(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
**26 December 2024 (26.12.2024)**

(10) **International Publication Number**
**WO 2024/260727 A1**

(51) **International Patent Classification:**
*G01N 15/04* (2006.01)

(21) **International Application Number:**
PCT/EP2024/065432

(22) **International Filing Date:**
05 June 2024 (05.06.2024)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
23382643.7 23 June 2023 (23.06.2023) EP

(71) **Applicants: UNIVERSIDAD DEL PAIS VASCO EUSKAL HERRIKO UNIBERTSITATEA** [ES/ES]; Barrio Sarriena, S/N, 48940 Leioa (ES). **UNIVERSIDAD DE CANTABRIA** [ES/ES]; Pabellón de Gobierno, Avenida de los Castros S/N, 39005 SANTANDER, CANTABRIA (ES).

(72) **Inventors: PÉREZ AGUIRRE, Rubén**; Barrio Sarriena, S/N, 48940 Leioa, BIZKAIA (ES). **CASTILLO GARCÍA, Oscar**; Barrio Sarriena, S/N, 48940 Leioa, BIZKAIA (ES). **BEOBIDE PACHECO, Garikoitz**; Barrio Sarriena, S/N, 48940 Leioa, BIZKAIA (ES). **DE PEDRO DEL VALLE, Manuel**; Pabellón de Gobierno, Avenida de los Castros S/N, 39005 SANTANDER, CANTABRIA (ES). **FERNÁNDEZ BARQUÍN, Luis**; Pabellón de Gobierno, Avenida de los Castros S/N, 39005 SANTANDER, CANTABRIA (ES). **RODRÍGUEZ FERNÁNDEZ, Jesús María**; Pabellón de Gobierno, Avenida de los Castros S/N, 39005 SANTANDER, CANTABRIA (ES).

(74) **Agent: BALDER IP LAW, S.L.**; Paseo de la Castellana 93, 5ª planta, 28046 Madrid (ES).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**
— *with international search report (Art. 21(3))*

# (54) Title: METHOD AND APPARATUS FOR MEASURING THE CAPACITY OF ADSORBENT MATERIALS TO ABSORB SUBSTANCES DISSOLVED IN A LIQUID MEDIUM

(57) **Abstract:** The invention relates to a method and a device for measuring the adsorption of adsorbent materials of chemical substances dissolved in a liquid medium. The method comprises a container containing a liquid medium with magnetically particles of an adsorbent material, and a substance dissolved in the liquid medium, and placing the container in proximity to at least one permanent magnet. The separation distance between the permanent magnet and the container is increased, until the magnetic attraction of the permanent magnet no longer holds the magnetically active particles. The method comprises measuring the separation distance between the permanent magnet and the container at which all or a predetermined amount of the magnetically active particles have fallen by gravity to the bottom of the container, and determining, by linear correlation, the mass of substance captured by the magnetically active particles based on the measured separation distance.

# METHOD AND APPARATUS FOR MEASURING THE CAPACITY OF ADSORBENT MATERIALS TO ABSORB SUBSTANCES DISSOLVED IN A LIQUID MEDIUM

## DESCRIPTION

## TECHNICAL FIELD

The invention can be framed in the area of chemistry and in the technical field dedicated to the development of scientific instrumentation.

The invention relates to a method and a device for measuring the capacity of adsorbent materials to absorb chemical substances dissolved in a liquid medium.

One of the objects of the invention is to provide a method and a device for the measurement of adsorption in adsorbent materials of chemical substances dissolved in a liquid medium, which is based on the direct measurement of a parameter for the determination of the amount of adsorbed mass. This does not require prior characterization of the variation of a magnetic field. The device is capable of operating autonomously (i.e., without the need to be provided with a power supply and a cooling circuit) for its application in the determination of adsorption in adsorbent solids.

## STATE OF THE ART

Adsorption is widely used for different purposes due to the advantages it offers, such as low-cost and high efficiency. For decades, a lot of effort has been concentrated on finding suitable adsorbents, but a few works have focused on developing suitable direct characterization techniques for adsorption processes in solution that do not rely on specific physicochemical properties of the adsorbate. The greatest advantages of adsorption in the removal and purification of chemicals are the low-cost, high efficiency and ease of operation comparing to conventional methods such as chemical precipitation, ion exchange, liquid extraction or filtration and the considerable variety of adsorbents available. For this reason, adsorption is a widely used process in different industrial and environmental protection applications such as catalysis, storage and purification of water and air. Therefore, adsorption capacity, kinetics and enthalpy are widely studied in order to analyze and evaluate the performance of the adsorbents.

Nowadays, the quantification of the adsorption of chemical species dissolved in a liquid medium is mostly carried out indirectly, using instruments that determine the variation of the concentration of the chemical species of interest in the solution, and not in the adsorbent support. These instruments include a wide variety of common analytical equipment that are chosen according to the problem to be analyzed, and are also capable of continuous or semi-continuous liquid phase analysis. Examples include HPLC-UV, GC-MS, GC-FID, ICP-AES, NMR, etc.

Although it is possible to extract the content of the adsorbent solid a posteriori, by extracting and analyzing the species of interest, there is no known universal technique that allows the adsorption process to be monitored directly on the solid.

Some studies analyze the adsorption of chemical species (drugs, alcohols...) on an adsorbent using the magnetic lift provided by an electromagnet. In this procedure, the variation of the current that feeds the electromagnet makes it possible to vary the magnetic field that supports the adsorbent solid contained in a liquid medium (water or other solvent). This allows to observe the critical magnetic field in which the solid detaches and falls down. The value of the critical magnetic field depends on the adsorbed mass and, therefore, the adsorption of the chemical species of interest can be determined from its value.

It should be noted that this technique determines the ratio of mass of the adsorbed compound with respect to the mass of the adsorbent material. This enables the measurement of the adsorbate in-situ without carrying out any manipulation of either the adsorbent material or the solution with which it is in contact, unlike other analytical techniques. It should also be stressed that it is a non-destructive technique.

The work described to date requires the use of an electromagnet, a relatively expensive element (20-30k €) which, in addition to an electrical power supply, requires a cooling system to prevent the coils from overheating. Moreover, a prior characterization of the electromagnet is necessary to determine how the magnetic field varies according to the current applied to the coils of the electromagnet.

On another note, in the vast world of porous materials used as adsorbent, an interesting class with intrinsic properties that can be directly correlated with the amount of captured adsorbate are paramagnetic Metal Organic Frameworks (MOFs). MOFs are a class of three-dimensional (3D) porous crystalline materials built from organic linkers (organic building units, OBUs) and metal centers or clusters (inorganic building units, IBUs) that are connected through strong coordination bonds. Their most outstanding properties include high and permanent porosity, large surface areas (surpassing that of the other adsorbents), structural and functional tenability, high thermal stability, tailorable pores and cavities, and high adsorption affinity.

MOFs offer the possibility to design and synthesize a targeted material with atomic precision. Thus, such materials have become very attractive, as their properties can be easily designed and tuned. Although many MOFs contain paramagnetic centers, there are very few characterization techniques that seize the advantage of their magnetic behavior to monitor the different physical/chemical parameters.

