

(43) International Publication Date
16 January 2014 (16.01.2014)(51) International Patent Classification:
G01R 33/12 (2006.01)Yuseong, Daejeon, Daejeon 305-335 (KR). **GANDIT, Philippe**; 292 chemin du Devier, F-38250 Saint-Nizier du Moucherotte (FR).

(21) International Application Number:

PCT/EP2013/064775 (74)

(22) International Filing Date:

12 July 2013 (12.07.2013)

(81)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12305852.1 13 July 2012 (13.07.2012) EP

(71) Applicants: UNIVERSITE MONTPELLIER 2, SCIENCES ET TECHNIQUES [FR/FR]; Place Eugène Bataillon, F-34095 Montpellier Cedex 5 (FR). CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE (C.N.R.S) [FR/FR]; 3, rue Michel Ange, F-75016 Paris (FR).

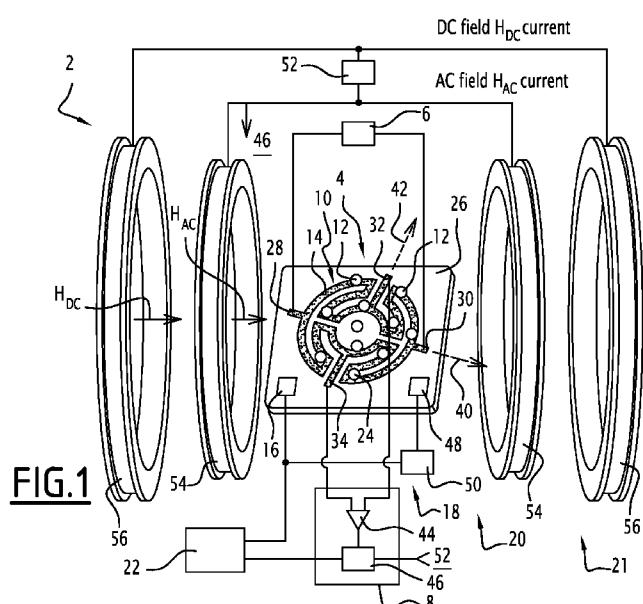
(72) Inventors: TERKI, Férial; 1 chemin de la bergerie, F-34270 Le Triadou (FR). BOUSSEKSOU, Azzedine; 8 rue du Médecin Colonel Calbairac, F-31100 Toulouse (FR). TRAN, Quang Hung; Bredeboevej 37 5 floor, DK-2800 Lyngby (DK). KAMARA, Souleymane; 27 allée de Bon accueil, app4, F-34090 Montpellier (FR). KIM, CheolGi; Songrim APT 509-203 Hagidong, Yuseong, Daejeon, Daejeon 305-759 (KR). KIM, Kun Woo; 302 1-10 Gungdong

(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, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, 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, 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).

[Continued on next page]

(54) Title: MICROMAGNETOMETRY DETECTION SYSTEM AND METHOD FOR DETECTING MAGNETIC SIGNATURES OF MAGNETIC MATERIALS.



(57) Abstract: A micromagnetometry system for detecting the presence of very small quantities of magnetic particles comprises a first magnetic hybrid AMR/PHR multi-ring sensor (4) using a Wheatstone bridge electrical configuration, a first current source (6), a first voltage measurement device (8), a set of at least one magnetic particles (12) deposited on the first magnetic sensor (4) and a processing unit (22) for detecting from a set of different measured differential voltages a magnetic flux shift representative of the presence of a least one deposited magnetic particle (12). The micromagnetometry system comprises means (20) for creating a magnetic excitation field H_{AC} to make produce by each motionless magnetic particle (12) a stray magnetic field oscillating along the time at a constant frequency w ranging from 10 Hz to 3 KHz.



Published:

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

Micromagnetometry detection system and method for detecting magnetic signatures of magnetic materials

Nowadays nano-sized Spin CrossOver (SCO) particles receive more and more interests not only for the exploration of the physical properties of these materials at the mesoscopic scale, but also for the development of new functional materials. Up to now observations of the spin transition property was essentially reduced to the simple investigation of temperature dependence of the magnetization or the optical absorption in a huge ensemble of nano-particles with different degrees of size and shape dispersion. The development of methods for single Spin CrossOver (SCO) particle measurements is desirable for both fundamental and applicative perspective even if such efforts remain scare so far.

In the field of nano-scale magnetic measurements, the state of the art is represented by the micro-SQUID and nano-SQUID devices. These devices can detect the magnetization reversal of small amount of magnetic nano-particles or single molecule magnets by depositing directly the nano-particles on the micro-bridge Josephson junctions.

However, for low noise operation, the micro-bridges are normally made of low temperature superconducting materials such as niobium. Such devices are for example described in the article entitled "Magnetic Anisotropy of a Single Cobalt Nanocluster" from M. Jamet and al., published in the Physical Review Letters, Vol. 86, number 20.

Hitherto the working temperature of such a magnetometry detection system is limited below few tens of Kelvin.

Consequently, the conventional micro-SQUID technique is not appropriate to study the magnetization properties within the room temperature range, especially to carry out precise measurements of room temperatures switching properties of a small volume or a single nano-particle of a SCO material.

The current ultra-sensitive SQUID detection method suffers from several drawbacks as being used at very low temperature and requiring complex instruments that are not portable and not flexible.

Alternative methods are proposed as described in the following documents:

- the article from Sunjong Oh et al. untitled "Analytes kinetics in lateral flow membrane analyzed by cTnI monitoring using magnetic method", published in Sensors and Actuators B: Chemical International devoted to Research and Development of Physical and Chemical Transducers, Elsevier S.A., Switzerland, vol. 160, n°1, 19 August 2011, pages 747-752 ;

- the article from Sunjong Oh et al. untitled "Hybrid AMR/PHR ring sensor", published in Solid State Communications, Pergamon, GB, vol. 151, n° 18, 29 May 2011, pages 1248-1251 ;

5 - the patent application US 2006/194327 A1 ;

- the patent application US 2010/231213 A1.

A technical problem is to avoid such disadvantages and to provide an ultra-sensitive magnetometry system that performs measurements at room temperature, which is less complex and offers a more portable and flexible implementation

10 In addition, another technical problem is to propose a magnetometry system and method that improves the sensitivity detection performance in order to detect nano or picotesla field generated by a "single micro/nano object" in the close vicinity of the sensor active surface.

15 Accordingly the invention relates to a first micromagnetometry system for detecting the presence of very small quantities of magnetic particles down to a single magnetic particle or a single magnetic object in nano or micro scale comprising a:

20 - a first magnetic hybrid AMR/PHR multi-ring sensor having an active surface including a magnetic track of a closed loop shape deposited on a substrate, a first current terminal and a second current terminal forming a pair of current terminals which face each other contacting with the closed loop magnetic track made of a magnetic material, a first voltage terminal and a second voltage terminal forming a pair of voltage terminals which face each other contacting with the closed loop magnetic track and from which an output differential voltage V_b is detected, a first axis passing through the first and second current terminals being parallel to the exchange bias field direction of the track material and perpendicular to a second axis passing through the first and second voltage terminals;

25 - a first current or voltage source connected between the first and second current terminals for injecting a current I therethrough;

- a first voltage measurement device connected between the first and second voltage terminals for measuring the differential voltage V_b between the pair of voltage terminals ;

30 - a set of at least one magnetic particles deposited on the active surface of the first magnetic sensor ;

- a processing unit for detecting from a set of different measured differential voltages a magnetic flux shift representative of the presence of a least one deposited magnetic particle ;

35 the magnetic track of the first AMR/PHR multi-ring magnetic sensor having :

- a first arm made of a first set of a predetermined ring number m lower than 18 of circular meander paths delimited within a first quarter surface of the first magnetic sensor, the outermost meander path being connected to the first current terminal and the innermost meander path being connected to the first voltage terminal,

5 - a second arm made of a second set of the same predetermined number m of circular meander paths delimited within a second quarter surface of the first magnetic sensor, the outermost meander path being connected to the second current terminal and the innermost meander path being connected to the first voltage terminal,

10 - a third arm made of a third set of the same ring number m of circular meander paths delimited within a third quarter surface of the first magnetic sensor, the outermost meander path being connected to the second current terminal and the innermost meander path being connected to the second voltage terminal,

15 - a fourth arm made of a fourth set of the same ring number m of circular meander paths delimited within a fourth quarter surface of the first magnetic sensor, the outermost meander path being connected to the first current terminal and the innermost meander path being connected to the second voltage terminal ;

20 - the magnetic track is a bi-layered structure including a ferromagnetic film and an anti-ferromagnetic films, or a spin-valve structure, or a tri-layered structure including a ferromagnetic film, a metal and an anti-ferromagnetic film;

characterized in that

25 - the micromagnetometry system comprises means for creating a magnetic excitation field H_{AC} to make produce by each magnetic particle a stray magnetic field, the magnetic excitation field H_{AC} oscillating along the time at a constant frequency ω ranging from 10 to 3 KHz; and

30 - the magnetic particles to be detected are motionless and placed close to or in contact with the active surface of the magnetic track ; and

- the current I injected by the first current or voltage source passing through the current terminals is a direct current (DC), or an alternating current (AC), or a sum of a direct and an alternating current; and

35 - the processing unit is configured to either

provide with a first calibration curve of a background thermal magnetic response of the first magnetic sensor without any magnetic particles deposited thereon, over a predetermined temperature range, under first known predetermined environmental physical conditions, and under a first set of known system operating conditions in terms of the injected current by the first current or voltage source and of the magnetic excitation field H_{AC} applied; then

after deposit of an unknown amount of magnetic particles upon the first magnetic sensor, determining a second curve of the evolution versus temperature of differential voltage measurements corrected or not from a set of differential voltage measurements output from the first magnetic sensor and carried out by varying the temperature over the same predetermined range of temperature, under the same first known predetermined environmental physical conditions and under the same first set of known system operating conditions , then

to determine a third curve as the difference the second curve and the first curve over the same range of temperature; and

to detect the presence of at least one magnetic particle when the absolute value of all the voltage differences of the third curve remains above a predetermined detection threshold or when the third curve exhibits a temperature interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10 nT;

either,

after deposit of an unknown amount of magnetic particles upon the first magnetic sensor, the magnetic particles being switchable molecular nanoparticles by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command, by varying the physical property magnitude over a predetermined range of the physical property under known predetermined physical conditions and under known system operating conditions, to determine a first curve of the evolution of differential voltage measurements corrected or not from the evolution of differential voltage measurements carried out by the first magnetic sensor versus the magnitude of the physical property; then

to determine over the predetermined range of the physical property magnitude a second curve as a fitting curve from a lower portion of the first curve, this lower portion of the first curve corresponding to a lower interval included within the predetermined range of the physical property, the lower interval having its upper bound lower than the predetermined switching threshold; then

to determine a third curve as the difference versus the magnitude of the switching physical property between the differential voltages of the first curve and the differential voltages of the second curve within the same range of magnitude of the physical property; and

to detect the presence of magnetic particles when the third curve exhibits a switching physical property interval over which a transition occurs having an amplitude

greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10 nT.

