.
2) The second hypothesis is that the porous structure would be damaged after its first passage under 60 bar. This would explain why the problem did not occur with the volumetric method, which only went up to about 32 bar.
3) Finally, the same hypothesis as for the calibration still holds, with static charges building up in the material and in the tube by the flow of CO_2, and influencing the result on the balance.

- **Relative weight uptake under CO_2 flow at atmospheric pressure**

The results of the gravimetric analysis done by the TGA analyzer under a periodic flow of CO_2 followed the pattern shown on Fig. 15 for all the MIL-100 samples. The HKUST sample didn't reach equilibrium so we will not take it into account.

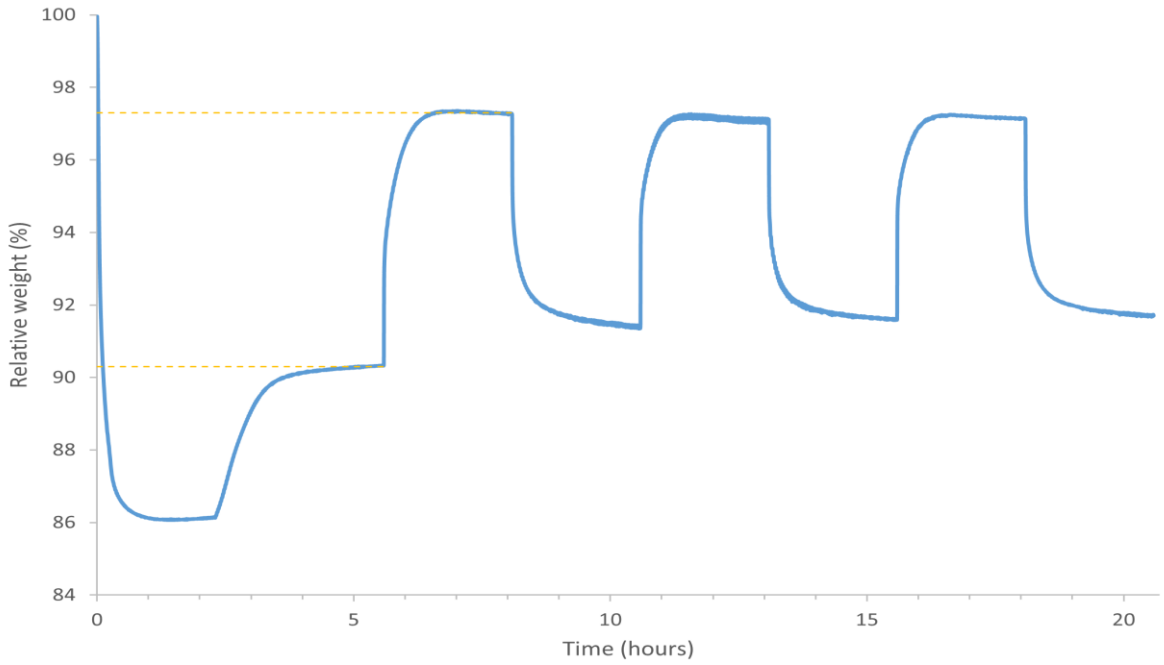

Figure 15 : Pattern followed by the results of the "TGA CO_2" experiment (here : MIL-100(Fe)).

The initial drop of weight corresponds to the activation of the sample at 200°C. After equilibration back to 25°C, the weight follows a periodic pattern corresponding to cycles of adsorption and desorption of CO_2. By taking the difference between the equilibrated adsorbed and desorbed states (and converting its units), we can compare that uptake with the interpolation at 1 atm of the volumetric isotherms previously determined. If both methods are correct, the results should match. The comparison is plotted in Fig. 16. (NB: the point for HKUST-1 has been excluded because the adsorption did not reach equilibrium in the TGA analysis)

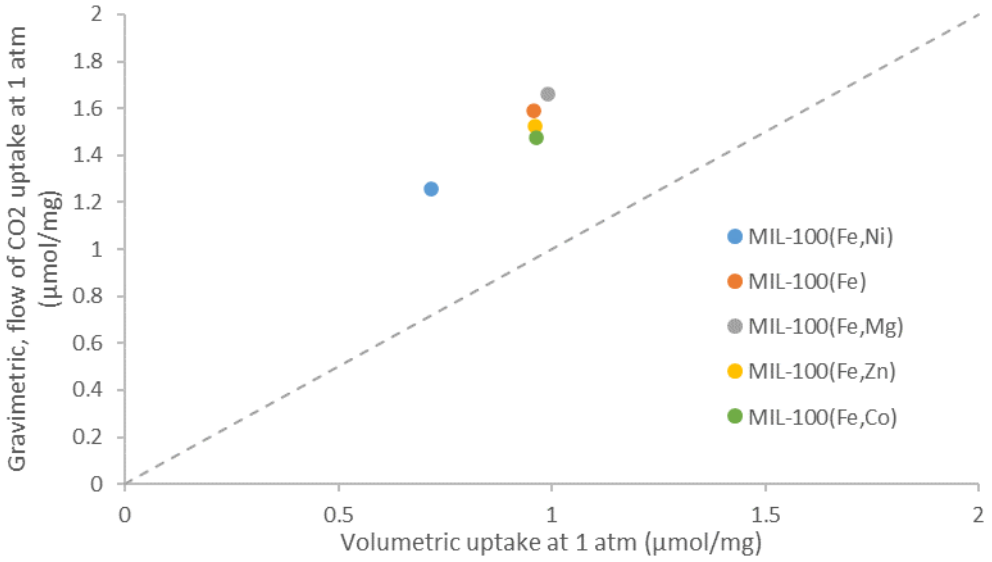

Figure 16 : Comparison of the CO_2 uptake at 1 atm by the TGA analyzer vs. the reference volumetric analysis. Dashed line corresponds to the hypothetical ideal match of the results for the two techniques.

Unfortunately, the enterprise was quite inconclusive. The uptake of weight recorded by the TGA analyzer under a flow of CO_2 is well above the reference value from the volumetrically determined isotherm, for all samples.