## DESCRIPTION OF THE INVENTION

The present invention provides a method and a device based on a maintenance-free permanent magnet capable of operating autonomously (i.e., without the need to be provided with a power supply and cooling circuit) for its application in the determination of adsorption on adsorbent solids. The scientific grounds are based on a linear correlation between a physical parameter, directly measurable, for example the separation distance between a permanent magnet and a recipient containing a liquid medium with magnetically active particles, and the amount of adsorbed mass. In other words, it does not require a prior characterization of the field variation, as is the case with an electromagnet.

More specifically, one aspect of the invention relates to a method for measuring the capacity of adsorbent materials to absorb substances dissolved in a liquid medium, wherein the method comprises:

providing a recipient containing a liquid medium with particles of an adsorbent material with positive magnetic susceptibility (magnetically active), and a substance dissolved in the liquid medium,

placing the recipient in proximity to at least one permanent magnet so that the magnetically active particles are retained in the liquid medium by the magnetic attraction of the permanent magnet,

increasing the separation distance between the permanent magnet and the recipient until the magnetic attraction of the permanent magnet no longer holds the magnetically active particles,

measuring the separation distance between the permanent magnet and the recipient at which all or a predetermined amount of the magnetically active particles have fallen by gravity to the bottom of the recipient, and

determining, by a linear correlation, the mass of the captured substance by the magnetically active particles on the basis of the measured separation distance.

Preferably, the adsorbent material is a material endowed with porosity, relatively high surface area and positive magnetic susceptibility.

The step of increasing the separation distance between the permanent magnet and the recipient is preferably carried out by keeping the permanent magnet in a fixed position, and moving the recipient linearly with respect to the permanent magnet in a direction orthogonal to the permanent magnet.

Preferably, the recipient is a test tube which is placed between two permanent magnets facing each other, and in close proximity or in contact with one of the magnets, and in a way that the bottom of the test tube is outside the magnetic field generated by the magnet.

The equation that mediates the attraction between the particles of the magnetically active material and the magnetic field implies: $F_{magnetism} = \nabla(m \cdot H)$, where the gradient $\nabla$ is the change of the quantity $m \cdot H$ per unit distance ($m$ magnetic dipole of the particle and $H$: external magnetic field), and the direction is that of the maximum increase of $m \cdot H$. As the magnetic dipole ($m$) of the particles is oriented in the same direction as $H$, the gradient attracts the particles towards the region of maximum $H$ field.

Since the magnetic dipole of the particles can be expressed as a function of the external magnetic field and the magnetic dipole gradient is negligible if the particles are small (< 1 mm), the magnetic dipole moment can be considered constant over the entire length of the particle and expressed as a function of the magnetic susceptibility of the particle material (Equation 1):

$$F_P = \mu_0 \frac{\chi_M}{MW} \cdot \rho_P \cdot V_P \cdot H \cdot \nabla(H_P) \qquad (1)$$

Where $F_P$ is the magnetic attraction force on the particle, $\mu_0$ the vacuum permeability, $\chi_M$ the molar susceptibility, $MW$ the molecular weight of the adsorbent structure (excluding solvent molecules located in the pores), $\rho_P$ the adsorbent density, $V_P$ the particle volume, $H$ and $\nabla(H_p)$ the magnetic field and the field gradient at the position occupied by the particle.

The magnetic lift experiments described are the result of a balance between the three forces to which the particles of the adsorbent material are subjected: Magnetic attraction, buoyancy (flotation) and gravitational force.

Magnetic force is defined as the force that is exerted on the particle by the magnet and lifts the particle up to the bottom border of the magnet pole (zone of maximum magnetic force) (Equation 2), gravity is the opposite force that pushes down the particles (Equation 3) and the buoyancy of the liquid medium that pushes the particles up (Equation 4). The equations governing each force described above are described below.

$$F_{magnetism} = \nabla(m \cdot H) = m \cdot \nabla H = \frac{\chi_M}{MW_F} \cdot \rho_F \cdot V_F \cdot H \cdot \nabla H \qquad (2)$$

$$F_{gravity} = \mathrm{M} \cdot \mathrm{g} = (\mathrm{M}_F + M_M) \cdot g = (\mathrm{V}_F \cdot \rho_F + V_M \cdot \rho_M) \cdot g \qquad (3)$$

$$F_{flotation} = (\mathrm{V}_F \cdot \rho_S + V_M \cdot \rho_S) \cdot g \qquad (4)$$

In these equations, an arbitrary separation has been made between the mass, volume and density corresponding to the adsorbent material ($M_F, V_F$ and $\rho_F$) and those of the adsorbate ($M_M, V_M$ and $\rho_M$). The other parameters ($\chi_M$) being the molar susceptibility, (*H)* the magnetic field, ($H \cdot \nabla H$) the magnetic field gradient and (*g)* the acceleration of gravity of the Earth.

The value of the critical magnetic field corresponds to the value at the moment when the forces exerted on the particle are equalised (Equation 5):

$$F_{magnetism} = F_{gravity} - F_{flotation} \qquad (5)$$

Replacing Equations (2-4) in Equation (5), Equation (6) is obtained:

$$\frac{\chi_M}{MW_F} \cdot \rho_F \cdot V_F \cdot H \cdot \nabla H = (\mathrm{V}_F \cdot \rho_F + V_M \cdot \rho_M) \cdot g - (\mathrm{V}_F \cdot \rho_S + V_M \cdot \rho_S) \cdot g \qquad (6)$$

Which can be simplified and rewritten as Equation (7):

$$\frac{\chi_M}{MW_F} \cdot \rho_F \cdot H \cdot \nabla H = (\rho_F - \rho_S) \cdot g + (\rho_M - \rho_S) \cdot \frac{\mathrm{V}_M}{\mathrm{V}_F} \cdot g \qquad (7)$$

On the other hand, $V_F$ and $V_M$ can be defined as:

$$V_F = \frac{M_F}{\rho_F} = \frac{n \cdot MW_F}{\rho_F} \quad \text{and} \quad V_M = \frac{M_M}{\rho_M} = \frac{n \cdot x \cdot MW_M}{\rho_M},$$

In order to have the ratio between the volumes of adsorbate captured *($V_M$)* and sorbent *($V_F$)* shown in Equation (8):

$$\frac{V_M}{V_F} = \frac{x \cdot MW_M \cdot \rho_F}{MW_F \cdot \rho_M} \qquad (8)$$

Replacing Equation (8) in Equation (7) gives Equation (9):

$$\frac{\chi_M}{MW_F} \cdot \rho_F \cdot H \cdot \nabla H = (\rho_F - \rho_S) \cdot g + (\rho_M - \rho_S) \cdot \frac{x \cdot MW_M \cdot \rho_F}{MW_F \cdot \rho_M} \cdot g \qquad (9)$$

Which can be rewritten as Equation (10):

$$x \cdot MW_M = \frac{\chi_M \cdot MW_F \cdot \rho_M}{MW_F \cdot (\rho_M - \rho_S) \cdot g} H \cdot \nabla H - \frac{(\rho_F - \rho_S) \cdot MW_F \cdot \rho_M}{(\rho_M - \rho_S) \cdot \rho_F} \qquad (10)$$