According to particular embodiments, the micromagnetometry system comprises at least one of the following features:

5 - a first environmental temperature sensor for measuring an environmental temperature and/or a second environmental sensor for measuring a physical property different from the environmental temperature placed close to the active surface of the first active sensor, the switching of a magnetization of the magnetic particles being actuated when temperature or the physical property different of temperature is above or below a predetermined switching threshold,

10 - means for controlling and/or regulating the environmental temperature and/or the physical environmental property different from the temperature,

15 - the means for creating a magnetic excitation field H_{AC} comprises a second current source supplying an AC current and a least one coil connected to the second AC current source, the at least one coil being positioned relative to the first magnetic sensor so that the magnetic excitation field H_{AC} has a main component collinear to the first axis,

20 - means for creating a magnetic sensor bias field H_{DC} to shift the operating point of the first magnetic sensor to a highest sensing region, the magnetic sensor bias field H_{DC} being constant along the time, and being collinear with the magnetic excitation field H_{AC} created by means for creating a magnetic excitation field H_{AC} ,

25 - wherein the angle α formed between the first axis passing through the first and second current terminals and the axis of magnetic sensor bias field H_{DC} is selected in the range [0 degree, 90 degrees] so that the sensitivity of the magnetic sensor is maximal, and preferably is comprised within the range [15 degrees, 25 degree],

30 - the means for creating a magnetic excitation field H_{AC} is the current or voltage source connected between the first and second current terminals, the current or voltage source being configured to generate an alternating current (AC) oscillating along the with time at a constant frequency ω ranging from 10 Hz to 3 KHz, preferably ranging from 50 Hz to 150 Hz,

35 - comprising further a second magnetic hybrid AMR/PHR multi-ring sensor having the same structure as the first magnetic hybrid AMR/PHR multi-ring sensor,

the first and the second magnetic hybrid AMR/PHR multi-ring sensors being placed close to each other on the same substrate under the same known physical conditions to measure the same magnetic field when no magnetic particles are deposited onto the sensors,

the second magnetic hybrid AMR/PHR multi-ring sensors having a first current terminal and a second current terminal forming a pair of current terminals connected in parallel to and sharing the same first current source of the first magnetic hybrid AMR/PHR multi-ring sensor ; and wherein

5 the micromagnetometry system is configured

to differentiate a first set of differential voltage measurements carried out by the first sensor corresponding to a first configuration wherein magnetic particles to be detected if they are contained in the solution dropped are deposited on the first magnetic sensor and placed under a set of known environmental conditions and system operating settings, and a second set of reference differential voltage measurements carried out by the second sensor corresponding to a second configuration wherein no magnetic particles are deposited thereon, under the same set of known environmental physical conditions and system operating settings and to provide a corresponding difference curve; and then

to detect from the difference curve an abrupt variation corresponding at least to a minimal magnetization field shift of 10nT.

The invention also relates to a second micromagnetometry system for detecting the presence of very small quantities of magnetic particles down to a single magnetic particle or a single magnetic object in nano or micro scale comprising :

- a first magnetic hybrid AMR/PHR sensor and a second magnetic hybrid AMR/PHR multi-ring sensor,

the first magnetic hybrid AMR/PHR sensor having a first active surface including a first magnetic track deposited on a substrate, a first current terminal and a second current terminal forming a pair of current terminals which face each other contacting with the first magnetic track made of a magnetic material, a first voltage terminal and a second voltage terminal forming a pair of voltage terminals which face each other contacting with the first magnetic track and from which an output differential voltage is detected, a first axis passing through the first and second current terminals being parallel to the exchange bias field direction of the track material and perpendicular to a second axis passing through the first and second voltage terminals;

30 characterized in that

the micromagnetometry system comprises a second magnetic hybrid AMR/PHR sensor being placed close to the second magnetic hybrid AMR/PHR sensor on the same substrate under the same known physical conditions to measure the same magnetic field when no magnetic particles are deposited onto the sensors,

35 the second magnetic hybrid AMR/PHR multi-ring sensor having a second active surface including a second magnetic track deposited on the same substrate, a first current

terminal and a second current terminal forming a pair of current terminals which face each other contacting with the second magnetic track made of a magnetic material, a first voltage terminal and a second voltage terminal forming a pair of voltage terminals which face each other contacting with the second magnetic track and from which an output differential voltage is detected, a first axis passing through the first and second current terminals being parallel to the exchange bias field direction of the track material and perpendicular to a second axis passing through the first and second voltage terminals,

5 the first and the second magnetic tracks having a same shape amongst a cross shape, a single ring closed loop shape and a multi-ring closed loop shape, and having a same layer structure,

10 the layer structure of the first and the second magnetic tracks being a bi-layered structure including a ferromagnetic film and an anti-ferromagnetic films, or a spin-valve structure, or a tri-layered structure including a ferromagnetic film, a metal and an anti-ferromagnetic film;

15 and in that the micromagnetometry system comprises:

- a same first current or voltage source connected to and supplying in parallel a current I to the first magnetic hybrid AMR/PHR sensor and the second magnetic hybrid AMR/PHR multi-ring sensor,

20 - a first voltage measurement device connected at its input to the first and second voltage terminals of the first magnetic hybrid AMR/PHR sensor and the second magnetic hybrid AMR/PHR sensor, and configured to determine the difference voltage between an amplified differential voltage detected at the voltage terminals of the first magnetic sensor and an amplified differential voltage detected at the voltage terminals of the second magnetic sensor ;

25 - a set of at least one magnetic particles deposited on the active surface of the first magnetic sensor ;

- a processing unit for detecting from a set of different measured differential voltages output by first voltage measurement device a magnetic flux shift representative of the presence of a least one magnetic particle deposited on the first magnetic sensor ;

30 - means for creating a magnetic excitation field H_{AC} to make produce by each magnetic particle a stray magnetic field, the magnetic excitation field H_{AC} oscillating along the time at a constant frequency ω ranging from 10 to 3 KHz; and in that

- the magnetic particles or the magnetic object to be detected are motionless and placed only close to or in contact with the active surface of the first magnetic track ; and

- the current I injected by the first current or voltage source passing through the current terminals is a direct current (DC), or an alternating current (AC), or a sum of a direct and an alternating current.

According to a particular of embodiment of the second micromagnetometry system, wherein

no magnetic particles or magnetic object in nano or micro scale are deposited on the second sensor, and

the processing unit is configured to

after deposit of an unknown amount of magnetic particles or a magnetic object upon the first magnetic sensor,

either

under known predetermined physical conditions,

to detect the presence of magnetic particles or a magnetic object when a second difference as the difference between a first difference and a reference difference has an amplitude greater than a predetermined detection threshold,

the reference difference being the difference between a first voltage measurement carried out by the first sensor that has no magnetic particles thereon and a second voltage measurement carried out by the second sensor that has no magnetic particles thereon under the same known predetermined physical conditions,

the first difference being determined by the first voltage measurement device as the difference between the first voltage measurement carried out by the first sensor that has magnetic particles thereon and the second voltage measurement carried out by the second sensor that has no magnetic particles thereon,

and the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT,

either

when the magnetic particles are molecular nanoparticles or a magnetic object switchable by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command ,

under known predetermined physical conditions, by varying the physical property magnitude over a predetermined range of the physical property,

to determine a curve as the evolution versus the physical property magnitude of the difference between a first set of differential voltage measurements and a second set of voltage measurements, the first set of voltage measurements being carried out by the first sensor that has magnetic particles thereon and the second set of voltage measurements carried out by the second sensor that has no magnetic particles thereon, and then

to detect the presence of magnetic particles or magnetic object when the curve exhibits a switching physical property interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

According to particular embodiments of the first and second micromagnetometry systems, wherein the magnetic particles are comprised in the family of:

- Any switchable molecular nanoparticles in form of $A_hB_k[M(CN)_6]_l \cdot mH_2O$, where A can be Co, Ni, Fe, etc, B and M can be various transition metals (Fe^{II}, Fe^{III}, Mn^{II}, Mn^{III}, fml aCo^{II}, Co^{III}, ...) and C is an alkali metal cation;

- Any paramagnetic particles: Fe₂O₃, Fe₃O₄, Fe@Fe₃O₄, CoFe@Fe₃O₄, Ni, ...;
- Any ferromagnetic particles: Fe, CoFe, Ni;
- Any antiferromagnetic particles;
- Any particles with multilayer structure Ti/Fe, Cr, NiO, Co₃O₄, a-Fe₂O₃, CuO, MnO, Cr₂O₃ nanoparticles;
- Any magnetic bead made of Fe₃O₄ in the polymer matrix with the sphere shape and any size ranging from 50 nm to 10 μ m.

The invention also relates to a first detection method for detecting the presence of very small quantities of magnetic particles carried out by a micromagnetometry system, comprising the following steps of

firstly, calibrating in temperature under first known predetermined physical conditions the first magnetic sensor when the system comprises a single first magnetic sensor, or the set of the first and second magnetic sensor when the magnetometry system comprises a first magnetic sensor and a second magnetic sensor by providing a first calibration background thermal noise curve; then

deposit an unknown amount of magnetic particles upon the first magnetic sensor; then,

under the same first known predetermined physical conditions, by varying temperature on a predetermined range of temperature,

when the magnetometry system comprises a first single magnetic sensor, outputting a second curve as the evolution of differential voltage measurements carried out by the first sensor versus temperature, or

when the magnetometry system comprises a first magnetic sensor and a second magnetic sensor, outputting a first set of differential voltage measurements carried out by the first sensor that has magnetic particles thereon and a second set of differential voltage measurements carried out by the second sensor that has no magnetic particles thereon,

and determining a second curve as the evolution versus temperature of the difference between the first set of differential voltage measurements and the second set of differential voltage measurements;

5 determining a third curve as the difference versus temperature between the differential voltages of the second curve and the differential voltages of the first curve within the same range of temperature; and

10 detecting the presence of magnetic particles when the absolute value of voltage differences of the third curve remains stable above a predetermined detection threshold or the third curve exhibits a temperature interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

15 The invention also relates to a second detection method for detecting the presence of very small quantities of magnetic particles carried out by a micromagnetometry system, comprising the following steps of

depositing an unknown amount of magnetic particles upon the first magnetic sensor, the magnetic particles being switchable molecular nanoparticles by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command, then

20 in a next step, under known predetermined physical conditions, by varying the physical property magnitude over a predetermined range of the physical property,

when the magnetometry system comprises a first single magnetic sensor, outputting a first curve as the evolution of differential voltage measurements carried out by the first sensor versus the magnitude of the physical property, or

25 when the magnetometry system comprises a first magnetic sensor and a second magnetic sensor, outputting a first set of differential voltage measurements carried out by the first sensor that has magnetic particles thereon and a second set of differential voltage measurements carried out by the second sensor that has no magnetic particles thereon, and determining a first curve as the evolution versus the physical property of the difference between the first set of differential voltage measurements and the second set of differential voltage measurements; then

30 determining over the predetermined range of the physical property a second curve as a fitting curve from a lower portion of the first curve, this lower portion of the first curve corresponding to a lower interval included within the predetermined range of the physical property having its upper bound lower than the predetermined switching threshold;

determining a third curve as the difference versus the magnitude of the switching physical property between the differential voltages of the first curve and the differential voltages of the second curve within the same range of magnitude of the physical property; and

5 detecting the presence of magnetic particles when the third curve exhibits a switching physical property interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

10 According to particular embodiments, in the second detecting method for detecting the presence of very small quantities of magnetic particles, the switching physical property is temperature, pressure, optical irradiation, electrical field, magnetic field, chemical guest molecules.