- **Relation between surface area, pore volume and uptake capacity**

With adsorption happening on the surfaces and in the pores of materials, it would make sense for it to follow some proportionality between either the surface area or the pore volume, and the uptake capacity, especially among highly analogous materials such as the MIL-100 series that we used. Here we tried to highlight this relation, plotting the uptake of CO_2 at 30 bar (from the volumetric method), versus the BET surface area and the total pore volume (from single point determination at P/P°=0.975, and pore diameter less than 747.6 Å), on Fig. 17.

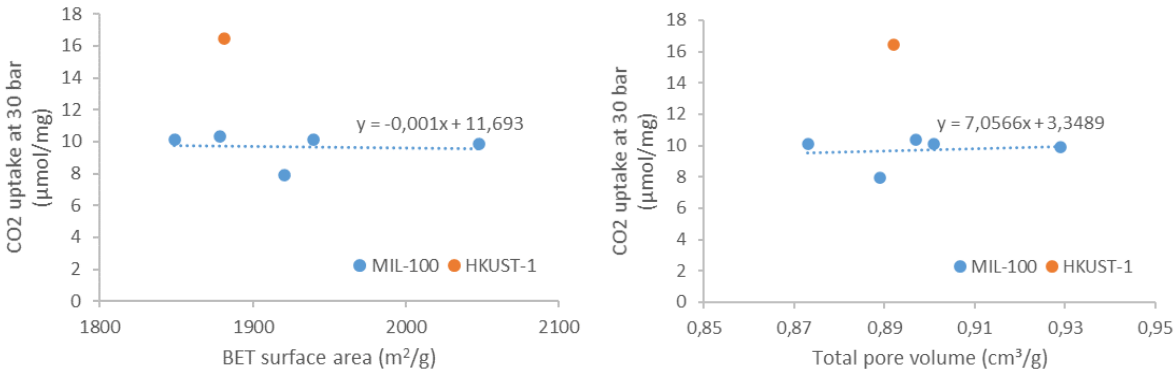

Figure 17 : CO_2 uptake at 30 bar vs. sample BET surface area and total pore volume.

Even though the proposed slope for the total pore volume makes sense by being positive, as opposed to the slope for surface area, which matches our hypothesis from the BET graphs that adsorption would be mainly micro- and meso-porous and thus follow the trend of the pore volume instead of surface area; unfortunately, the data points for the MIL-100 series are not spread on a wide enough range to seriously infer any proportionality. On the other hand, the MIL-100's uptakes are closer together than with HKUST-1's one, which highlights the importance of the influence of the microstructure, and of the density of "open-metal sites", higher in HKUST-1.

- **TSD and Gain**

As explained earlier, the GT method was developed to propose and easier and more accurate method to quantify the gas storage capacity of materials. In both the GT and WGT method, the measuring setup is in the same state as a practical gas storage unit would be: it is composed of a tank, filled with adsorbent and under pressure. This similarity allows the use of new parameters to describe the materials, simpler but only useful in the context of gas storage applications: the TSD and the Gain. [26]

The TSD is defined as the total mass of gas (adsorbed and in the gas phase) per unit volume, and the Gain is, in percent, the improvement of the TSD provided by the material, compared to an empty tank. A precision must be added for the TSD, as it can refer to the whole tank (TSD_{tank}) or to the material itself (TSD_{mat}). The TSD_{tank} is the simplest quantity to calculate ($\frac{measured\ mass}{tank\ volume}$), but only describes the gas storage capacity of the material in that one tank, and is therefore not scalable or applicable practically. The TSD_{mat} addresses this by subtracting from the volume and the measured mass, the dead volume and the mass of the associated gas phase. Only the volume taken up by the material remains, making this parameter scalable to any storage tank. That volume is calculated by division of the mass of sample by its bulk density.

Unfortunately, as we lack the values for the bulk density, we can only relate the non-scalable data associated with the tank. However, it is important to note that for a well filled tank, the dead space is very small and therefore the TSD_{mat} and $_{tank}$ are nearly equal.

Table 2 : WGT results at 60 bar in terms of TSD_{tank} and $Gain_{tank}$

	TSD_{tank} (mg/cm³)	$Gain_{tank}$ (%)
MIL-100(Fe,Ni)	222.4	22.0
MIL-100(Fe)	219.2	20.3
MIL-100(Fe,Mg)	222.0	21.8
MIL-100(Fe,Zn)	238.7	30.9
MIL-100(Fe,Co)	213.3	17.1
HKUST-1	208.3	14.3

Perspectives

Sources of error

The results of the WGT method that we reported present non negligeable differences with those of the reference method, which itself, along with any experimental measurement, carries a certain load of errors. In this section, we will discuss a list of experimental factors that influence the outcome of the measurement, while putting them into perspective with the other related methods and seeking solutions to diminish their importance.

The theory behind the WGT method was practically implemented in this thesis at a very early stage in its development. To render this contrast, we classify the sources of errors in 2 groups. What we call *theoretical errors* are linked with the theoretical model on which the method is based. It comprises physical parameters needed for calculations and the degree of precision that can be achieved for them, which rely on the quality of the analytical equipment. On the other hand, *practical errors* are linked with the imperfection of the setup (which was built from spare parts), and could be greatly avoided by proper manufacture of the setup.

- **Theoretical errors**

- *Accuracy of measurements : weight, pressure and temperature*

It is the most fundamental source of error relevant here. A hypothetic perfectly idealized version of the WGT method would only ever be as accurate as the measurement tools it comprises for these 3 parameters. It can be noted that the weight measurement has 2 roles: the quantity of gas entering the tank during the adsorption, and also the quantity of material put into the tank beforehand.

In the present case, even though we already argued that the quality of our probes and balance was far from the best available today, this source of error is quite anecdotic in our results, as its influence remained well below that of other sources.

The particularity of this source is that, providing good calibration, its error should be randomly spread across the mean, and its influence is then easily calculable.

- *Accuracy of variables : wool density, material density, gas compressibility*

The same comment holds for variables that are to be measured in independent experiments. While the compressibility is easily accessible for most gases, and the wool density should be provided by the manufacturer, the material density can be a more complicated question. The WGT method does not include a procedure for the determination of either kind of density (bulk or skeletal). Although it is technically possible, analogously to what is done in the volumetric method, to measure the tank's weight increase upon addition of helium and deduce the sample's skeletal density based on the assumption of no helium adsorption; doing so would not resolve the controversies around this parameter. The result would always be of poorer quality than what could be achieved with the volumetric method, considering that the WGT method's experimental error decreases with increasing pressure, while the problem of helium sorption increases. About the bulk density, the question of the packing arises, which can depend on the sample's particle size, and on the way of filling the tank, with eventual compression. This issue also holds for the GT method. One way to address it would be to systematically mention the bulk density when presenting results in terms of TSD or Gain.