Taking into account that all parameters are constant with the exception of "$H \cdot \nabla H$" and “$x \cdot MW_M$" , the above equation can be simplified to the form of Equation (11):

$$x \cdot MW_M = A \cdot H \cdot \nabla H - B \quad (11)$$

We can define $M_{M(F)} = x \cdot MW_M$, wherein $M_{M(F)}$ is the mass of adsorbate captured per weight formula of the adsorbent to obtain Equation (12), which gives a linear relationship between the mass captured and the $H \cdot \nabla H$ to which particles fall.

$$M_{M(F)} = A \cdot H \cdot \nabla H - B \qquad (12)$$

If a magnetic field configuration that shows a linear variation of "$H \cdot \nabla H$" with respect to an easily measurable physical parameter (D) is available (Equation 13), where *a* and *b* are the corresponding constants representing the slope and y-intercept of the corresponding straight line, Equation (12) could be rewritten as Equation (14):

$$H \cdot \nabla H = a \cdot D + b \quad (13)$$

$$M_{M(F)} = aA \cdot D + bA - B \quad (14)$$

Equation (14) can be simplified further *as a, b, A* and *B* parameters are constants in the form of Equation (15):

$$M_{M(F)} = A' \cdot D - B' \quad (15)$$

In this arrangement of permanent magnets, this physical parameter is the lateral displacement of the recipient containing the particles of adsorbent material suspended in a liquid and can be obtained directly from the reading of the actuator integrated in the equipment. This linearity remains within the ranges of displacements observed in the experimental measurements as represented in Figures 6 and 7.

Therefore, once the values of the constants *A'* and *B'* have been determined for the adsorbent used, by means of a calibration with samples with a known amount of captured mass, the equipment provides easily quantitative information on the amount of mass captured of any adsorbate by the adsorbent material.

The calibration process for each adsorbent material is carried out by measuring the parameter D (lateral displacement) at which the last particles fall on the device of the invention and also for the same adsorbent materials but incorporating adsorbed molecules in a known mass amount. The captured adsorbate mass amount of the samples employed for the calibration, is calculated from the difference between the initial adsorbate containing solution concentration and the remaining one after the in-solution adsorption process. The measurement of the adsorbate concentration in the solution requires the use of analytical techniques, such as UV-Vis spectroscopy, NMR or chromatography according to the intrinsic characteristics of the adsorbate molecule. The representation of both values in a Mass (%) vs. lateral displacement (D) diagram allows to establish the calibration straight line. This result subsequently allows to quantify the percentage of adsorbate mass captured by the adsorbent directly from the reading of D parameter in this device, as represented in Figures 8 and 9.

Another aspect of the invention refers to a device for measuring the absorption capacity of adsorbent materials of substances dissolved in a liquid medium.

The device comprises:

a support of ferromagnetic material and two permanent magnets placed on the support of ferromagnetic material in such a way that they face each other, and with a gap between them,

an elongated recipient for containing a liquid medium containing magnetically active particles of an absorbing material, and

a substance dissolved in the liquid medium, and a platform configured to retain the recipient between the two permanent magnets, so that the bottom of the recipient is outside the magnetic field generated by the magnets.

The device further includes a mechanical actuator coupled to the platform and configured to move the recipient relative to the permanent magnets, and means for measuring the separation distance between the recipient and one of the magnets.

The device additionally includes computing means adapted to determine the mass of substance captured by the linear correlation in accordance with the method defined above.

## BRIEF DESCRIPTION OF THE DRAWINGS

To complete the description and in order to provide a better understanding of the invention, a set of illustrations is provided. These form an integral part of the description and depict embodiments of the invention, which should not be interpreted as restricting the scope of the invention, but just as examples of how the invention can be implemented. The illustrations comprise the following figures:

Figure 1.- shows a perspective view of the metal frame where the permanent magnets are placed, wherein their components are shown decoupled to facilitate their identification.

Figure 2.- shows the methacrylate support attached to the mobile axis in charge of increasing or decreasing the distance between the test tube and the magnet surface.

Figure 3.- shows a view of the metal frame and magnets mounted with the methacrylate support. An enlarged view in this figure shows the methacrylate plate where the test tube is supported, which moves away from the permanent magnet thanks to the mobile axis.

Figure 4.- shows a test tube touching one of the magnets.

Figure 5.- shows how, as the test tube is displaced away, a distance is reached where the particles of the porous material fall due to the weakening of the external magnetic field, which will be characteristic of each porous material and the mass of adsorbate captured.

Figure 6.- shows a graph of the parameter $H\cdot\nabla H$ (magnetic field and magnetic field gradient) versus lateral displacement (D) within the range measured for the adsorbent material MIL-100(Fe) showing the linear dependence between both parameters.

Figure 7.- shows a plot of the parameter $H\cdot\nabla H$ versus lateral displacement (D) within the range measured for the adsorbent material MIL-101(Cr) showing the linear dependence between both parameters.

Figure 8.- shows a graph of the adsorbed mass versus lateral displacement for the adsorbent material MIL-100(Fe). Molecules whose adsorbed mass has been corroborated by another analytical technique to determine the equation of the line are identified with a circle, while molecules whose mass has been determined by the extrapolation of their lateral parameter

(D) value are identified with a square.

Figure 9.- shows a plot with a linear representation of the adsorbed mass versus lateral displacement for the adsorbent material MIL-101(Cr). Molecules whose adsorbed mass has been corroborated by another analytical technique to determine the equation of the calibration line are identified with a circle, while molecules whose mass has been determined by the extrapolation of their lateral parameter (D) value are identified with a square.

## PREFERRED EMBODIMENTS OF THE INVENTION

Figures 1 to 3 show a preferred embodiment of a device (1) for measuring the absorption capacity of adsorbent materials of substances dissolved in a liquid medium according to the invention.

The device (1) is provided with at least one and preferably two permanent magnets (marked as 2 and 2´) arranged in a facing configuration and with a reduced distance between them (3-10 cm) to concentrate the field lines in the confined zone between both magnets (2, 2´). A sufficiently high field gradient is generated away from this intermediate zone, so that the test tube (3) containing particles (4) of the magnetically active porous material can be placed at the boundary of this zone. There, the magnetic field gradient will be at its maximum value.

The high magnetic field gradient at the lower boundary between the inter-magnet zone and the outside exerts a sufficiently strong attraction on the particles (4) of the magnetically active adsorbent or porous material (paramagnetic or functionalised with ferromagnetic particles), so that they are retained and do not fall down to the bottom.

Additionally, the device (1) comprises a lateral displacement actuator (5) to modify and measure the relative distance of the porous material from the area of maximum magnetic field gradient. This actuator (5) is adapted to allow homogeneous, smooth displacement and an accuracy of, at least, one tenth of a millimetre.

The value of the magnetic field and its gradient shall decrease as the test tube (3) is moved away from the magnet surface. The value of the distance at which the last particle falls down, which depends, as described above, on the balance of the forces of gravity, the attraction exerted by the magnetic field and the buoyancy effect of the solvent, will be characteristic of each porous material and of the amount of adsorbate captured.