15 The invention also relates to a third detection method for detecting the presence of very small quantities of magnetic particles down to a single magnetic particle or a single magnetic object in nano or micro scale carried out by a micromagnetometry system, comprising the following steps of

depositing an unknown amount of magnetic particles or a single magnetic object upon the first magnetic sensor, then

either

20 under known predetermined physical conditions,

outputting a first voltage measurement carried out by the first sensor that has magnetic particles thereon and a second voltage measurement carried out by the second sensor that has no magnetic particles thereon, and determining a first difference between the first voltage measurement and the second voltage measurement; then

25 detecting the presence of magnetic particles or a magnetic object when a second difference as the difference between the first difference and a reference difference has an amplitude greater than a predetermined detection threshold,

30 the reference difference being the difference between a first voltage measurement carried out by the first sensor that has no magnetic particles thereon and a second voltage measurement carried out by the second sensor that has no magnetic particles thereon under the same known predetermined physical conditions, and the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT,

either

when the magnetic particles are molecular nanoparticles or a single object switchable by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command ,

under known predetermined physical conditions, by varying the physical property magnitude over a predetermined range of the physical property, then

outputting a first set of voltage measurements carried out by the first sensor that has magnetic particles thereon and a second set of voltage measurements carried out by the second sensor that has no magnetic particles thereon, and determining a curve as the evolution versus the physical property magnitude of the difference between the first set of differential voltage measurements and the second set of voltage measurements; then

detecting the presence of magnetic particles or magnetic object when the curve exhibits a switching physical property interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT,

The invention also relates to a humidity or gas sensing measurement system comprising a micromagnetometry system, wherein the particles are molecular nanoparticles are switchable by overstepping a predetermined temperature switching threshold, the predetermined temperature switching threshold depending on the humidity of the degree environment, or on the environment concentration of any vapour of external molecules,

and wherein

the processing unit is configured to determine the humidity degree or the environment concentration of the vapour of external molecules from magnetic field change measurements of magnetic particles that are sensitive to the humidity degree or the environment concentration of the vapour of external molecules, and from a previously determined mapping curve between a calibrated humidity degree or a calibrated environment concentration of the vapour of external molecules measured by another method and a corresponding parameter such as a temperature threshold, a transition temperature, or a width of an hysteresis loop determined through the magnetic property change of the magnetic particles detected by the micromagnetometry method as defined hereabove.

According to a particular embodiment, in the humidity or gas sensing measurement system, the vapour of external molecules that can be detected are amongst the external molecules of the family consisting of N₂, He, I₂, CO₂, ethanol, methanol, 2-propanol, acetone, D₂O, CS₂ , CO, Iode (I), brome (Br), chlore (Cl), benzene, toluene,

chlorobenzene, bromobenzene, iodobenzene, dichlorobenzene, trichlorobenzene, pyrazine, pyridine, pyrrole, thiophene, furane, thf.

A better understanding of the invention will be facilitated by reading the following description, which is given solely by way of examples and with reference to drawings in which:

- Figure 1 is a view of the architecture of a micromagnetometry system according to a first embodiment of the invention wherein an exciting magnetic field H_{AC} is generated by means external to the sensor;

- Figure 2 is a planar detailed view of the hybrid AMR/PHR multi-ring magnetic sensor used by the micromagnetometry system of Figure 1;

- Figure 3 is an electrical schematic view of the hybrid AMR/PHR multi-ring magnetic sensor of Figure 2;

- Figure 4 is a view of different profiles of the detection voltage versus the bias magnetic field, each profile being characterized by the orientation angle α formed between the easy axis of the magnetic sensor and the external magnetic field direction;

- Figure 5 is a view of the evolution of the sensitivity deduced from the profiles of Figure 4 versus the orientation angle α ;

- Figure 6 is a view of the architecture of a micromagnetometry system according to a second embodiment of the invention wherein the exciting magnetic field H_{AC} is generated partly by the first magnetic sensor itself;

- Figure 7 is a view of the architecture of a micromagnetometry system according to a third embodiment of the invention wherein a second magnetic sensor has been added as a calibrating magnetic sensor;

- Figure 8 is an example of a flow diagram of a micromagnetometry detection method according a first embodiment of the invention, the method being carried out when magnetic particles are switchable molecular nanoparticles by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command;

- Figure 9 is an exemplary view of a first curve of the evolution versus temperature of measurement voltages provided by the micromagnetometry system of Figure 1 when SCO particles are deposited on the active surface of the first magnetic sensor the temperature ranging from 300 K to 350 K, and of a corresponding fitting second curve determined by the method of Figure 6;

- Figure 10 is a view of the third curve determined from the first and second curves of Figure 7 according to the method of Figure 6;

- Figure 11 is an example of flow diagram of a micromagnetometry detection method according a second embodiment of the invention carried out for a broader family of magnetic particles including magnetization switchable molecular nanoparticles, paramagnetic particles, ferromagnetic particles, anti-ferromagnetic particles, magnetic beads made of Fe_3O_4 in a polymer matrix;

5 - Figure 12 is a view of a calibration background noise curve representative of the thermal magnetic response of the first magnetic sensor without any magnetic particles deposited thereon;

10 - Figure 13 is a view of transition temperatures of SCO particles detected under two different humidity conditions, 80% and 60% respectively,

- Figure 14 is a partial view of an example of a variant of the micromagnetometry system of Figure 7 wherein the two multi-ring magnetic sensors are replaced by cross shape magnetic sensors.

15 According to Figure 1, a micromagnetometry system 2 for detecting the presence of very small quantities of magnetic particles comprises a first magnetic hybrid Anisotropic Magneto-Resistive AMR/ Planar Hall Resistive PHR multi-ring magnetic sensor 4, a first current or voltage source 6, a first voltage measurement device 8, a set 10 of at least one magnetic particles 12 deposited on an active surface 14 of the first magnetic sensor 4, a first environmental temperature sensor 16, means 18 for controlling and/or regulating the 20 environmental temperature of the magnetic particles, means 20 for creating a magnetic alternating excitation field H_{AC} to produce by each magnetic particle a stray magnetic field, means 21 for creating a magnetic sensor bias field H_{DC} , and a processing unit 22.

25 The first magnetic hybrid AMR/PHR multi-ring magnetic sensor 4 or first magnetic sensor includes on its active surface 14 a magnetic track 24 of a closed loop shape deposited on a substrate 26.

The first magnetic sensor 4 has a first current terminal 28 and a second current terminal 30 forming a pair of current terminals which face each other contacting with the closed loop magnetic track 24.

30 The first magnetic sensor 4 has a first voltage terminal 32 and a second voltage terminal 34 forming a pair of voltage terminals which face each other contacting with the closed loop magnetic track 24 and from which an output differential voltage is detected.

35 The first magnetic sensor 4 has a first axis 40 or easy axis passing through the first and second current terminals 28, 30 being parallel to the exchange bias field direction of the material and perpendicular to a second axis 42 passing through the first and second voltage terminals 32, 34.

The first current or voltage source 6, connected between the first and second current terminals, is configured to inject a DC bias current I for the first magnetic sensor 4 through the pair of the first and second current terminals 28, 30. The first current source 6 is for example a Keithley 2400 current source and the amplitude of the DC bias current is set 5 equal to 1mA.

The first voltage measurement device 8 is connected between the first and second voltage terminals 32, 34 for measuring a differential voltage V_b between the pair of voltage terminals 32, 34.

The first voltage measurement device 8 comprises a low noise amplifier 44 with a 10 gain of 20 dB for amplifying the detected differential voltage and driving the output signal obtained to a synchronizing amplifying device 46 based on a phase lock loop. The synchronizing amplifier is configured to lock the measured differential voltage signal onto the magnetic alternating excitation field signal and to detect the peak measured differential voltage measured at the output of the pair of voltage terminals 32, 34.

The first environmental temperature sensor 16 is configured to measure a 15 temperature representative of the actual environmental temperature T of the magnetic particles 12 and the first magnetic sensor 4, and is preferably located close to the active surface 14 of the first magnetic sensor 4. For instance, the environmental temperature sensor 16 is a platinum resistance of 100 Ohms.

The means 18 for controlling and/or regulating the temperature T are configured to 20 heat by a heater 48 in a controlled way the environment of the magnetic particles 12 and are preferably located close to the active surface 14 of the first magnetic sensor 4. The heater 48 is for instance a resistance Minco attached to the first magnetic sensor 4 and connected to a Lakeshore 332 temperature controller 50 that controls the environmental 25 temperature T variation by varying the temperature T from 300 K to 350 K.

The means 20 for creating an alternating magnetic excitation field H_{AC} is configured to make produce by each magnetic particle 12 a stray magnetic field oscillating along the time at a constant frequency ω ranging from 10 to 3 KHz, here set to 100 Hz.

The means 20 for creating the alternating magnetic excitation field H_{AC} comprises 30 here a second current source 52 supplying a AC current oscillating at the frequency of 100 Hz, and at least one coil, here two Helmholtz coils 54, connected to the second AC current source 52.

The two Helmholtz coils 54 are positioned relative to the first magnetic sensor 4 so 35 that a main component of the magnetic excitation field H_{AC} is collinear with the first axis 40.

The means 20 for creating an alternating magnetic sensor bias field H_{DC} is configured to shift the operating point of the first magnetic sensor 4 to a highest sensitivity region, the magnetic sensor bias field H_{DC} being constant along the time, and being collinear with the alternating magnetic excitation field H_{AC} .

5 The bias angle α formed between the first axis 40 passing through the first and second current terminals and the axis of the magnetic sensor bias field H_{DC} is selected in the range of [0 degree, 90 degree] so that the sensitivity S of the first magnetic sensor 4 is maximal. Here, this angle α equals to 20 degrees.