- *Elasticity of the tube*

It seems at first counter-intuitive to weigh on a balance anything that is not physically disconnected from the outside of the balance. The weight of the tube itself is irrelevant since, providing no movement of the whole system, the part of it weighing on the balance is constant. However, the tube has other actions. By seeing it as an object fixed to the tank and lying on the same "ground" as the balance, we understand that the force of gravity pushing the tank downwards, which should be entirely compensated by the balance to be precisely measured, would be partly compensated by the reaction of this object. This reaction is modulated by the elasticity of the tube.

Another related problem is the curvature of the tube under its own weight. As the tube must be long and flexible enough to avoid the precedent issue, its curvature cannot be ignored. The consequence of an overpressure of gas inside a curved tube is a force pushing to straighten the tube, influencing, in this case, the weight on the balance.

This system could probably be modelled and put into equations, but this is outside the scope of this work. We addressed the problem by choosing a long, thin and flexible tube, and maintaining it as straight as possible by tension between its two ends. It is difficult to give an estimation of the extent of these influences, or even of their significance. However, what can be noted is that if they have significance, it must increase along with the pressure. This motivates further the need to model and calculate these phenomena, as increasing precision at higher pressures should be one of the main assets of the WGT method.

- *Equilibration time*

This point is analogous to any method of adsorption analysis. After setting the system under the desired pressure, it must be given enough time to reach equilibrium before recording the outcome, and diffusion through porous materials can be a very slow process. There are two possible ways to determine the equilibrium point in our system. First, by setting the pressure close to the target pressure, then closing the inflow of gas and monitoring when the pressure finally stabilizes. The other way is to keep the inflow open and blocked at the target pressure, and monitoring when the weight stabilizes. This has the advantage of yielding the data points exactly at the target pressures. However, in our experiment, because of the smaller precision of the balance than the pressure probe and the lack of automated pressure transducer, we performed in the first way.

In any case, and whether the detection of the equilibrium is performed by a software or manually by the operator, it actually comes down to detecting when the change in the chosen parameter (pressure or weight) falls below a certain increment per increment of time. While this is already not so trivial (considering the low precision of the balance and the important noise at the millibar scale from the pressure probe), it must also be verified independently that the chosen increments are adequate to consider that the equilibrium is reached, i.e. that there is no ongoing slow process which could still significantly change the outcome over time.

- *Tank volume determination*

The tank volume is a parameter in the calculation of the results of the adsorption, whether they are given in terms of excess surface sorption, or in terms of TSD_{mat} and $Gain_{mat}$. Its (im)precision is therefore spread to precision of the result. However, since the procedure for its determination is analogous to the procedure for the adsorption measurements, its precision is restricted by the same phenomena. This means that, in the case where every other source of error would be resolved, this one would be resolved by itself to the same extent. Apart from that ideal case, as we have seen previously, the volume should be determined at high pressure to enhance the relative precision of the weight measurement.

Similarly, another way to improve the tank volume precision independently from other parameters, would be to perform the calibration with other gases than the adsorbate, i.e. heavier gases.

- **Practical errors**

- *Instability of the setup (+ hardness of the valves)*

Every movement of the valve board relative to the balance has a consequence on the repartition of the tube's weight between those 2 parts. At the milligram scale, this had a huge influence relative to the adsorption's gravimetric response. It has been a real challenge for the operator to manipulate the valves without making the whole valve board move, as it was simply lying on the table and the valves were quite hard. Considering the stepwise procedure of the isotherm determination, any movement has an influence not only on the next data point, but on all downstream points. Of course, every time a significant movement was noted, the procedure was started over. However, this was probably still the main source of error of our experiments, with the slightest slips remaining unnoticed while still having a significant impact on the outcome.

Fortunately, this issue is quite easy to solve. The valve board needs to be fixed firmly onto a stable structure with the balance. Another additional precaution would be to fix a receptacle onto the balance's plate, where the tank could fit perfectly. This would prevent the tank from moving on the plate by accidentally touching the tube.

- *Equilibration of temperature*

Relative to the other methods of adsorption analysis, the lack of a thermostatic chamber is an undeniable flaw, and it is an essential addition if one considers to build a WGT setup to match or surpass the precision of the other methods. In the GT method [26], the tank was thermostated during its pressurizing, then closed. The weight measurement could thus be done outside of the thermostat, as the gas quantity inside the tank was fixed. In our method, only the tank and the balance need to be thermostated during the procedure, and the gas must have time to equilibrate in temperature at each step.

Instead of a thermostat, we had a thermometer in our setup, which allowed to take the temperature into consideration in our equations. However, its position was not ideal (see Fig. 4, scheme of the setup). Because of its distance to the sample, it could only record the temperature of the gas at the board, where small fluctuations happened due to gas relaxation and skin contact with the valves. Another consequence of its bad location is that it didn't allow to determine when the sample had cooled back to room temperature after its activation, so that the experiment could begin.

- *Outflow of sample*

As explained earlier, samples under the form of a fine powder can be carried out from the tank by the important gas flow when decreasing the pressure. This eventual source of error is shared by the other methods of adsorption analysis and is simply avoided by putting quartz wool, or any kind of non-adsorbing filter of known density at the exit of the tube. Note that the volume of this filter must be taken into account in the calculation of the volume of the gas phase. Failure of the filter will be noticed by the presence of powder at the exit when opening the tank.

On top of causing an error in the measurement, outflow of sample could cause clogging of the tube or, in more advanced machines, contamination of inaccessible zones, it must then be paid good attention to.

- *Plastic tube maximum allowable temperature*

As with the other methods of adsorption analysis, the activation must be carried out in situ to avoid atmospheric contamination of the sample during its transfer into the tank. In

our method, this poses a problem due to the high temperatures needed and the proximity to the plastic tube. As we have seen, activation at a lower temperature than needed causes an important underestimation of the adsorption, since pores are still filled with synthesis solvents or atmospheric water. The challenge here is to find a material for the tube, that would remain flexible while being resistant enough for the high pressures and able to hold under the high temperatures needed for the activation, which depend on the material.