The measurement starts with the test tube (3) containing the liquid in the area of the maximum field gradient (bottom part of the permanent magnet pole) and the porous material or a suspension of it is added to the test tube (3). The adsorbent material (4) is retained in the area where the field gradient is at its maximum and then the actuator (5) is used to increase the distance (D) of the test tube (3) with respect to this area of maximum magnetic field gradient until the necessary separation is reached for the particles of the material to fall. This distance value is the one that provides, after calibration of the equipment, a parameter directly linked to the percentage of mass adsorbed by the porous material (4). The calibration of the equipment is carried out for each adsorbent material and requires several preparations of the adsorbent material with different percentages of known mass captured. Both the calibration measurements and the adsorption quantification measurements must be carried out at the same temperature.

For the construction of the device (1) as shown in Figure 1, three pieces (6a, 6b, 6c) of magnetic steel or ferromagnetic metal capable of condensing the magnetic field lines of a magnet are used. These three are fixed together in a U-shaped arrangement, with the longest one acting as the base, configuring a U-shaped support of ferromagnetic material. Two circular spacers (7, 7´) of ferromagnetic steel or other ferromagnetic metal/alloy are attached to the upper inner ends of the U-shape with a screw. Two circular permanent magnets (2, 2´) are attached to the spacers (7, 7´) by the magnetic attraction force itself.

A methacrylate support (8) is provided with an indentation (12) of the width and length of the metal support in a U-shape, so that the metal U-shaped support can be positioned and cannot move or shift.

A plate of methacrylate (or any other non-ferromagnetic material) (9) with a hole (10) is fixed on the shaft (13) of the actuator (5), in such a way that when the test tube (3) is inserted into this hole (10), it becomes firmly attached to the surface of a magnet (2), as shown in Figure 4 at the beginning of the measurement, but it can also be displaced laterally.

The test tube (3) is positioned with respect to the magnets (2, 2´), so that the level of the liquid (11) contained inside the test tube (3), is above the lower edge of the magnet (2) and the bottom of the tube, in this case, below the lower edge of the magnet. In this way the test tube (3) is within the same plane defined by the U-shaped support and the magnets (2, 2´), and in contact to one of the permanent magnets, as shown in Figure 4.

The test tube (3) is filled with water or any other liquid (11) and placed in the measuring device

(1) attached to one of the permanent magnets (2, 2´). Subsequently, particles of the magnetically active adsorbent material are dropped, either directly or contained in a suspension. The buoyancy effect exerted by the liquid (11) medium decreases the force of gravity and slows down the rate of their fall, allowing the magnetic field of the permanent magnet to retain the particles in the area of the test tube (3) adjacent to the lower edge of the permanent magnet (2). Once attached, the shaft (13) of the actuator (5) is used to slowly pull the test tube (3) away from the surface of the magnet (2), as represented in Figure 5.

As the distance *D* between the attached particles and the magnets increases, as shown in Figure 5, the gradient of the magnetic field allowing these particles to avoid falling down to the bottom of the tube decreases. At some point, there will be a distance at which the magnetic force is too small to counteract the weight of the porous material, causing it to descend. The distance *D* at which the last of the particles fall from the adsorbent material, a value obtained directly from the linear actuator, is the parameter that allows the quantification of the adsorption. As the adsorbent material (4) captures a larger mass of adsorbate, the distance at which this fall occurs decreases.

# CLAIMS

1.- Method for measuring the absorption capacity of adsorbent materials to absorb substances dissolved in a liquid medium, comprising:

providing a recipient containing a liquid medium with magnetically active particles of an adsorbent material, and a substance dissolved in the liquid medium,

placing the recipient in proximity to or in contact with at least one permanent magnet, so that the magnetically active particles are retained in the liquid medium by the magnetic attraction of the permanent magnet,

increasing the separation distance between the permanent magnet and the recipient until the magnetic attraction of the permanent magnet no longer holds the paramagnetic particles,

measuring the separation distance between the permanent magnet and the recipient at which all or a predetermined amount of the magnetically active particles have fallen down by gravity to the bottom of the recipient, and

determining, by a linear correlation, the mass of substance captured by the magnetically active particles based on the measured separation distance.

2.- Method according to claim 1, wherein the linear correlation for determining the mass of substance captured is the following:

$$M_{M(F)} = A' \cdot D - B'$$

where: ($M_{M(F)}$) is the mass of adsorbate captured per weight formula of the adsorbent; (*D*) is the lateral separation distance between the permanent magnet and the recipient; (*A' and B'*) are constants determined through a calibration procedure.

3.- Method according to claim 2, wherein the constants *A´* and *B´* are obtained for each adsorbent through a calibration procedure in which *D* parameter is measured on several samples of the adsorbent containing known adsorbate mass percentages with respect to the adsorbent mass, and wherein the linear fitting of the obtained Mass percentage vs. *D* representation provides the values of *A'* from the slope of the fitting to a straight line and *B'* from the extrapolated value of the straight line at *D* = 0.

4.- Method according to any of the preceding claims, wherein the recipient is placed between two permanent magnets facing each other and such that great $H \cdot \nabla H$ product values are achieved at the bottom part of the space between the magnets ($H$ being the magnetic field and $\nabla H$, being the gradient of the magnetic field).

5.- Method according to any one of the preceding claims, wherein increasing the separation distance between the permanent magnet and the recipient is carried out by keeping the permanent magnet in a fixed position and moving the recipient linearly with respect to the permanent magnet in a direction orthogonal to the permanent magnet.

6.- Method according to any one of the preceding claims, wherein the absorbing material is a metal-organic framework (MOF).

7.- Method according to any one of the preceding claims, wherein the permanent magnet is cylindrical.

8.- Method according to any of the previous claims, where the recipient is elongated and is positioned in front of the permanent magnet, in such a way that the bottom of the recipient is outside the magnetic field generated by the magnet.

9.- Device for measuring the absorption capacity of adsorbent materials of substances dissolved in a liquid medium, comprising:

a ferromagnetic material support and two permanent hard magnets placed on the ferromagnetic material support in such a way that they face each other and with a separation space between them,

an elongated recipient for containing a liquid medium containing magnetically active particles of an absorbing material, and a substance dissolved in the liquid medium,

and a platform configured to retain the container between the two permanent hard magnets, and so that the bottom of the recipient is outside the magnetic field generated by the magnets,

a mechanical actuator coupled to the platform and configured to move the recipient relative to the permanent magnets,

means for measuring the separation distance between the recipient and one of the magnets, and computing means adapted to determine the mass of substance captured by the linear correlation of claim 2 or claims 2 and 3.

10.- Device according to claim 9, wherein the ferromagnetic material support has a U-shaped configuration, and wherein the elongated recipient is positioned within a plane defined by the U-shaped support.