10 Whole the first magnetic sensor 4 and subsequently all the magnetic particles 12 deposited thereon are thus placed under an hybrid alternative and continuous magnetic field ($H_{AC} + H_{DC}$) the direction thereof forms an angle of 20 degree with the easy axis 40 of the first magnetic sensor 4.

15 With the combination of both H_{AC} and H_{DC} field, the sensitivity S of the first magnetic sensor 4 is enhanced.

15 Here, H_{DC} shifts the operating point of the magnetic sensor 4 to the highest sensitivity region, the optimized magnitude of the magnetic field being equal here to 1.4 mT.

20 The field H_{AC} introduced to generate the stray field of the SCO nano-particles 12 equals here to 0.5 mT in rms value at the frequency of 100 Hz.

20 The set 10 of the at least one magnetic particles 12 are deposited on the surface of the magnetic sensor.

25 Here, the magnetic particles 12 are $[Fe(hptrz)_3](OTs)_2$ Spin-Crossover nanoparticles elaborated in an homogenous solution of chloroform. They are directly dropped on the whole active surface 14 of the first magnetic sensor.

25 The magnetic particles 12 to be detected are thus motionless and placed close to or in contact with the active surface 14 of the first magnetic sensor 4.

30 These magnetic SCO nanoparticles 12 exhibit a magnetic signature corresponding to the diamagnetic to paramagnetic transition wherein the transition temperatures or switching temperatures under open air with a predetermined degree of humidity are $T_{1/2\downarrow}$ equal to 325 K and $T_{1/2\uparrow}$ equal to 331 K while cooling and heating respectively.

These transition temperatures have been verified by an optical reflectance change test that shows the same values under the same humidity conditions.

35 The processing unit 22 is configured for detecting from a set of different differential voltages measured by the first voltage measurement device 8 a magnetic flux shift representative of the presence of at least one deposited magnetic particle 12 on the active surface 14 of the first magnetic sensor 4.

The magnetic particles 12 are assumed here to be molecular nanoparticles switchable in terms of a transition between two magnetic states when overstepping a predetermined temperature switching threshold, the temperature operating as a switching or actuating command.

5 The processing unit 22 is configured to, after the deposit of an unknown amount of magnetic particles 12 upon the first magnetic sensor 22 and after varying the temperature T over the predetermined temperature range, determine a first curve of the evolution versus temperature of the differential voltage measurements outputted by the first voltage measurement device 8 and carried out under the known environmental physical 10 conditions and operating system settings.

The processing unit 22 is configured to subsequently determine over the predetermined range of temperature a second curve as a fitting curve from a lower portion of the first curve, this lower portion of the first curve corresponding to a lower interval included within the predetermined range of temperature, the lower interval having its 15 upper bound lower than the temperature switching threshold.

The processing unit 22 is configured to, subsequently determine a third curve as the difference versus the temperature of the differential voltages of the first curve and the differential voltages of the second curve within the same range temperatures, namely [300K, 350K].

20 The processing unit 22 is configured to subsequently detect the presence of at least one magnetic particle when the third curve exhibits a temperature interval wherein a voltage transition occurs and when the amplitude of this transition is greater than a predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10 nT.

25 As a variant, the micromagnetometry system comprises a second sensor for measuring a physical property different from temperature, placed close to the active surface of the active sensor, the switching of a magnetization of the magnetic particles between two magnetization states being actuated when the physical property different from temperature is above or below a predetermined switching threshold.

30 As a variant, the micromagnetometry system comprises second means for controlling and/or regulating a physical environmental property different from temperature, placed preferably close to the active surface of the active sensor.

35 As a variant, the processing unit is configured to provide of a first calibration background thermal noise curve by calibrating in temperature under first known predetermined physical conditions the first magnetic sensor that has no magnetic particles thereon.

The processing unit is configured to after deposit of an unknown amount of magnetic particles upon the first magnetic sensor, by varying temperature on a predetermined range of temperature under the same first known predetermined physical conditions, to subsequently determine a second curve of the evolution versus temperature of differential voltage measurements corrected or not from the evolution of differential voltage measurements carried out by the first magnetic sensor.

The processing unit is configured to subsequently determine a third curve as the difference versus temperature between the differential voltages of the second curve and the differential voltages of the first curve within the same range of temperature.

The processing unit is configured to detect the presence of magnetic particles when the absolute value of voltage differences of the third curve remains stable above a predetermined detection threshold or the third curve exhibits a temperature interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

According to figure 2, the first magnetic sensor 4 is based on a multi-ring architecture and is manufactured using a lithography technique in a clean-room of class 1000 with a lift-off process.

Here, the magnetic track 24 is a tri-layered material, for example Ta(3)/NiFe(20)/Cu(0.2)/IrMn(10)/Ta(3) (nm). In this structure, the soft magnetic layer NiFe is the sensing material that is weakly coupled to an anti-ferromagnetic layer (IrMn) by a long range exchange bias field through a few atomic Cu layer.

The tri-layer structure Ta(3)/NiFe(20)/Cu(0.2)/IrMn(10)/Ta(3) nm is deposited by a 6 gun-magnetron sputtering system with a based vacuum of about 10^{-8} Torr.

To prevent the contamination, the magnetic sensor is passivated by a $\text{Si}_2\text{O}_3/\text{Si}_3\text{N}_4$ bi-layer with a nominal thickness of 200 nanometers.

The outer diameter of the first magnetic sensor 4 is equal here to 300 μm and the width w of the magnetic track 24 is equal to 10 μm .

The magnetic track 24 of the first magnetic sensor 4 has:

- a first arm 102 made of a first set of a predetermined ring number m of circular meander paths 104 delimited within a first quarter surface 126 of the magnetic sensor 4, the outermost meander path 128 being connected to the first current terminal 30 and the innermost meander path 110 being connected to the first voltage terminal 32,

- a second arm 112 made of a second set of the same predetermined number m of circular meander paths 114 delimited within a second quarter surface 116 of the magnetic sensor 4, the outermost meander path 118 being connected to the second current

terminal 30 and the innermost meander path 120 being connected to the first voltage terminal 32,

5 - a third arm 122 made of a third set of the same ring number m of circular meander paths 124 delimited within a third quarter surface 126 of the magnetic sensor 4, the outermost meander path 128 being connected to the second current terminal 30 and the innermost meander path 130 being connected to the second voltage terminal 34,

10 - a fourth arm made 132 of a fourth set of the same ring number m of circular meander paths 134 delimited within a fourth quarter surface 136 of the magnetic sensor 4, the outermost meander path 138 being connected to the first current terminal 30 and the innermost meander path 140 being connected to the second voltage terminal 34.

This multi-ring architecture enhances the sensitivity of the magnetic sensor in a compact region.

As the length of the arms increases with the ring number, filling the sensing meander paths enhances the active sensing area.

15 The current direction alternately changes for successive ring paths, i.e. there is a current angle range $\theta = \pi/2$ to 0 for path 1 shown in the inset of Figure 2, and $\theta = \pi$ to $3\pi/2$ for path 2 in the inset of Figure 2. The sign of the calculated value for path 1 and 2 is the same, which means that AMR effect for both currents is additive. Thus, the maximum voltage variation in the profiles and accordingly the field sensitivity of the arm 20 resistance increases the ring number.

The voltage profile for the full magnetic ring, that is the sum of the AMR and PHR effects, reveals anti-symmetric behavior with the applied field due to self-balancing of ring arm resistances, where the voltage variations are additive for all junction components.

25 The sensitivity of first magnetic sensor is enhanced by using a tri-layer structure which has a small exchange coupling field and high active current.

This multi-ring architecture enhances the field sensitivity and the active area of the magnetic sensor.

30 Thus, the first magnetic sensor is a highly sensitive hybrid magneto-resistive (MR) sensor combining Anisotropic Magneto Resistive (AMR) and Planar Hall Effect (PSE) that is capable to detect the switching of the spin states of SCO nano-particles.

Preferably the ring number m of circular meander paths is comprised between 9 and 13. Here, each arm has eleven meander paths or quarters of circular rings, this number maximizing the sensitivity of the first magnetic sensor 4.

35 This multilayer stack exhibits a very high sensitivity of about $S = 15 \text{ volts} / \text{T}^{-1}$ and a low white noise of about $1 \text{ nV} \cdot \text{Hz}^{-1/2}$ at 100 Hz.

According to the electrical scheme of Figure 3, the multi-ring geometry of the track and the connectivity of the four arms lead to a Wheatstone bridge configuration.

The output voltage of first the magnetic sensor is known as the planar effect Hall effect and is given the equation:

5 $V_{PHE} = V_0 \sin \theta \cos \theta$

Where V_0 depends upon the structure parameter of the sensor such as parallel resistivity ρ_{\parallel} and perpendicular resistivity ρ_{\perp} relative to magnetization of the sensor, the thickness t of the sensor, and the size of the sensor, θ is the angle between the direction of the actual magnetization and the applied magnetic field.

10 The ring architecture advantageously provides with high sensing performance due to the Wheatstone bridge electrical configuration.

In the general case, the differential voltage V_b detected between the first voltage $V1$ of the first voltage terminal and the second voltage $V2$ of the second voltage terminal is described by the following equation:

15
$$V_b = \left(\frac{R_4}{R_3 + R_4} - \frac{R_2}{R_1 + R_2} \right) V_0$$

where R_1 , R_2 , R_3 , R_4 designates the resistance of the first, second, third and fourth arms 102, 112, 122, 132 respectively.

Three different detection loading configurations are contemplated.

20 In a first configuration referenced as "quarter bridge configuration", the magnetic particles are deposited on a single arm, for instance on the fourth arm 132, the remaining three arms 102, 112, 122 having no magnetic particles thereon.

In this first configuration, the resistances R_1 , R_2 , R_3 of the first, second, third arms 102, 112, 122 equal to a same reference resistance value R , and the resistance R_4 of the fourth arm 132 equals to $R + \Delta R$.

25 In this first case, the detected different voltage denoted V_{b1} follows the equation:

$$V_{b1} = \left(\frac{\Delta R / R}{2(2 + \Delta R / R)} \right) V_0$$

30 In a second configuration case referenced as "half bridge configuration", the magnetic particles 12 are deposited onto two opposite arms, for instance onto the second and the third arms 112, 122, the remaining two arms 102, 132 having no magnetic particles thereon.

In this second configuration, the resistances R_1, R_4 of the first and fourth arms 102, 132 equal to the same reference resistance value R , and the resistance R_2, R_3 of the loaded second and third arms 112, 122 equals to $R + \Delta R$.