- *Leaks*

As with all gas handling systems, attention must be paid to leaks. This is simply mentioned here in an attempt to exhaustivity, but our experiments have normally not been impacted by this possible source of error. Checking for leaks is a simple procedure of putting the whole setup under high pressure and monitoring that the pressure stays constant.

- *Static charge build-up*

This source of error was proposed here as a probable cause to the descending tendency of the results between the weight measurements, that should have been constant during the calibration or at least randomly spread, and between successive measurements of the same isotherm.

Further research is needed to verify or invalidate this as the real source of the problem. If it is verified and located mainly in the plastic tube of the setup (a scenario that is coherent with our experiment since the effect was mainly noticeable during the calibration, i.e. with no sample), the problem could be addressed rather simply by replacing the tube by a conductive material. On the other hand, if this phenomenon occurs significantly also inside the porous material, this source of error would be better placed in the category of *theoretical errors* as it would be unavoidable and could only be diminished by a slower gas flow when adjusting the pressure. Another solution could be an adapted design of the balance, without influence of the charge on the result.

- *Collapse of the porous structure under too high pressure*

Another hypothesis explaining the lower results for second isotherms, which could be verified by X-ray re-analysis of the samples' crystallinity after the experiments, but this is outside the scope of this work. This is a sample-related problem, independent from the

concept of adsorption. It is however of great importance in the context of “gas storage capacity” research. Therefore, the maximum allowable pressure or gas flow inside a porous material should be determined independently by a dedicated method of analysis.

About the modus operandi

During the isotherm measurements as well as during the calibration, we used stepwise increases and decreases in pressure, which is similar to the functioning of the volumetric and gravimetric methods. However, considering that a great part of the errors we encountered would come from the manipulation of the system, this mean of operation may have unnecessarily propagated these errors. We argued that one of the main points of our method was its increasing precision with increasing pressures, but this is not true if the errors coming from the first manipulations at low pressure, which would have given the worst results anyway, end up accumulating and “spoiling” the precision that could have been achieved at higher pressure.

This issue could be solved by re-equilibrating the sample under 0 bar and taring the balance between each step of the isotherm. However, doing so would significantly increase the time needed for an experiment, probably making it comparable to what would be achieved through single point determinations such as performed with the GT method.

Another procedure, mentioned in [20], would be suitable with the WGT method. The *continuous mode* consists of doing the experiment with a continuous flow of gas rather than stepwise admittance. With a constant and slow enough flow rate, the system can be considered under quasi-equilibrium, and the evolution of weight and pressure can be monitored with minimum manipulations. However, to operate in this way, it is needed to know enough about the kinetics of the system to be able to compensate for the quasi-equilibrium, or assess its non-significance.

Improvement of the equipment

Introducing the motivation for the development of their GT method with a section devoted to the reasons of the controversies in adsorption measurements and irreproducibility of the older methods, Iakunkov et al. [26] state beautifully : “*Since the main principle of the method is rather simple, very often some homemade systems are assembled for sorption measurements without taking into account all important details and error sources*”.

In our own attempt to develop a substitute method, we faced that exact problem: the homemade character of our setup was the cause of its main error sources. Now for our WGT method to ever be able to compete in terms of precision with the well-established methods involving expensive dedicated equipment and software, it must be given the same opportunity. Therefore, a more reliable setup should be implemented. This would include a stable structure for all components, a thermostat, a suitable tube, automated precision probes and valves with a dedicated software, to begin with. Removing the human influence wherever it is possible, is necessary to set the stage for further investigations concerning potentially more fundamental issues, such as the tube's influence or the static charge build-up.

Conclusion

This first implementation of the *Wired Gravimetric Tank* method yielded promising results. Coherent adsorption isotherms were obtained for all tested samples, and most were in good agreement with the isotherms obtained by the volumetric method, used as a reference. The few big deviations from the expected results have had their causes identified, and other sources of error have been listed to explain the remaining internal variability of the results.

This method will not replace the other methods of adsorption analysis, some of which will always have an advantage in precision in the low-pressure range. In the context of research for gas storage application, it could become a good alternative for rapid testing of the materials. It allows the user to calculate the outcome in terms of surface excess amount for comparison with data from the literature, and in terms of TSD and Gain, some very relevant parameters to communicate gas storage capacity. However, for the precision achieved through the other common methods in automated systems to be matched, an important upgrade of the setup is still necessary.