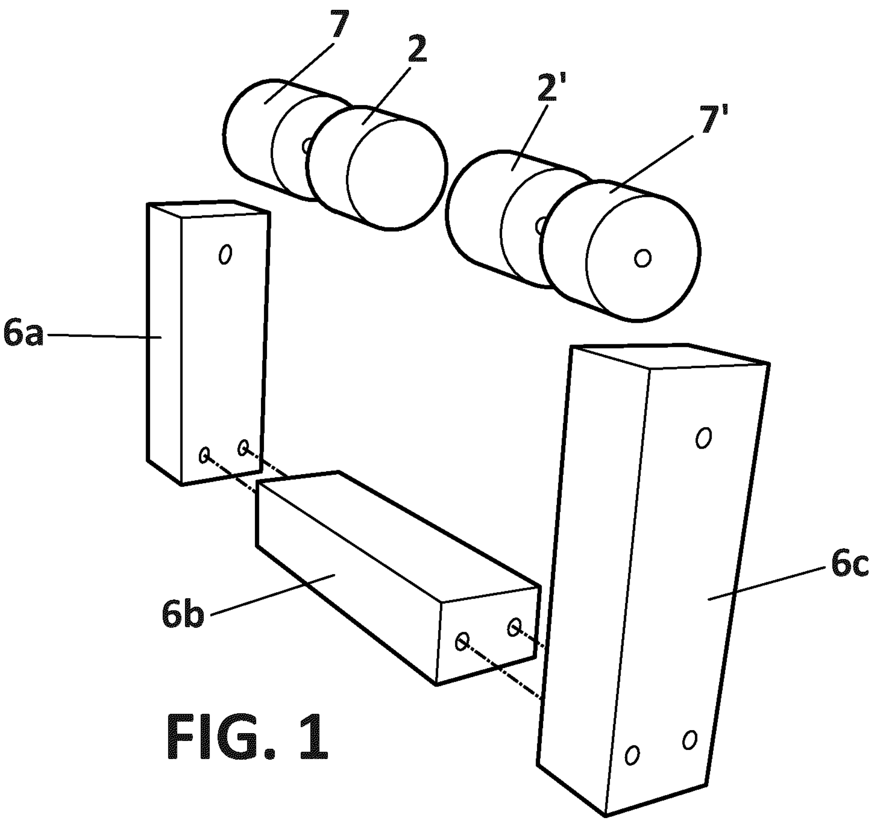

FIG. 1

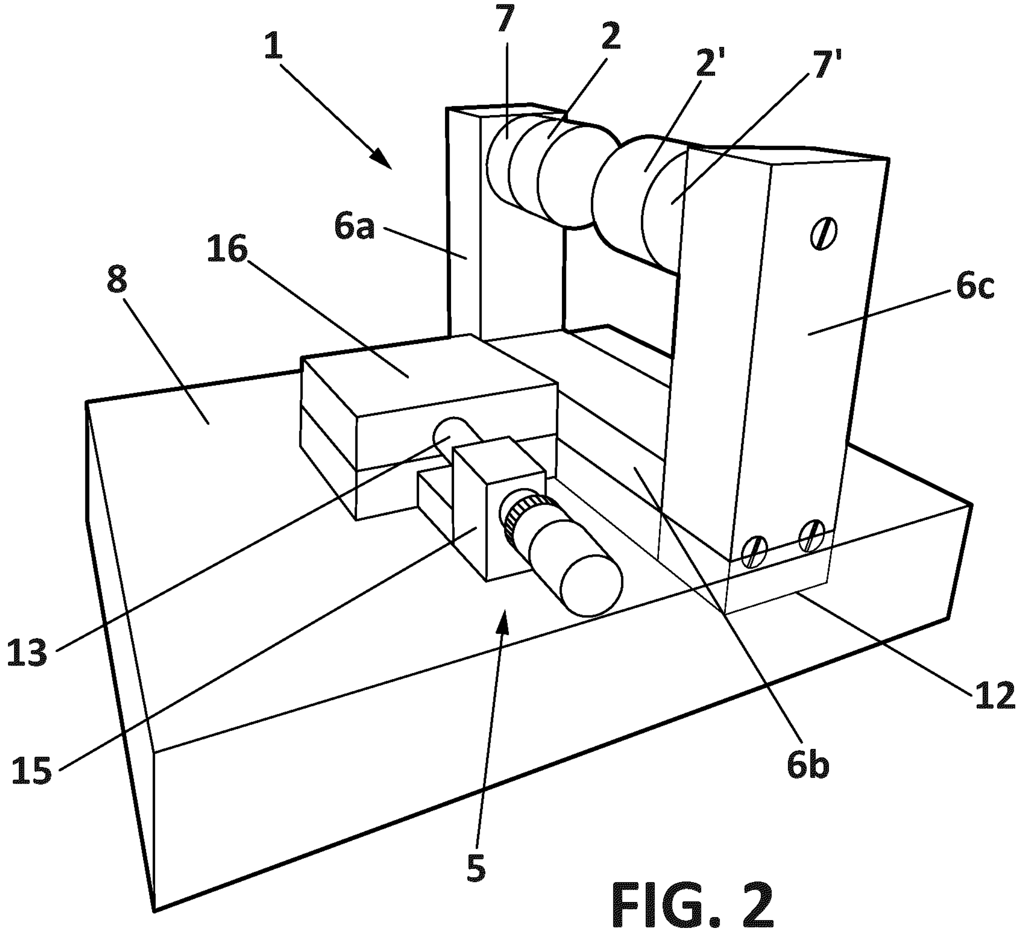

FIG. 2

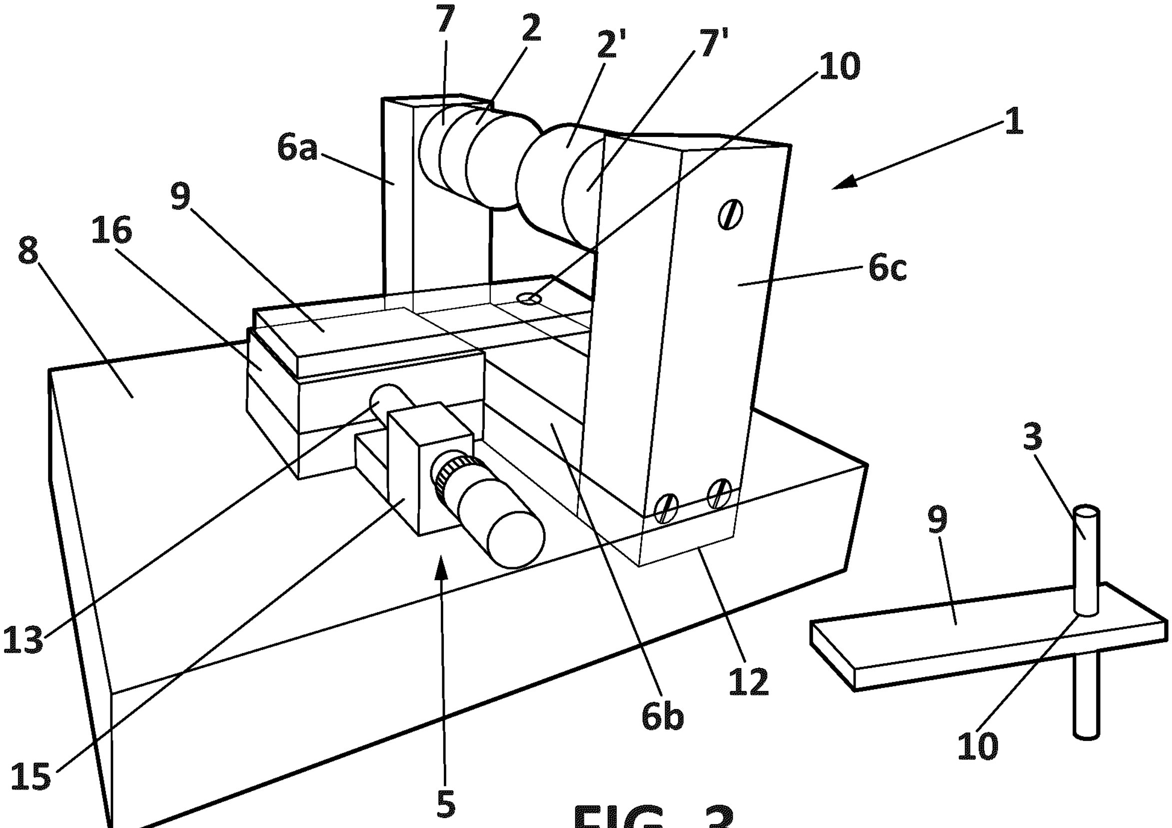

FIG. 3

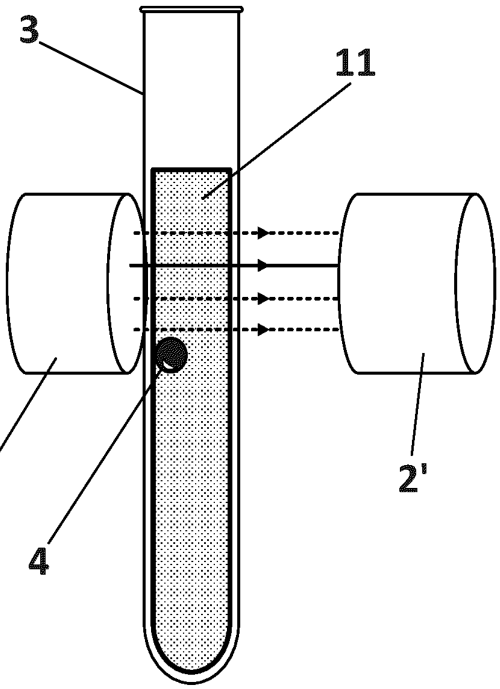

FIG. 4