In this second configuration the detected different voltage denoted V_{b2} follows the equation:

$$V_{b2} = \left(\frac{\Delta R / R}{2 + \Delta R / R} \right) V_0$$

In a third configuration referenced as "full bridge configuration", the magnetic particles are deposited onto whole the surface of magnetic sensor, namely the four arms.

In this third configuration, the resistances R_1, R_4 of the first and fourth arms 102, 132 equal to the same resistance value $R + \Delta R$, whereas the resistances R_2, R_3 of the loaded second and third arms 112, 122 equals to $R - \Delta R$.

In this third configuration the detected different voltage denoted V_{b3} follows the equation:

$$V_{b3} = \frac{\Delta R}{R} \cdot V_0$$

Among the three above described configurations, the full bridge configuration exhibits the highest sensitivity.

According to Figure 4, the first micro-magnetometry magnetic sensor as described in Figure 3 is characterized with different values of the bias angle α formed between the easy axis 40 of the magnetic sensor and the magnetic bias field direction.

A set 200 of various profiles 202, 204, 206, 208, 210, 212 are shown corresponding to a bias angle α set to 0, 10, 20, 45, 60, 90 degrees, respectively.

The bias current of the magnetic sensor 4 remains set to 1 mA. The bias magnetic field H_{DC} is swept in the range of -20 to 20 mT.

The sensitivity S at a point of a profile, defined as the slope dV/dH , is deduced from the voltage profiles, the maximum of the sensitivity for each bias angle α value being sketched in the curve 220 as shown in Figure 5.

The bias angle α formed between the bias magnetic field H_{DC} and the easy axis 40 is selected so that the sensitivity S is maximal.

From the curve 220 shown in the Figure 5, the sensitivity S is maximal for α equal to 20 degrees and is equal to the 16 V.T^{-1} . This value of 20 degrees for the bias angle α has been chosen in the Figure 1.

When a micromagnetometry system 2 is used, the effective measured voltage V_{eff} between the two voltage terminals and output from the measurement voltage device contains two contributions: a concave voltage response V_{drift} and a voltage response horizontally caused by the straight field generated from the magnetic particles V_{stray} .

5 Thus, the effective voltage V_{eff} can be expressed as:

$$V_{\text{eff}} = V_{\text{drift}} + V_{\text{stray}}$$

The voltage response of the sensor can be well described by the following expression:

$$V_{\text{drift}} = C \frac{I}{t} (\rho_{\parallel} - \rho_{\perp})$$

10 Where I is the DC bias current applied to the magnetic sensor 4, t, ρ_{\parallel} , ρ_{\perp} are, respectively, the thickness and the resistivity of the sensing layer in case of current parallel an perpendicular to magnetization.

According to Figure 6, a second embodiment of a micromagnetometry system 302 according to the invention is derived from the micromagnetometry system 2 of Figure 1 and comprises some parts that are designated by the same reference numerals.

15 The micromagnetometry system 320 of Figure 6 differs from the micromagnetometry system of Figure 1 in that the means 20 for creating the magnetic excitation field H_{AC} external to the first magnetic sensor 4 are removed and replaced by the set 320 formed by the first magnetic sensor 4 and a modified first current source 326, connected between the first and second current terminals 28, 30.

20 In this second embodiment, the modified first current source is configured to generate an alternating current (AC) oscillating along the time at a constant frequency ω ranging from 10 to 3 KHz, here set to 100 Hz.

25 By self-induction, the magnetic track 24 of the first magnetic sensor 4 supplied with an alternating current (AC) by the first modified current source 326 generates a magnetic excitation field H_{AC} to make produce by each magnetic particle a stray magnetic field, the stray magnetic field being detectable by the first magnetic sensor.

30 In other words, when the AC bias current I is applied to the first magnetic sensor 4, the magnetic sensor 4 generates a magnetic field globally surrounding the easy axis 40, the direction of the flux obeying the Ampere's law.

The measured voltage V_b between the voltage terminals can be written as:

$$V_b = S_0 \langle H_{\perp} \rangle + I \cdot R_{\text{offset}}$$

Where I is the magnetic sensor current, S_0 is the sensitivity of the magnetic sensor, $\langle H_{\perp} \rangle$ is the magnetic field averaged over the surface of the magnetic sensor.

In these measurements, the motionless magnetic particles disposed close to the active surface of the sensor are magnetized by the sensor self magnetic field H_{self} .

5 Using that H_{self} is proportional to I and assuming that the particle magnetization is directly proportional to the applied field, the stray field $\langle H_{stray} \rangle$ from the magnetic particles averaged over the magnetic sensor surface can be written as:

$$\langle H_{stray} \rangle = \gamma \cdot \chi \cdot I$$

10 where χ is the susceptibility of the magnetic particle and γ is a constant of proportionality depending on the magnetic sensor geometry and on the volume distribution of the magnetic particles.

Using the self field to magnetize the magnetic particles ensures that only the magnetic particles deposited close to the active surface of the first magnetic sensor will be magnetized.

15 Similarly to the micromagnetometry system of Figure 1, the measured voltage V_{eff} between the two voltage terminals and output from the measurement voltage device contains two contributions: a concave voltage response V_{drift} and a voltage response horizontally caused by the straight field generated from the magnetic particles V_{stray} , and can be expressed as:

$$V_{eff} = V_{drift} + V_{stray}$$

According to Figure 7, a third embodiment of a micromagnetometry system 402 according to the invention is derived from the micromagnetometry system 2 of Figure 1 and comprises some parts that are designated by the same reference numerals.

25 The micromagnetometry system 402 of Figure 7 differs from the micromagnetometry system of Figure 1 in that it comprises further a second hybrid AMR/PHR multi-ring magnetic sensor 404 and in that the first voltage measurement device 8 of Figure 1 is replaced by a modified voltage measurement device 408.

The second magnetic sensor 404 has the same structure as the one of the first magnetic sensor and has closed loop magnetic track 424 with the same shape pattern.

30 The second magnetic sensor 404 has a first current terminal 428 and a second current terminal 430 forming a pair of current terminals which face each other contacting with the closed loop magnetic track 424.

The second magnetic sensor 404 has a first voltage terminal 432 and a second voltage terminal 434 forming a pair of voltage terminals which face each other contacting with the closed loop magnetic track 424 and from which an output differential voltage is detected.

5 The second magnetic sensor 404 has an easy axis 440 defined as the axis passing through the first current terminal 428 and the second current terminal 430.

The first and the second magnetic sensors 4, 404 are placed so that their respective easy axis 40, 440 are collinear.

10 The first and the second magnetic sensors 4, 404 are placed close to each other on the same substrate under the same known physical conditions so that the same magnetic field when no magnetic particles are deposited onto the sensors with the same noise are received and detected.

15 The first current terminal 428 and the second current terminal 430 of the second magnetic sensor are respectively connected to the first current terminal 28 and the second current terminal 30 of the first magnetic sensor 4.

Thus, the first current or voltage source 6 supplies with in parallel the first magnetic sensor 4 and the second magnetic sensor 404 with respective current having the same noise characteristics.

20 The modified first voltage measurement device 408 is based upon the first voltage measurement device 8 of Figure 1, wherein a second low noise amplifier 444 and a differential unit 450.

25 The second low noise amplifier 444 with a gain of 20 dB is connected at its inputs to a first voltage terminal 432 and a second voltage terminal 434 and at its output to a first input of the differential unit 450.

The first low noise amplifier 4 is connected at its output to a second input of the differential unit 450.

The differential unit 450 has an output connected to the synchronizing amplifying device 46 based on a phase lock loop.

30 The differential unit 450 is configured to determine the difference voltage between the amplified differential voltage detected at the voltage terminals of the first magnetic sensor 4 and the amplified differential voltage detected at the voltage terminals of the second magnetic sensor 404.

Thus the sources of noises common to the two magnetic sensors are canceled by the subtraction unit 450.

35 As a variant of the micromagnetometry system 402 of Figure 7, the means 20 for creating the magnetic excitation field H_{AC} external to the first magnetic sensor 4 are

removed and replaced by the set 320 formed by the first magnetic sensor 4 and a modified first current source 326, connected between the first and second current terminals 28, 30.

According to Figure 8, a first embodiment of a micromagnetometry detection method 500 for detecting the presence of very small quantities of magnetic particles is carried out by a micromagnetometry system as defined in the Figures 1, 6 and 7.

This method 500 is applicable to any for magnetic particles that are switchable molecular nanoparticles by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command. Such magnetic particles are any switchable molecular nanoparticles in form of $A_hB_k[M(CN)_6]_l \cdot mH_2O$, where A can be Co, Ni, Fe, etc, B and M can be various transition metals (Fe^{II}, Fe^{III}, Mn^{II}, Mn^{III}, fml aCo^{II}, Co^{III}, ...) and C is an alkali metal.

The micromagnetometry detection method 500 comprises the following steps executed successively.

In a first step 502, an unknown amount of magnetic particles is deposited upon the first magnetic sensor, the magnetic particles being switchable molecular nanoparticles by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command.

In a following step 504, under known predetermined physical conditions, by varying the physical property magnitude over a predetermined range of the physical property,

when the magnetometry system comprises a first single magnetic sensor, a first curve as the evolution of differential voltage measurements carried out by the first sensor versus the magnitude of the physical property is provided, or

when the magnetometry system comprises a first magnetic sensor and a second magnetic sensor, a first set of differential voltage measurements carried out by the first sensor that has magnetic particles thereon and a second set of differential voltage measurements carried out by the second sensor that has no magnetic particles thereon are outputted, and a first curve is determined as the evolution versus the physical property of the difference between the first set of differential voltage measurements and the second set of differential voltage measurements.

Then, in a following step 506, over the predetermined range of the physical property a second curve is determined as a fitting curve from a lower portion of the first curve, this lower portion of the first curve corresponding to a lower interval included within the predetermined range of the physical property having its upper bound lower than the predetermined switching threshold.

Then, in a step 508, a third curve is determined as the difference versus the magnitude of the switching physical property between the differential voltages of the first curve and the differential voltages of the second curve within the same range of magnitude of the physical property.

5 In a next step 510, the presence of magnetic particles is detected when the third curve exhibits a switching physical property interval over which a transition occurs and when the amplitude of the transition is greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

10 According to Figure 9, a representative voltage profile 522 evolution of the effective voltage V_{eff} outputted by the micromagnetometry system 2 versus the environmental temperature T, and a fitting curve 524 are shown in a representation frame 520.

15 The representation frame 520 comprises an ordinate axis 526 of the outputted voltage expressed in mV and an abscissa axis 538 of the environmental temperature axis expressed in degree Kelvin.

The voltage profile 522 exhibits two contributions: a concave voltage response V_{drift} and a voltage response horizontally caused by the straight field generated from the SCO particles V_{stray} .