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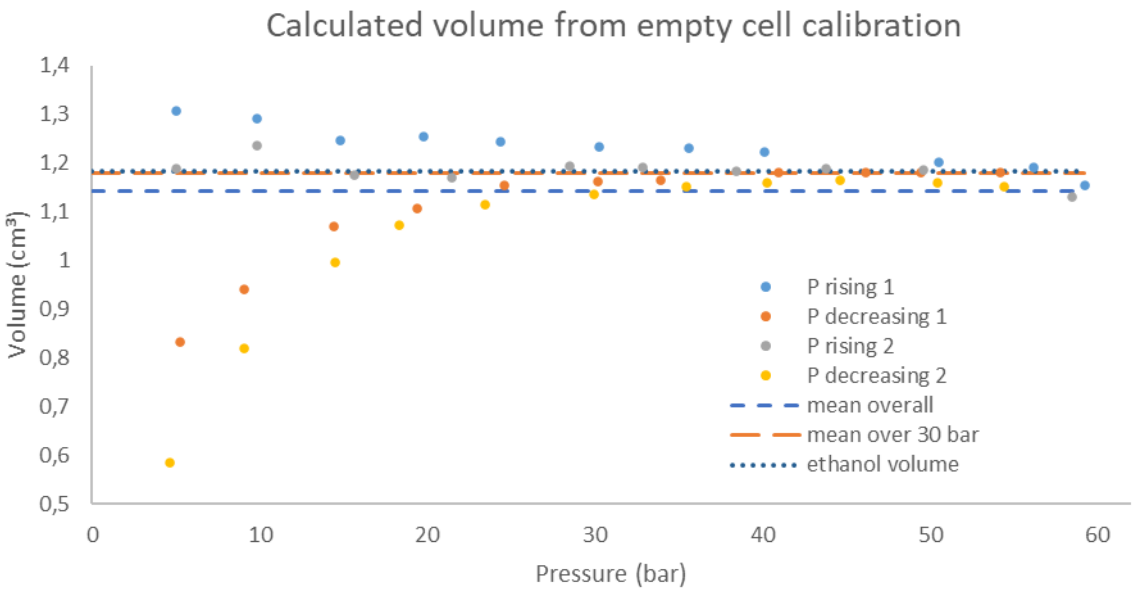
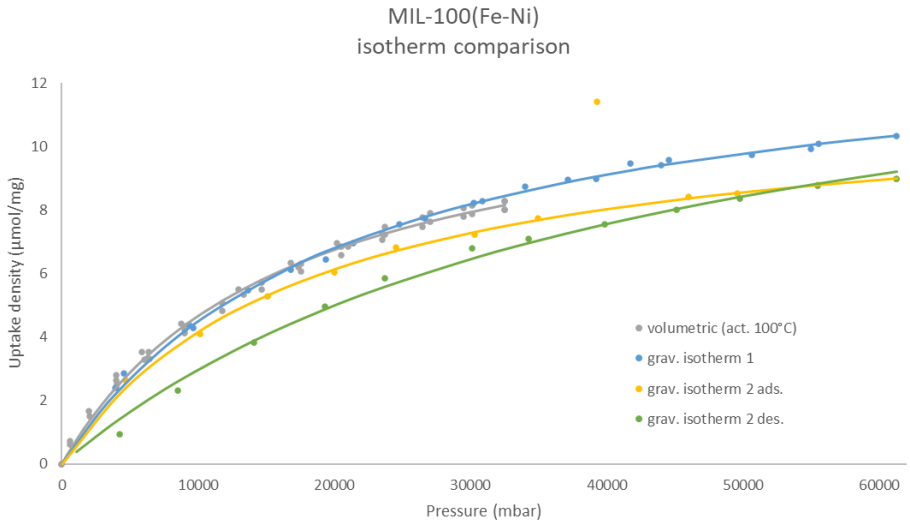
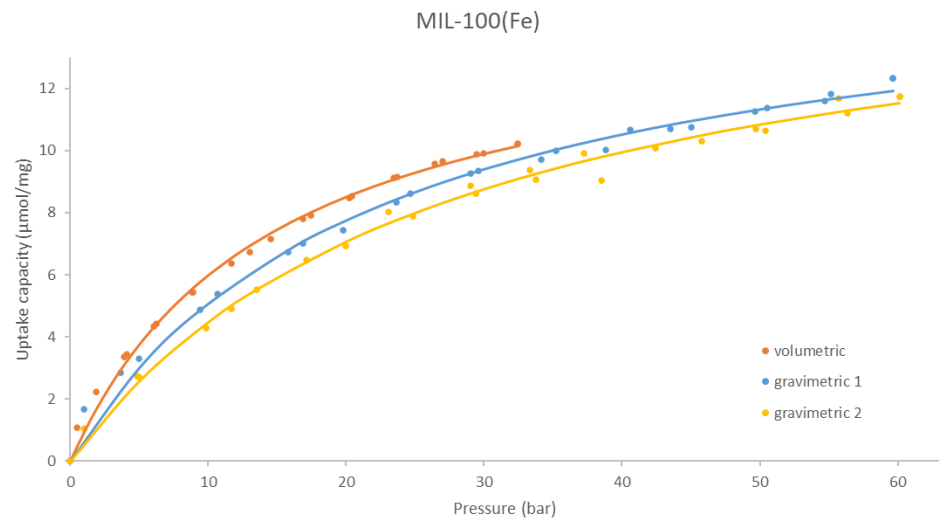
Appendices

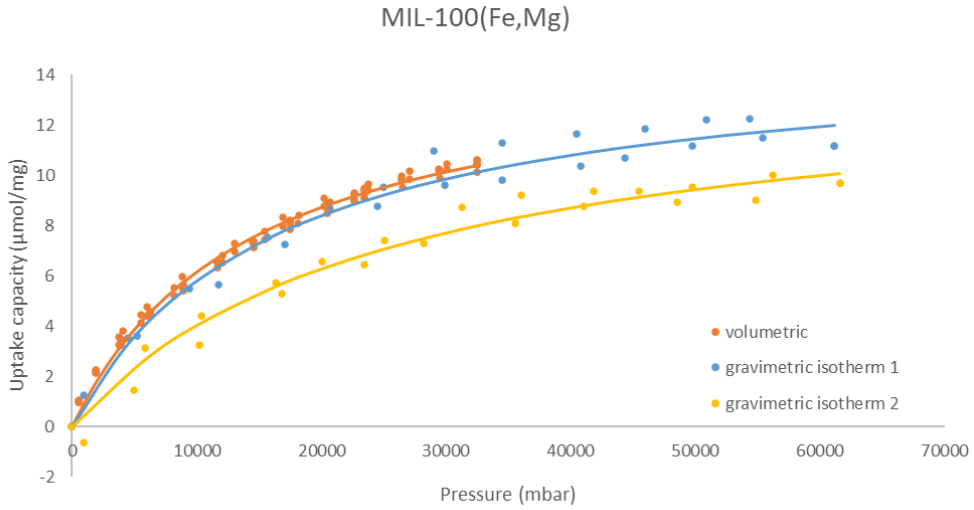
Appendix 1 : Calibration results including excessive errors at low pressure



Appendices 2-7 : adsorption isotherms : gap between first and second measurements