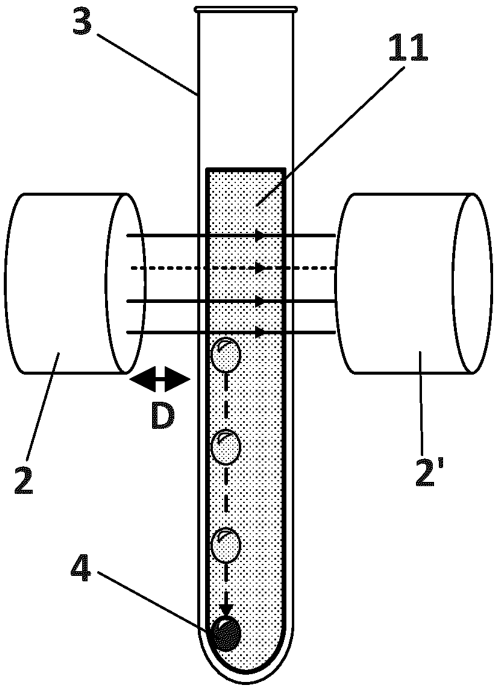

FIG. 5

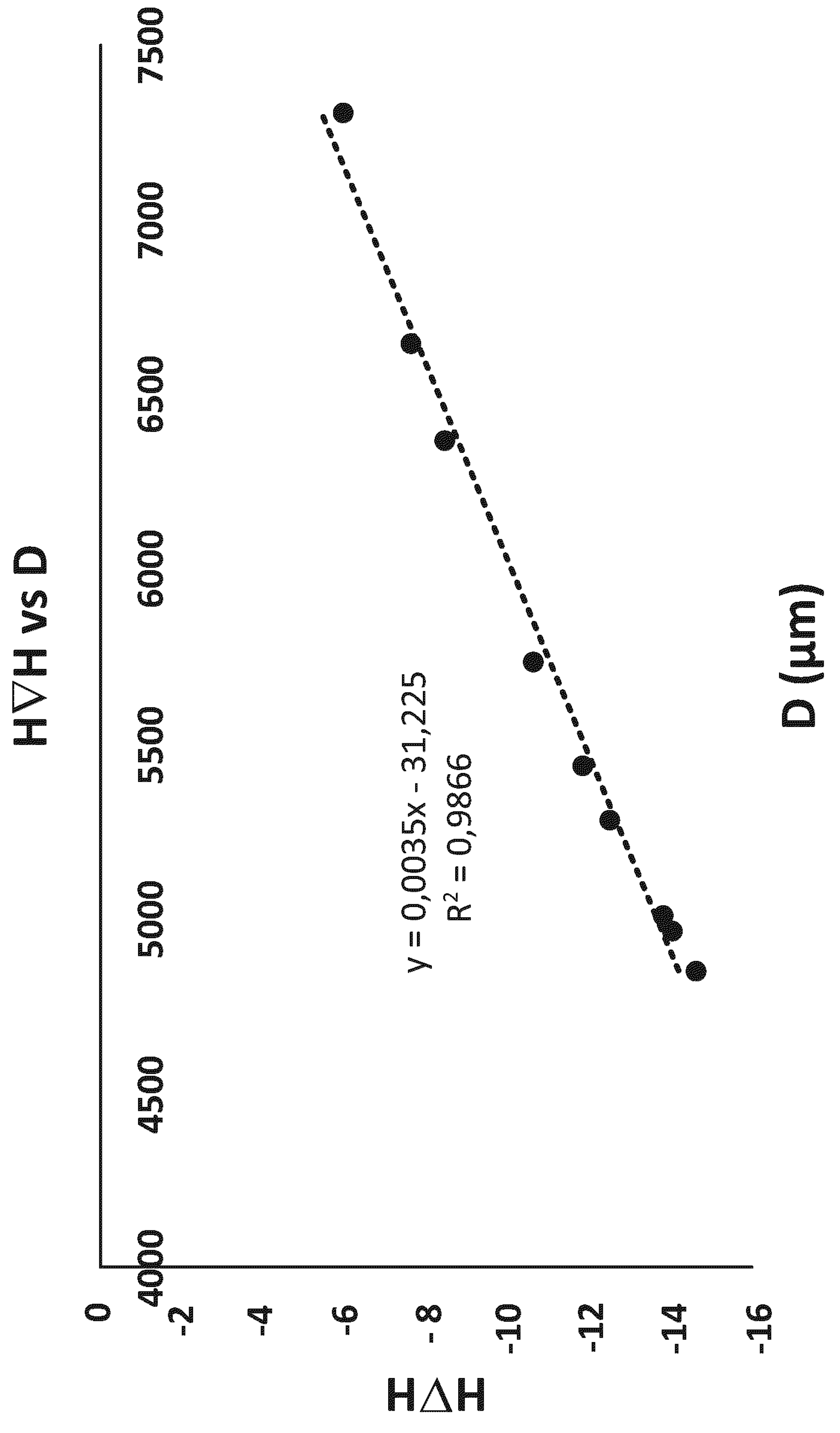
H▽H vs D
y = 0,0035x - 31,225
$R^2$ = 0,9866
HΔH
0
-2
-4
-6
-8
-10
-12
-14
-16
4000
4500
5000
5500
6000
6500
7000
7500
D (µm)