Thus, the effective voltage V_{eff} can be expressed as:

$$20 \quad V_{\text{eff}} = V_{\text{drift}} + V_{\text{stray}}$$

The voltage profile 522 also exhibits a hysteresis loop 530 having an upper curve portion in heating direction 532 and an lower curve portion in cooling direction 534. This hysteresis loop 530 is a magnetic signature of the SCO particles transition.

25 In practice, the voltage response of the magnetic sensor V_{drift} curve 524 is determined over the range of temperature [300 K, 350 K] as a fitting curve from a lower portion of voltage profile 522, this lower portion of the voltage profile 522 corresponding to a lower temperature interval included within the predetermined range of the physical property having its upper bound lower than the predetermined switching threshold. For example, the lower temperature interval is [300 K, 320 K].

30 According to Figure 10, a voltage profile 552 evolution of the stray field voltage V_{stray} versus the environmental temperature T is shown in a representation frame 550.

The voltage profile 552 evolution of the stray field voltage V_{stray} is derived from the subtraction of the voltage drift V_{drift} curve 524 to the effective voltage V_{eff} 522.

35 The subtraction is carried out by the processing unit 22 in the step 508 of the detection method 500.

The representation frame 550 comprises an ordinate axis 554 of the stray field voltage V_{stray} expressed in mV and an abscissa axis 556 of the environmental temperature axis expressed in degree Kelvin.

The voltage profile 552 exhibits a hysteresis loop 560 having a lower curve portion 562 in heating direction 564 and an upper curve portion 566 in cooling direction 568.

5 This hysteresis loop 560 is a magnetic signature of the SCO particles transition.

The transition temperatures are picked up at the middle eight of the hysteresis curves of the hysteresis loop 560.

10 With the dimensioning and the performance of the first magnetic sensor 4 as described here above, and with an average diameter of 250 nm for the SCO particles, the minimum magnetic field that can be detected by the magnetic sensor is equal to 10 nT.

15 As the detection capability of the magnetometer 2 depends on the sensor area, it is expected that by sizing the magnetic sensor to 500 nm, a single magnetic particle will deduce an amount of 25 nV. This makes possible to detect the magnetic signature of a single SCO particle at room temperature.

By integrating an amplifier in the close vicinity of the magnetic sensor or near the two magnetic sensors in the differential configuration, a local magnetic field down to one pico-Tesla (10^{-12} T) can be detected.

20 Generally, the width of one arm of the sensor ring is ranging from the nano-scale to the micro-scale and the effective size of the magnetometry is ranging from 50 nm to 1mm.

According to Figure 11, a second embodiment of a micromagnetometry detection 600 method is carried out for detecting the presence of very small quantities of magnetic particles.

25 This method 600 is applicable to any for magnetic particles that are switchable molecular nanoparticles by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command. Such magnetic particles are any switchable molecular nanoparticles in form of $A_hB_k[M(CN)_6]_l \cdot mH_2O$, where A can be Co, Ni, Fe, etc, B and M can be various transition metals (Fe^{II}, Fe^{III}, Mn^{II}, Mn^{III}, fml aCo^{II}, Co^{III}, ...) and C is an alkali metal cation .

30 This method is also applicable to any paramagnetic particles such as Fe_2O_3 , Fe_3O_4 , $Fe@Fe_3O_4$, $CoFe@Fe_3O_4$, Ni, to any ferromagnetic particles such as Fe, CoFe, Ni, to any antiferromagnetic particles i.e any particles with multilayer structure Ti/Fe, Cr, NiO, Co_3O_4 , a- Fe_2O_3 , CuO, MnO, Cr_2O_3 nanoparticles, and to any magnetic bead made of Fe_3O_4 in the polymer matrix with the sphere shape and any size ranging from 50 nm to 10 μ m.

The micromagnetometry detection method 600 for detecting the presence of very small quantities of magnetic particles can be carried out by a micromagnetometry system as defined in the Figures 1, 6 and 7.

The micromagnetometry detection method 600 comprises the following steps 5 executed successively.

In a first step 602, under first known predetermined physical conditions, when the system comprises a single first magnetic sensor 4 the first magnetic sensor is, or when the magnetometry system comprises a first magnetic sensor 4 and a second magnetic sensor 404 the set of the first and second magnetic sensor is calibrated in temperature and a first calibration background thermal noise curve is provided.

In a following step 604, an unknown amount of magnetic particles 12 is deposited upon the first magnetic sensor 4.

Then in a next step 606, under the same first known predetermined physical conditions, by varying temperature on a predetermined range of temperature, when the magnetometry system 2, 302 comprises a first single magnetic sensor 4, a second curve is outputted as the evolution of differential voltage measurements carried out by the first sensor versus temperature, or when the magnetometry system 402 comprises a first magnetic sensor 4 and a second magnetic sensor 404, a first set of differential voltage measurements carried out by the first sensor 4 that has magnetic particles thereon and a second set of differential voltage measurements carried out by the second sensor 404 that has no magnetic particles thereon are outputted. In the same step 506 a second curve is determined as the evolution versus temperature of the difference between the first set of differential voltage measurements and the second set of differential voltage measurements.

In a following step 608, a third curve is determined as the difference versus temperature between the differential voltages of the second curve and the differential voltages of the first curve within the same range of temperature.

Then, in a next step 610, the presence of magnetic particles is detected when the absolute value of voltage differences of the third curve remains stable above a predetermined detection threshold or the third curve exhibits a temperature interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

According to Figure 12, an example of a first calibration background thermal noise 35 profile is shown.

This calibration of the first magnetic sensor 4 or the set of the first and second magnetic sensor 4, 44 is carried out in the step 602 of the detection method 600.

During this thermal calibration step the first magnetic sensor 4 is unloaded i.e. without any magnetic particles deposited thereon and temperature is varied in the temperature once by increasing the temperature and once by decreasing the temperature.

The profile 650 comprises a first curve 652 corresponding to a heating direction and a second curve 654 corresponding to a cooling direction. These curves are identical and the calibration profile 650 does not exhibit any hysteresis cycle.

According to Figure 13, a set of two different hysteresis cycles or loops 672, 674 with their corresponding transition temperatures are shown for same used SCO particles detected under two different humidity conditions, 80% and 60% respectively.

These two hysteresis cycles 672, 674 are shown in a representation frame 670 that comprises an ordinate axis 676 of the normalized output voltage to an upper voltage and lower voltage of the hysteresis cycle and an abscissa axis 678 of the environmental temperature axis expressed in Kelvin degree.

The hysteresis loop 672 corresponding to 80% humidity exhibits a first transition temperature 680 and a second transition temperature 682.

The hysteresis loop 674 corresponding to 60% humidity exhibits a first transition temperature 692 and a second transition temperature 694.

It can be seen here that the transition temperatures as well as the width of a hysteresis loop can be used to estimate the humidity degree.

Such behaviour is therefore exploited to build a humidity measurement system comprising a micromagnetometry system as described in Figures 1, 6, and 7 wherein the particles are molecular nanoparticles switchable by overstepping a predetermined temperature switching threshold and sensitive to humidity degree, the predetermined temperature switching threshold or an hysteresis loop width depending on the humidity degree environment.

The processing unit is configured to determine the humidity degree from magnetic change measurements of the magnetic particles and a previously determined mapping curve between calibrated humidity degrees measured by another humidity measurement method and a corresponding temperature transition or hysteresis cycle width measured by the micromagnetometry method as described in Figure 8 or Figure 11.

In fact, by combining the magnetometry method of Figure 8 or Figure 11 and spin crossover, the system can be used as a gas sensor for detecting gas. Any external gas that affects the system like the humidity also shifts the spin crossover curves as a function of the environment gas concentration.

Thus any molecular nano-particles which are switchable by overstepping a predetermined temperature switching threshold, the predetermined temperature switching threshold depending on the environment concentration of some vapour of external molecules, can be used.

In such case, the processing unit is configured to determine the environment concentration of the vapour of external molecules from magnetic change measurements of magnetic particles that are sensitive to the environment concentration of the vapour of external molecules, and from a previously determined mapping curve between a calibrated environment concentration of the vapour of external molecules measured by another method and a corresponding parameter such as a temperature threshold, a transition temperature, or a width of an hysteresis loop determined through the magnetic property change of the magnetic particles detected by the micromagnetometry method described in Figure 8 or Figure 11.

The vapour of external molecules or the gas that can be detected are for example the following ones:

N₂, He, I₂, CO₂, ethanol, methanol, 2-propanol, acetone, D₂O, CS₂, CO, Iode (I), brome (Br), chlore (Cl), benzene, toluene, chlorobenzene, bromobenzene, iodobenzene, dichlorobenzene, trichlorobenzene, pyrazine, pyridine, pyrrole, thiophene, furane, thf.

The detection method 600 as described above in Figure 11 can be used for detection of the following particles:

- Any switchable molecular nanoparticles in form of A_hB_k[M(CN)₆]_l.mH₂O, where A can be Co, Ni, Fe, etc, B and M can be various transition metals (Fe^{II}, Fe^{III}, Mn^{II}, Mn^{III}, Co^{II}, Co^{III}, ...) and C is an alkali metal cation;
- Any paramagnetic particles: Fe₂O₃, Fe₃O₄, Fe@Fe₃O₄, CoFe@Fe₃O₄, Ni, ...;
- Any ferromagnetic particles: Fe, CoFe, Ni;
- Any antiferromagnetic particles: any particles with multilayer structure Ti/Fe, Cr, NiO, Co₃O₄, a-Fe₂O₃, CuO, MnO, Cr₂O₃ nanoparticles;
- Any magnetic bead made of Fe₃O₄ in the polymer matrix with the sphere shape and any size ranging from 50 nm to 10 µm.

This system can be used to detect a magnetization variation (magnetization commutation) of all magnetic materials (paramagnetic, diamagnetic, ferromagnetic, antiferromagnetic, ferrimagnetic) in different forms (materials in the form of microcristalline powders, nanoparticles, thin layer, etc.) and at any temperature. As representative examples, the following can be cited: metallic materials, metallic oxides, rare earth elements, organometallic complexes, coordination complexes (magnetic molecules, magnet chains, and in particular spin cross-over materials, transfer of load materials, etc.

Metals, metal oxides

As representative metal derivatives, the following can be cited : compounds such as Co, Ni, Fe, etc., as well as alloys AB, with A = Co, Ni, Fe, etc. and B = Pt, Fe, etc.

As representative metal oxides derivatives, the following can be cited: FeO, Fe₂O₃, CuO,

5 ZnO, etc.

Magnetic compounds and molecular complexes

As representative magnetic compounds and molecular complexes can be cited magnet molecules (Mn₁₂, etc.), magnet chains (homopolynuclear and heteropolynuclear compounds), etc.