MIL-100(Fe)
Uptake capacity (µmol/mg)
Pressure (bar)
volumetric
gravimetric 1
gravimetric 2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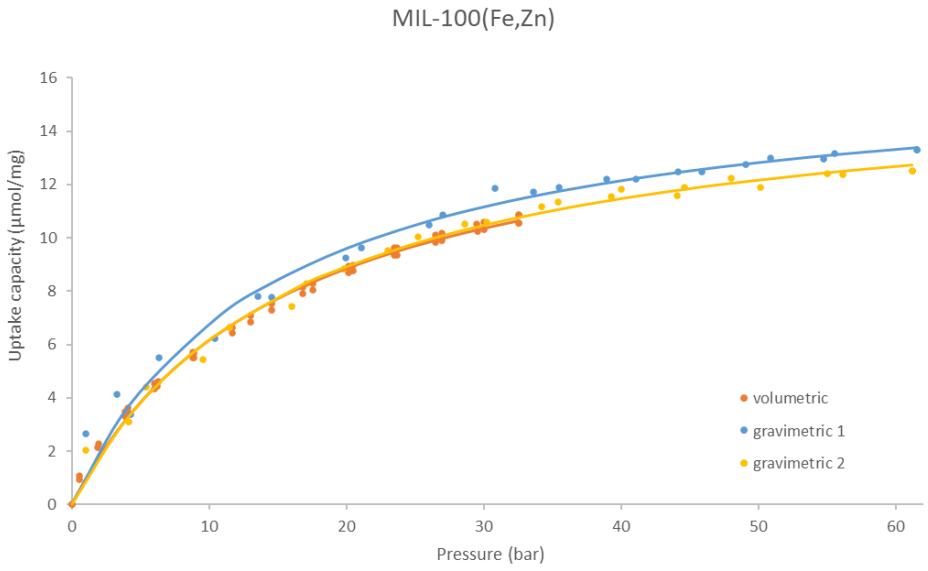
Uptake capacity (µmol/mg)
Pressure (mbar)
volumetric
gravimetric isotherm 1
gravimetric isotherm 2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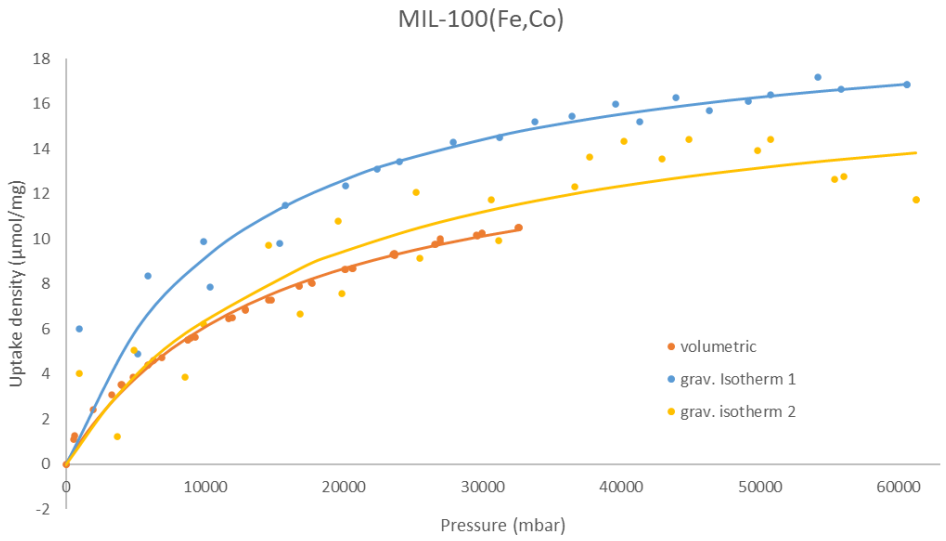
Uptake capacity (µmol/mg)
Pressure (bar)
volumetric
gravimetric 1
gravimetric 2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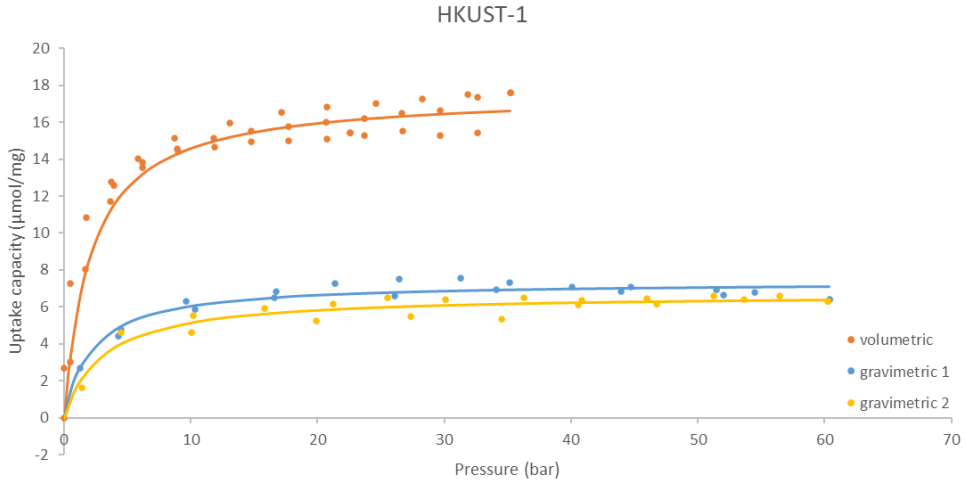
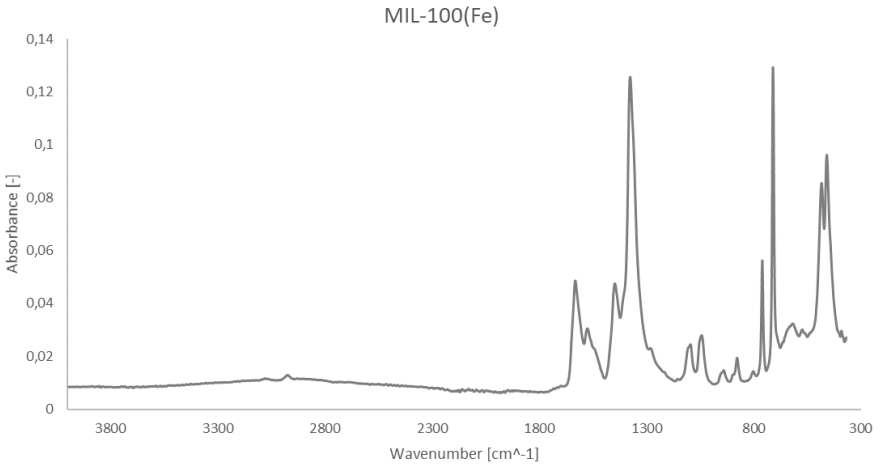
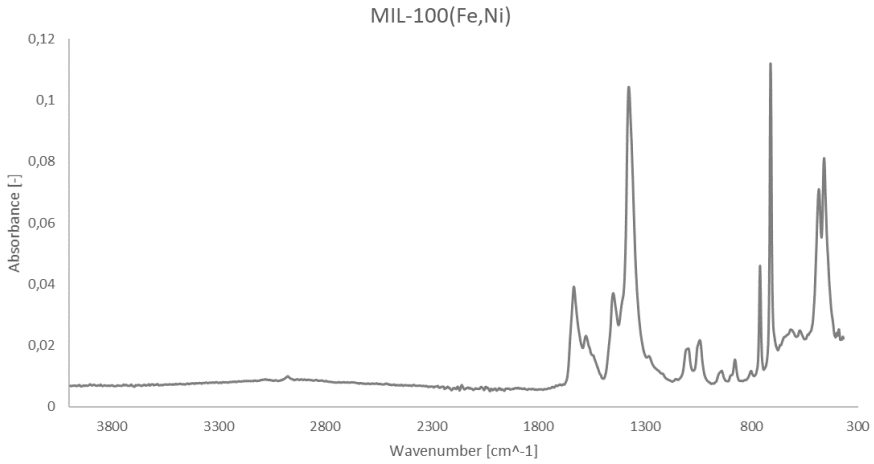
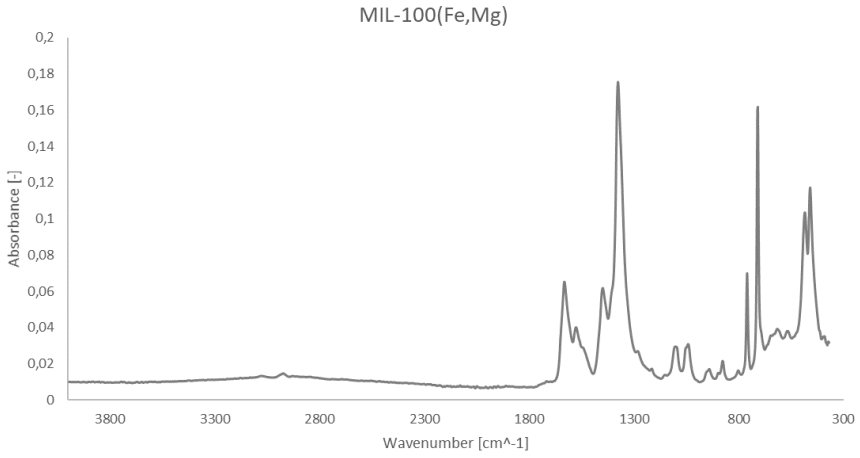
Uptake density (µmol/mg)
Pressure (mbar)
volumetric
grav. Isotherm 1
grav. isotherm 2