FIG. 6

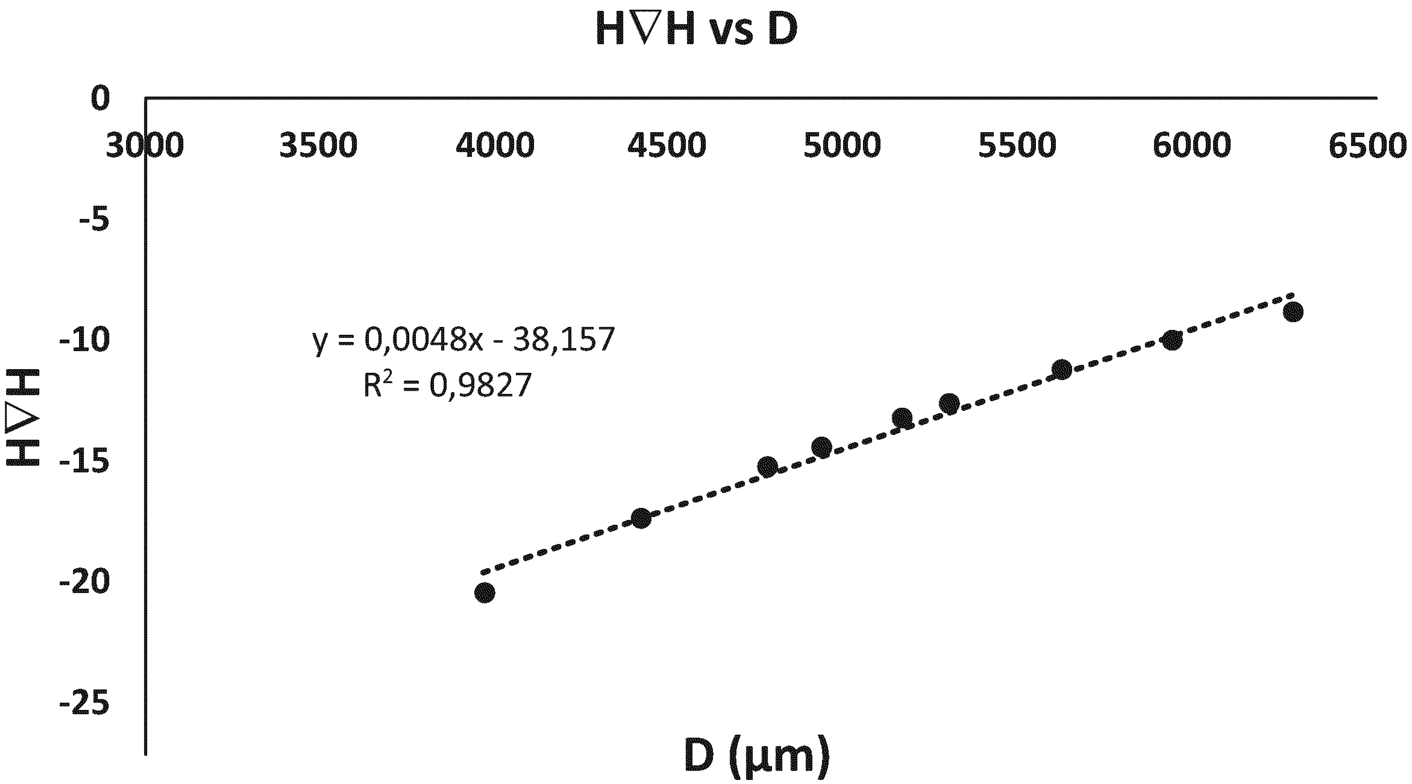
H∇H vs D
y = 0,0048x - 38,157
R² = 0,9827
0
-5
-10
-15
-20
-25
H∇H
3000
3500
4000
4500
5000
5500
6000
6500
D (µm)

FIG. 7

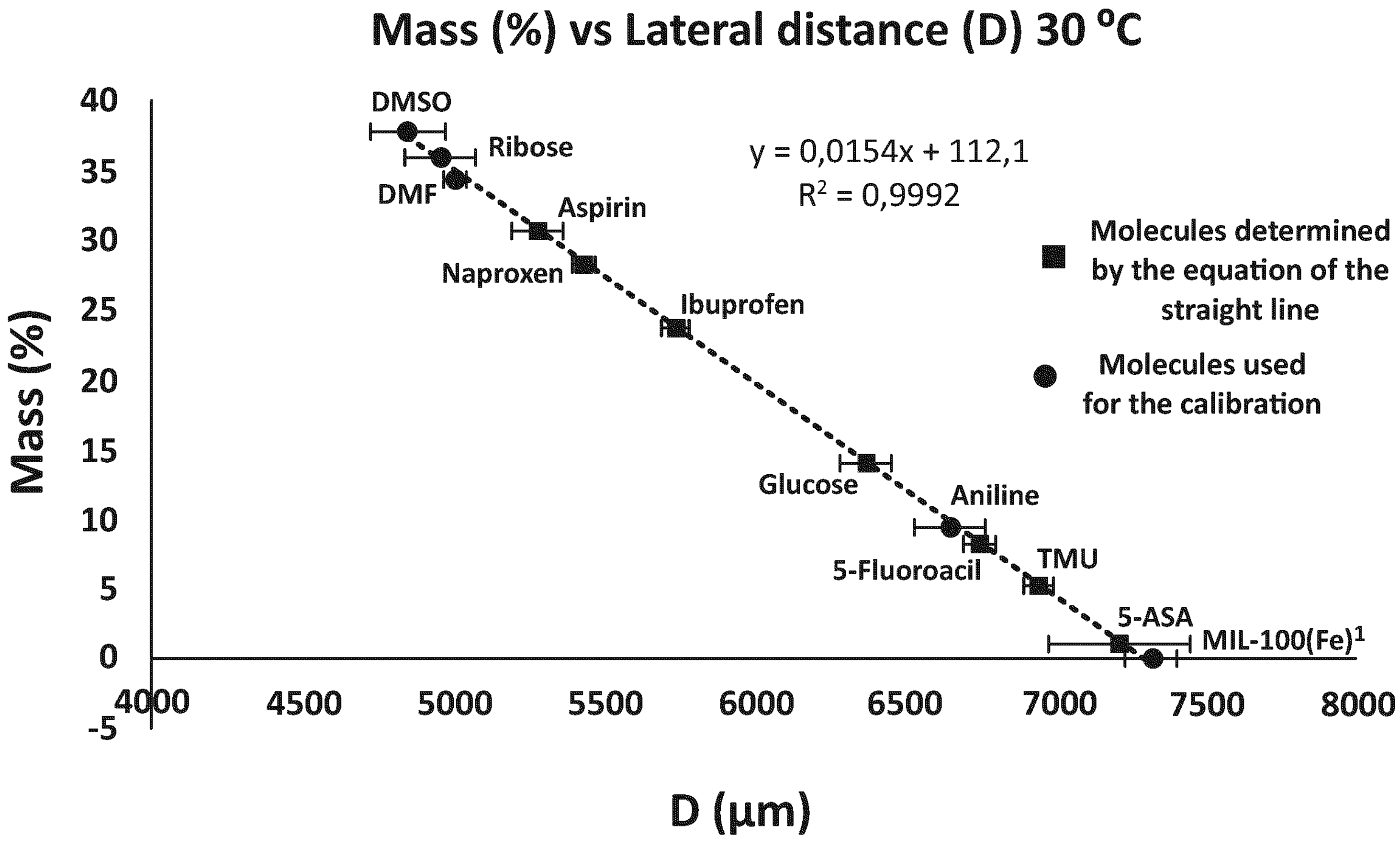
Mass (%) vs Lateral distance (D) 30 °C
y = 0,0154x + 112,1
R² = 0,9992
■ Molecules determined by the equation of the straight line
● Molecules used for the calibration
DMSO
Ribose
DMF
Aspirin
Naproxen
Ibuprofen
Glucose
Aniline
5-Fluoroacil
TMU
5-ASA
MIL-100(Fe)¹
Mass (%)
40
35
30
25
20
15
10
5
0
-5
4000
4500
5000
5500
6000
6500
7000
7500
8000
D (µm)