10 As heteropolynuclear magnetic compounds, one can cite Prussian Blue and its analogues of general formula M_x[M'(CN)₆]_y.nH₂O et A_xM_y[M'(CN)₆]. nH₂O where A represents an alkaline cation and M and M' represent cations of divalent or trivalent transition metals such as Fe₄[Fe(CN)₆]₃.15H₂O, CsNi[Cr(CN)₆], etc.

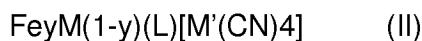
As spin cross-over materials can be cited iron complexes, in particular of formula (I):



in which :

- L represents a ligand such as trz (triazole), NH₂trz, Fatrz ((4-formylamino-1,2,4-triazol), Hptrz (heptyltriazole), etc. ;
- X represents an anionic counterion such as OTf (triflate ou trifluoromethanesulfonate), p-tol or tof (p-tolylsulfonate or tosyl), tetrafluoroborate, nitrate, Br, Cl, etc. ;
- x is an integer comprised between 0 et 10.

20 As alternative spin cross-over materials, one can cite the derivatives of general formula (II):



25 where :

- M represents a metal such as Ni or Co;
- M' represents a metal, identical or different from M, chosen from Ni, Pd, Pt, etc;
- L represents a bis-monodente ligand such as pyrazine (pz), azopyridine (azpy), bis(4-pyridyl)acetylene (bpac), etc. ;
- y is strictly comprised between 0 and 1, being different from 0 and from 1.

30 As a load transfer compounds, one can cite the derivatives formed by donor/acceptor pairs such as compound of formula [Fe(Cp^{*})₂][TCNE] (TCNE = tetracyanoethylene), [Mn(Cp^{*})₂][TCNQ] (TCNQ = tetracyanoquinodimethane), etc.

Other load transfer materials according to the invention also include the analogues of 35 Prussian Blue of general formula A_xM_y[M'(CN)₆]. nH₂O with A being a alkaline cation and

M and M' representing cations of divalent or trivalent transition metals such as $\text{Na}_x\text{Co}_y[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$, etc.

The detection method 500 as described above in Figure 8 can be used for detection of any switchable molecular nanoparticles as described above.

5 In a variant the current injected by the first current source passing through the current terminals is a sum of a direct current (DC) and an alternating current (AC).

Generally, the magnetic track is a bi-layered structure including a ferromagnetic film and an anti-ferromagnetic film, or a spin-valve structure, or a tri-layered structure including a ferromagnetic film, a metal and an anti-ferromagnetic film.

10 In a variant of the micromagnetometry system 402 of Figure 7, the first and second hybrid AMR/PHR multi-ring magnetic sensors 4, 404 are replaced by magnetic sensors having a same magnetic structure and a same shape amongst a cross shape or a single ring closed loop shape.

15 The first and the second magnetic sensors with a same shape amongst a cross shape or a single ring closed loop shape are placed so that their respective easy axis, are collinear in terms of direction i.e are parallel between each other.

20 The first and the second magnetic sensors are placed as close as possible on the same substrate under the same known physical conditions so that the same magnetic and temperature response when no magnetic particles are deposited onto the sensors with the same noise are received and detected.

The first current terminal and the second current terminal of the second magnetic sensor are respectively connected to the first current terminal and the second current terminal of the first magnetic sensor.

25 Thus, the first source current supplies with in parallel the first magnetic sensor and the second magnetic sensor with respective current having the same noise characteristics.

30 The structure of the modified voltage measurement device 408 remains the same and the modified voltage measurement device is configured to determine the difference voltage between the amplified differential voltage detected at the voltage terminals of the first magnetic sensor and the amplified differential voltage detected at the voltage terminals of the second magnetic sensor.

Thus the sources of noises common to the two magnetic sensors are canceled.

35 As for the micromagnetometry system 402 of Figure 7, the means 20 for creating the magnetic excitation field H_{AC} external to the first magnetic sensor 4 can be removed and replaced by a set formed by the first magnetic sensor, the second magnetic sensor and a modified first current source generating an alternating current between the first and

second current terminals of the first magnetic sensor, and between the first and second current terminals of the second magnetic sensor.

In fact all the variants described for a magnetometry system using one or two multi-ring magnetic sensors as described here above in terms of current biasing and means for creating an external magnetic field can be used for a magnetometry system using two magnetic sensors having a same shape amongst a cross shape or a single ring closed loop shape, and connected between each other in a differential way.

The same detection methods as described in Figure 5 and 8 can also be used.

An example of such a variant of micromagnetometry system 702 is partly illustrated in Figure 14 wherein the two multi-ring magnetic sensors 4, 404 of Figure 7 are replaced by two cross shape magnetic sensors 706, 726.

The first and the second magnetic sensors 706, 726 with the same cross shape are placed close to each other on the same substrate under the same known physical conditions so that the same magnetic field when no magnetic particles are deposited onto the sensors with the same noise are received and detected.

The first and the second magnetic sensors 706, 726 are placed so that their respective easy axis are collinear in terms of direction i.e are parallel between each other.

In a variant, when the micromagnetometry system used comprises a first and a second hybrid AMR/PHR multi-ring magnetic sensors 4, 404 as described in Figure 7 or comprises two magnetic sensors having a same magnetic structure and a same shape amongst a cross shape or a single ring closed loop shape, a direct detection method can be used.

Such a micromagnetometry direct detection method is used for detecting the presence of very small quantities of magnetic particles down to a single magnetic particle or a single magnetic object in nano or micro scale.

A micromagnetometry direct detection method according to a first embodiment comprises the following steps.

After depositing an unknown amount of magnetic particles or a magnetic object upon the first magnetic sensor, in a first step, under known predetermined physical conditions, a first voltage measurement carried out by the first sensor that has magnetic particles thereon and a second voltage measurement carried out by the second sensor that has no magnetic particles thereon are outputted.

In a second step, a first difference between the first voltage measurement and the second voltage measurement is determined.

In a third step, the presence of magnetic particles or a magnetic object is detected when a second difference as the difference between the first difference and a reference

difference has an amplitude greater than a predetermined detection threshold, the reference difference being the difference between a first voltage measurement carried out by the first sensor that has no magnetic particles thereon and a second voltage measurement carried out by the second sensor that has no magnetic particles thereon under the same known predetermined physical conditions, and the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

5 A micromagnetometry direct detection method according a second embodiment is applicable when the magnetic particles are molecular nanoparticles or a single object switchable by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command.

10 The direct detection method comprises the following steps.

15 After depositing an unknown amount of magnetic particles or a magnetic object upon the first magnetic sensor, in a first step, under known predetermined physical conditions, the physical property magnitude is varied over a predetermined range of the physical property.

20 In a second step carried in parallel with the first step, a first set of voltage measurements carried out by the first sensor (4) that has magnetic particles thereon and a second set of voltage measurements carried out by the second sensor (404) that has no magnetic particles thereon are outputted.

In a third step, a curve is determined as the evolution versus the physical property magnitude of the difference between the first set of differential voltage measurements and the second set of voltage measurements.

25 In a fourth step, the presence of magnetic particles or magnetic object is detected when the curve exhibits a switching physical property interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

CLAIMS

1.- Micromagnetometry system for detecting the presence of very small quantities of magnetic particles down to a single magnetic particle or a single magnetic object in nano or micro scale comprising a:

- a first magnetic hybrid AMR/PHR multi-ring sensor (4) having an active surface (14) including a magnetic track (14) of a closed loop shape deposited on a substrate (26), a first current terminal (28) and a second current terminal (30) forming a pair of current terminals which face each other contacting with the closed loop magnetic track (24) made of a magnetic material, a first voltage terminal (32) and a second voltage terminal (34) forming a pair of voltage terminals which face each other contacting with the closed loop magnetic track (24) and from which an output differential voltage V_b is detected, a first axis (40) passing through the first and second current terminals (28, 30) being parallel to the exchange bias field direction of the track material and perpendicular to a second axis (42) passing through the first and second voltage terminals;

- a first current or voltage source (6) connected between the first and second current terminals (28, 30) for injecting a current I therethrough;

- a first voltage measurement device (8) connected between the first and second voltage terminals (32, 34) for measuring the differential voltage V_b between the pair of voltage terminals (32, 34);

- a set of at least one magnetic particles (12) deposited on the active surface (14) of the first magnetic sensor (4);

- a processing unit (22) for detecting from a set of different measured differential voltages a magnetic flux shift representative of the presence of a least one deposited magnetic particle (12);

the magnetic track (24) of the first AMR/PHR multi-ring magnetic sensor (4) having :

- a first arm (102) made of a first set of a predetermined ring number m lower than 18 of circular meander paths (104) delimited within a first quarter surface (106) of the first magnetic sensor (4), the outermost meander path (108) being connected to the first current terminal (28) and the innermost meander path (110) being connected to the first voltage terminal (32),

- a second arm (112) made of a second set of the same predetermined number m of circular meander paths (114) delimited within a second quarter surface (116) of the first magnetic sensor (4), the outermost meander path (118) being connected to the second current terminal (30) and the innermost meander path (120) being connected to the first voltage terminal (32),

- a third arm (122) made of a third set of the same ring number m of circular meander paths (124) delimited within a third quarter surface (126) of the first magnetic sensor (4), the outermost meander path (128) being connected to the second current terminal (30) and the innermost meander path (130) being connected to the second voltage terminal (34),

- a fourth arm (132) made of a fourth set of the same ring number m of circular meander paths (134) delimited within a fourth quarter surface (136) of the first magnetic sensor (4), the outermost meander path (138) being connected to the first current terminal (30) and the innermost meander path (140) being connected to the second voltage terminal (34);

- the magnetic track (24) is a bi-layered structure including a ferromagnetic film and an anti-ferromagnetic films, or a spin-valve structure, or a tri-layered structure including a ferromagnetic film, a metal and an anti-ferromagnetic film;

characterized in that

- the micromagnetometry system comprises means (20) for creating a magnetic excitation field H_{AC} to make produce by each magnetic particle a stray magnetic field, the magnetic excitation field H_{AC} oscillating along the time at a constant frequency ω ranging from 10 to 3 KHz; and

- the magnetic particles (12) to be detected are motionless and placed close to or in contact with the active surface (14) of the magnetic track (24); and

- the current I injected by the first current or voltage source (6) passing through the current terminals (28, 30) is a direct current (DC), or an alternating current (AC), or a sum of a direct and an alternating current; and

- the processing unit (22) is configured to either provide with a first calibration curve of a background thermal magnetic response of the first magnetic sensor (4) without any magnetic particles deposited thereon, over a predetermined temperature range, under first known predetermined environmental physical conditions, and under a first set of known system operating conditions in terms of the injected current by the first current or voltage source (6) and of the magnetic excitation field H_{AC} applied; then

after deposit of an unknown amount of magnetic particles (12) upon the first magnetic sensor (4), determining a second curve of the evolution versus temperature of differential voltage measurements corrected or not from a set of differential voltage measurements output from the first magnetic sensor (4) and carried out by varying the temperature over the same predetermined range of temperature, under the same first

known predetermined environmental physical conditions and under the same first set of known system operating conditions, then

to determine a third curve as the difference the second curve and the first curve over the same range of temperature; and

5 to detect the presence of at least one magnetic particle when the absolute value of all the voltage differences of the third curve remains above a predetermined detection threshold or when the third curve exhibits a temperature interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10 nT;

10 or,

15 after deposit of an unknown amount of magnetic particles (12) upon the first magnetic sensor (4), the magnetic particles being switchable molecular nanoparticles by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command, by varying the physical property magnitude over a predetermined range of the physical property under known predetermined physical conditions and under known system operating conditions, to determine a first curve of the evolution of differential voltage measurements corrected or 20 not from the evolution of differential voltage measurements carried out by the first magnetic sensor (4) versus the magnitude of the physical property; then

25 to determine over the predetermined range of the physical property magnitude a second curve as a fitting curve from a lower portion of the first curve, this lower portion of the first curve corresponding to a lower interval included within the predetermined range of the physical property, the lower interval having its upper bound lower than the predetermined switching threshold; then

to determine a third curve as the difference versus the magnitude of the switching physical property between the differential voltages of the first curve and the differential voltages of the second curve within the same range of magnitude of the physical property; and

30 to detect the presence of magnetic particles when the third curve exhibits a switching physical property interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10 nT.