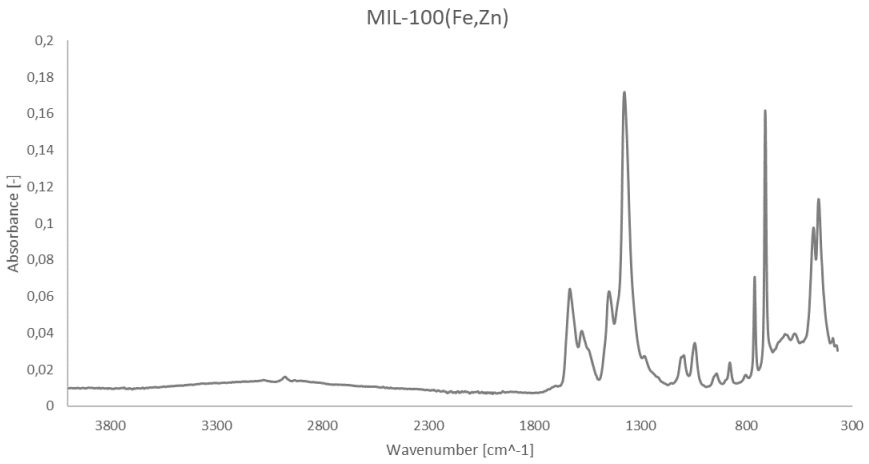

HKUST-1
Uptake capacity (µmol/mg)
Pressure (bar)
volumetric
gravimetric 1
gravimetric 2

Appendix 8 : FTIR data





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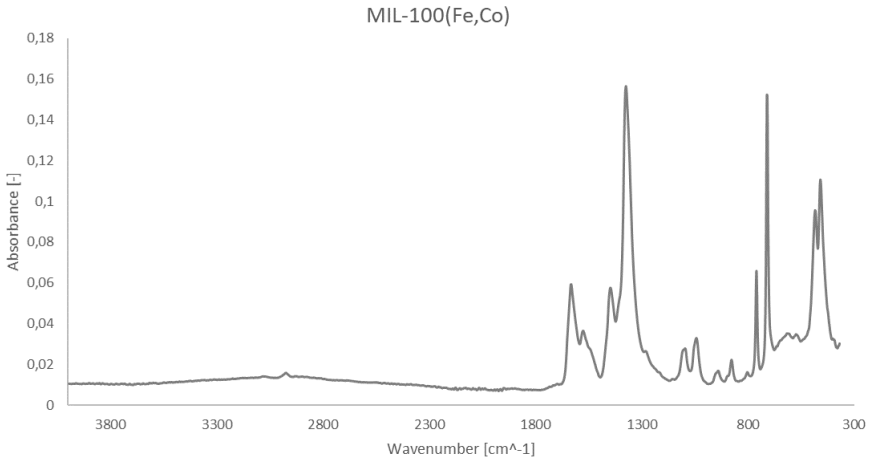
Absorbance [-]
0,2
0,18
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
3800
3300
2800
2300
1800
1300
800
300
Wavenumber [cm^-1]