FIG. 8

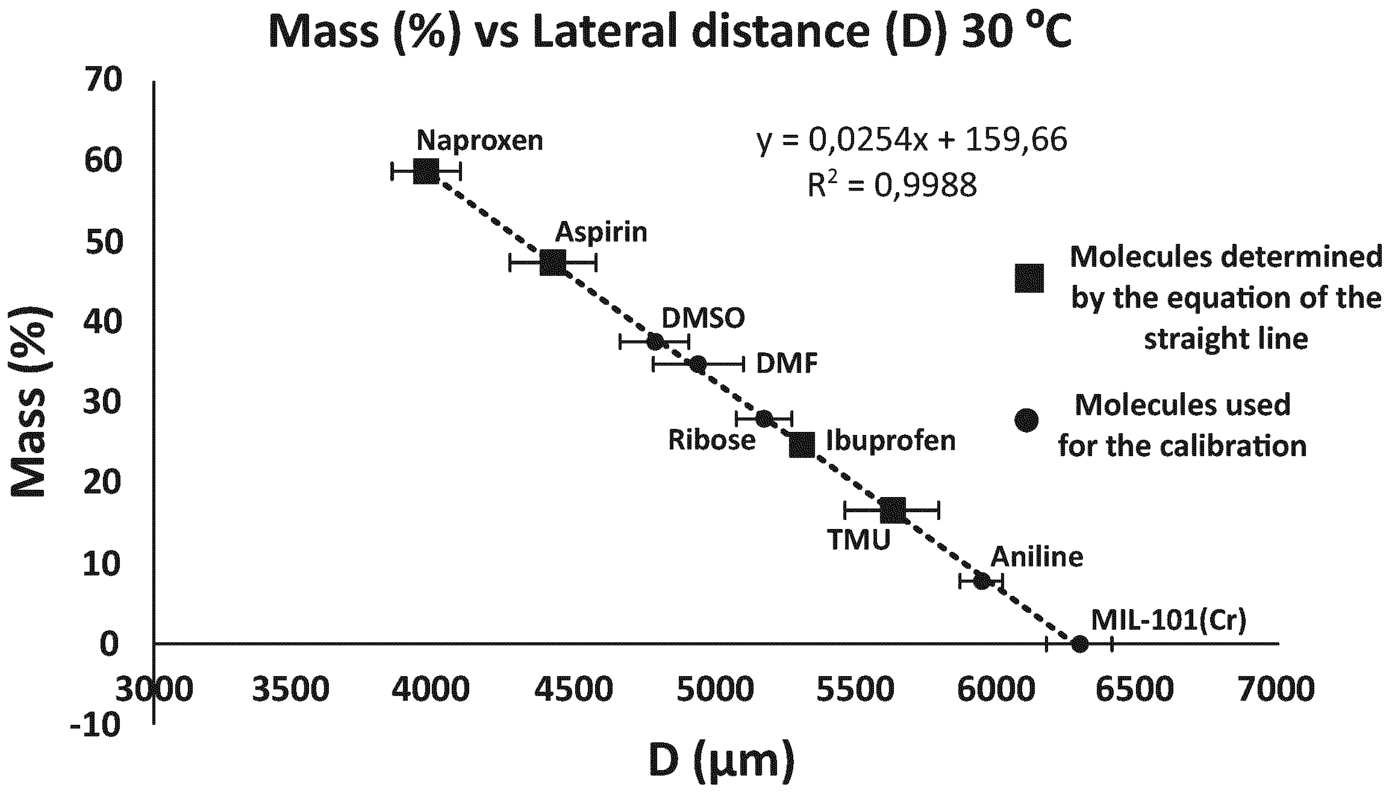
Mass (%) vs Lateral distance (D) 30 °C
y = 0,0254x + 159,66
R² = 0,9988
■ Molecules determined by the equation of the straight line
● Molecules used for the calibration
Naproxen
Aspirin
DMSO
DMF
Ribose
Ibuprofen
TMU
Aniline
MIL-101(Cr)
Mass (%)
70
60
50
40
30
20
10
0
-10
3000
3500
4000
4500
5000
5500
6000
6500
7000
D (µm)

FIG. 9

# INTERNATIONAL SEARCH REPORT

**International application No**

PCT/EP2024/065432

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. G01N15/04

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | BARROSO NAGORE ET AL: "Magnetic sustentation as an adsorption characterization technique for paramagnetic metal-organic frameworks", COMMUNICATIONS CHEMISTRY<br>,<br>vol. 6, no. 1<br>5 January 2023 (2023-01-05), XP093100585,<br>DOI: 10.1038/s42004-022-00799-w<br>Retrieved from the Internet:<br>URL:https://www.nature.com/articles/s42004-022-00799-w<br>the whole document<br>-----<br>-/-- | 1-10 |

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>23 August 2024 | Date of mailing of the international search report<br>16/09/2024 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Dekker, Derk |

1

Form PCT/ISA/210 (second sheet) (April 2005)

**C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | Barroso García Nagore: "A STUDY OF METAL-ORGANIC FRAMEWORK SORPTION PHENOMENA IN SOLUTION",<br>,<br>4 May 2023 (2023-05-04), pages 1-197, XP093100647,<br>Retrieved from the Internet:<br>URL:https://addi.ehu.es/handle/10810/61382<br>[retrieved on 2023-11-13]<br>Chapter 3<br>----- | 1-10 |
| A | Pascual-Colino Jon ET AL: "An in solution adsorption characterization technique based on the response to an external magnetic field of porous paramagnetic materials: application on supramolecular metal-adenine frameworks containing heterometallic heptameric clusters",<br>Inorganic chemistry frontiers,<br>11 April 2023 (2023-04-11), XP093100568, London<br>DOI: 10.1039/d2qi01994a<br>Retrieved from the Internet:<br>URL:https://pubs.rsc.org/en/content/articlelanding/2023/QI/D2QI01994A<br>[retrieved on 2023-11-13]<br>the whole document<br>----- | 1-10 |

1