MIL-100(Fe,Co)
Absorbance [-]
0,18
0,16
0,14
0,12
0,1
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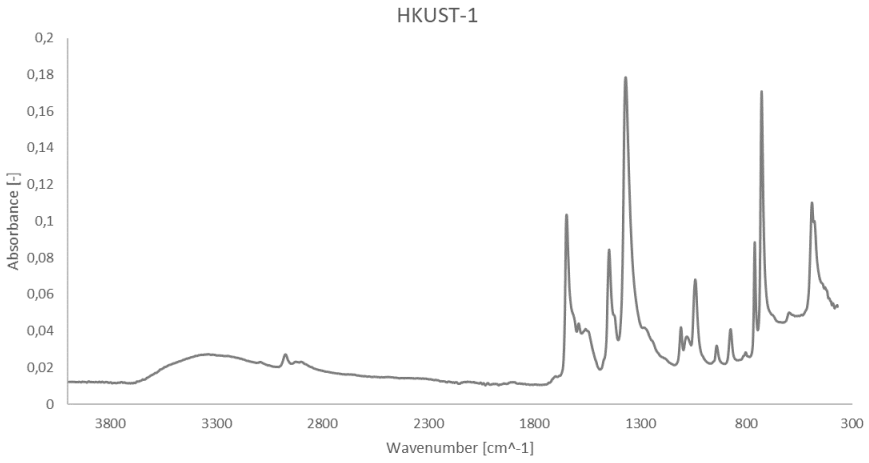
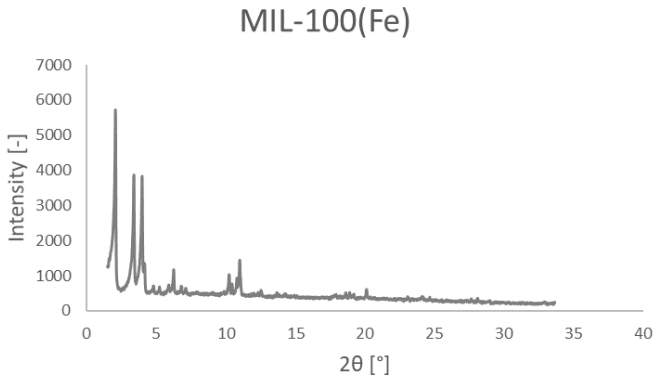
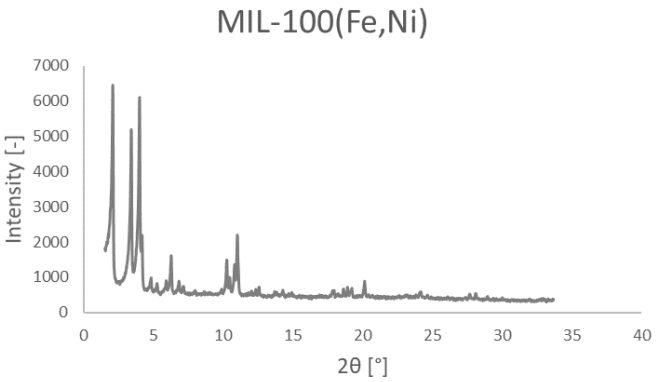
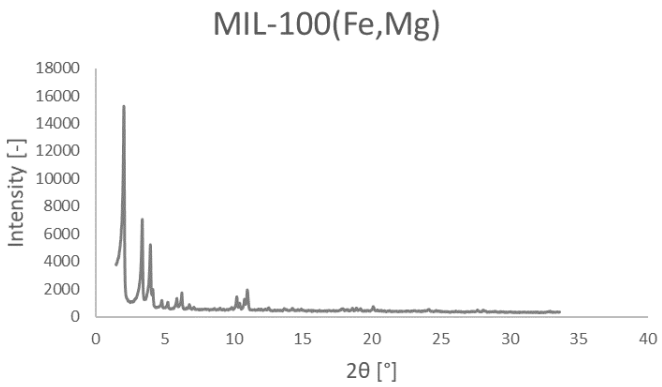
0
3800
3300
2800
2300
1800
1300
800
300
Wavenumber [cm^-1]

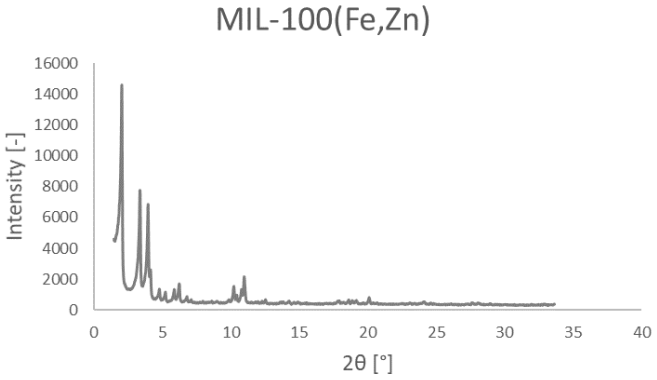

HKUST-1
Absorbance [-]
0,2
0,18
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
3800
3300
2800
2300
1800
1300
800
300
Wavenumber [cm^-1]

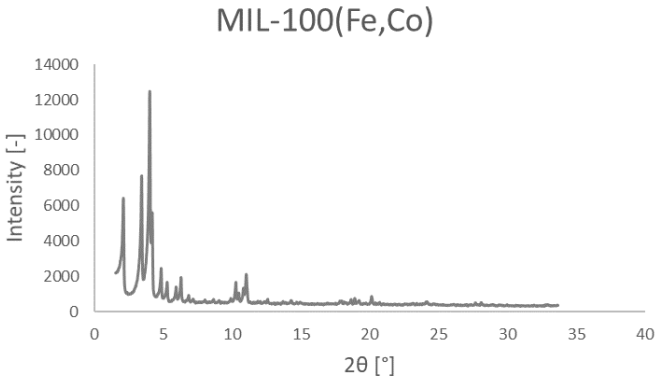
Appendix 9 : PXRD data











The gravimetric tank method to evaluate CO2 adsorption in MOFs

Julien Delderenne

Adsorption is at the heart of a lot of research in today's background of environmental challenges, as it can be applied for gas storage and separations. However, it is not a trivial phenomenon, and the methods and models to evaluate it are complicated, often prone to errors and controversies, and extremely time-consuming. In 2018, Iakunkov et al. proposed a new method : the gravimetric tank method. It uses a model based on simpler variables, focusing more on the practical aspect of gas storage, as opposed to the precise material characterization. In this thesis, we push their idea further by setting up a modified version of their method, which allows for a continuous monitoring of the adsorption through the filling and emptying of the test tank, while reducing greatly the time needed for a measurement, restoring the possibility to make full adsorption isotherms in a reasonable time. The method was tested by applying it to CO_2 adsorption on MOFs and comparing the results with a reference volumetric method, and the MOFs were characterized through BET, TGA, and other analyses to try and explain the observations more deeply. Encouraging results were obtained, even though their precision does not allow the method, at this stage of development, to be used on its own. Many sources of error were identified, as well as the next steps to be taken in the development of the method to make it competitive and complementary with the other ones available.

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