35 2.- Micromagnetometry system according to claim 1, comprising further a first environmental temperature sensor (4) for measuring an environmental temperature and/or a second environmental sensor for measuring a physical property

different from the environmental temperature placed close to the active surface (14) of the first active sensor (4), the switching of a magnetization of the magnetic particles being actuated when temperature or the physical property different of temperature is above or below a predetermined switching threshold.

5 3.- Micromagnetometry system according to claim 2, comprising further means (18) for controlling and/or regulating the environmental temperature and/or the physical environmental property different from the temperature.

10 4.- Micromagnetometry system according to any of claims 1 to 3, wherein the means (20) for creating a magnetic excitation field H_{AC} comprises a second current source (52) supplying an AC current and a least one coil (54) connected to the second AC current source (52), the at least one coil (54) being positioned relative to the first magnetic sensor (4) so that the magnetic excitation field H_{AC} has a main component collinear to the first axis (40).

15 5.- Micromagnetometry system according to claim 4, comprising further means (21) for creating a magnetic sensor bias field H_{DC} to shift the operating point of the first magnetic sensor (4) to a highest sensing region, the magnetic sensor bias field H_{DC} being constant along the time, and being collinear with the magnetic excitation field H_{AC} created by means (20) for creating a magnetic excitation field H_{AC} .

20 6.- Micromagnetometry system according to claim 5, wherein the angle α formed between the first axis (40) passing through the first and second current terminals (28, 30) and the axis of magnetic sensor bias field H_{DC} is selected in the range [0 degree, 90 degrees] so that the sensitivity of the magnetic sensor is maximal, and preferably is comprised within the range [15 degrees, 25 degree].

25 7.- Micromagnetometry system according to any of claims 1 to 3, wherein the means (20) for creating a magnetic excitation field H_{AC} is the current or voltage source (326) connected between the first and second current terminals (28, 30), the current or voltage source (326) being configured to generate an alternating current (AC) oscillating along the with time at a constant frequency ω ranging from 10 Hz to 3 KHz, preferably ranging from 50 Hz to 150 Hz.

30 8.- Micromagnetometry system according to any of claims 1 to 7, comprising further a second magnetic hybrid AMR/PHR multi-ring sensor (404) having the same structure as the first magnetic hybrid AMR/PHR multi-ring sensor (4),

35 the first and the second magnetic hybrid AMR/PHR multi-ring sensors (4, 404) being placed close to each other on the same substrate under the same known physical conditions to measure the same magnetic field when no magnetic particles are deposited onto the sensors (4, 414),

the second magnetic hybrid AMR/PHR multi-ring sensors (404) having a first current terminal (428) and a second current terminal (430) forming a pair of current terminals connected in parallel to and sharing the same first current source (326) of the first magnetic hybrid AMR/PHR multi-ring sensor (4); and wherein

5 the micromagnetometry system is configured to differentiate a first set of differential voltage measurements carried out by the first sensor (4) corresponding to a first configuration wherein magnetic particles to be detected if they are contained in the solution dropped are deposited on the first magnetic sensor (4) and placed under a set of known environmental conditions and system 10 operating settings, and a second set of reference differential voltage measurements carried out by the second sensor (404) corresponding to a second configuration wherein no magnetic particles are deposited thereon, under the same set of known environmental physical conditions and system operating settings and to provide a corresponding difference curve; and then

15 to detect from the difference curve an abrupt variation corresponding at least to a minimal magnetization field shift of 10nT.

9.- Micromagnetometry system for detecting the presence of very small quantities of magnetic particles down to a single magnetic particle or a single magnetic object in nano or micro scale comprising :

20 - a first magnetic hybrid AMR/PHR sensor (4) and a second magnetic hybrid AMR/PHR multi-ring sensor (404),

the first magnetic hybrid AMR/PHR sensor (4) having a first active surface (14) including a first magnetic track (14) deposited on a substrate (426), a first current terminal (28) and a second current terminal (30) forming a pair of current terminals which face 25 each other contacting with the first magnetic track (24) made of a magnetic material, a first voltage terminal (32) and a second voltage terminal (34) forming a pair of voltage terminals which face each other contacting with the first magnetic track (24) and from which an output differential voltage is detected, a first axis (40) passing through the first and second current terminals (28, 30) being parallel to the exchange bias field direction of 30 the track material and perpendicular to a second axis (42) passing through the first and second voltage terminals;

characterized in that

35 the micromagnetometry system comprises a second magnetic hybrid AMR/PHR sensor (404) being placed close to the second magnetic hybrid AMR/PHR sensor (404) on the same substrate (426) under the same known physical conditions to measure the same magnetic field when no magnetic particles are deposited onto the sensors (4, 414),

the second magnetic hybrid AMR/PHR multi-ring sensor (404) having a second active surface including a second magnetic track deposited on the same substrate (426), a first current terminal (428) and a second current terminal (430) forming a pair of current terminals which face each other contacting with the second magnetic track made of a magnetic material, a first voltage terminal (432) and a second voltage terminal (434) forming a pair of voltage terminals which face each other contacting with the second magnetic track and from which an output differential voltage is detected, a first axis (440) passing through the first and second current terminals (428, 430) being parallel to the exchange bias field direction of the track material and perpendicular to a second axis (442) passing through the first and second voltage terminals,

the first and the second magnetic tracks having a same shape amongst a cross shape, a single ring closed loop shape and a multi-ring closed loop shape, and having a same layer structure,

the layer structure of the first and the second magnetic tracks being a bi-layered structure including a ferromagnetic film and an anti-ferromagnetic films, or a spin-valve structure, or a tri-layered structure including a ferromagnetic film, a metal and an anti-ferromagnetic film;

and in that the micromagnetometry system comprises:

- a same first current or voltage source (6) connected to and supplying in parallel a current I to the first magnetic hybrid AMR/PHR sensor (4) and the second magnetic hybrid AMR/PHR multi-ring sensor (404),

- a first voltage measurement device (8) connected at its input to the first and second voltage terminals (32, 34; 432, 434) of the first magnetic hybrid AMR/PHR sensor (4) and the second magnetic hybrid AMR/PHR sensor (404), and configured to determine the difference voltage between an amplified differential voltage detected at the voltage terminals (32, 34) of the first magnetic sensor (4) and an amplified differential voltage detected at the voltage terminals (432, 434) of the second magnetic sensor (404);

- a set of at least one magnetic particles (12) deposited on the active surface (14) of the first magnetic sensor (4);

- a processing unit (22) for detecting from a set of different measured differential voltages output by first voltage measurement device (8) a magnetic flux shift representative of the presence of a least one magnetic particle (12) deposited on the first magnetic sensor (4);

- means (20) for creating a magnetic excitation field H_{AC} to make produce by each magnetic particle a stray magnetic field, the magnetic excitation field H_{AC} oscillating along the time at a constant frequency ω ranging from 10 to 3 KHz; and in that

- the magnetic particles (12) or the magnetic object to be detected are motionless and placed only close to or in contact with the active surface (14) of the first magnetic track (24); and

5 - the current I injected by the first current or voltage source (6) passing through the current terminals (28, 30) is a direct current (DC), or an alternating current (AC), or a sum of a direct and an alternating current.

10.- Micromagnetometry system according to claim 9, wherein

no magnetic particles or magnetic object in nano or micro scale are deposited on the second sensor (404), and

10 the processing unit (22) is configured to

after deposit of an unknown amount of magnetic particles (12) or a magnetic object upon the first magnetic sensor (4),

either

15 under known predetermined physical conditions,

to detect the presence of magnetic particles or a magnetic object when a second difference as the difference between a first difference and a reference difference has an amplitude greater than a predetermined detection threshold,

20 the reference difference being the difference between a first voltage measurement carried out by the first sensor (4) that has no magnetic particles thereon and a second voltage measurement carried out by the second sensor (404) that has no magnetic particles thereon under the same known predetermined physical conditions,

25 the first difference being determined by the first voltage measurement device (8) as the difference between the first voltage measurement carried out by the first sensor (4) that has magnetic particles thereon and the second voltage measurement carried out by the second sensor (404) that has no magnetic particles thereon,

and the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT,

30 or

when the magnetic particles are molecular nanoparticles or a magnetic object switchable by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command ,

under known predetermined physical conditions, by varying the physical property magnitude over a predetermined range of the physical property,

35 to determine a curve as the evolution versus the physical property magnitude of the difference between a first set of differential voltage measurements and a second set of voltage measurements, the first set of voltage measurements being carried out by the first

sensor (4) that has magnetic particles thereon and the second set of voltage measurements carried out by the second sensor (404) that has no magnetic particles thereon, and then

5 to detect the presence of magnetic particles or magnetic object when the curve exhibits a switching physical property interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

10 11.- Micromagnetometry system according to any of claims 1 to 10, wherein the magnetic particles are comprised in the family of:

- Any switchable molecular nanoparticles in form of $A_hB_k[M(CN)_6]_l \cdot mH_2O$, where A can be Co, Ni, Fe, etc, B and M can be various transition metals (Fe^{II}, Fe^{III}, Mn^{II}, Mn^{III}, fml aCo^{II}, Co^{III}, ...) and C is an alkali metal cation;

- Any paramagnetic particles: Fe₂O₃, Fe₃O₄, Fe@Fe₃O₄, CoFe@Fe₃O₄, Ni, ...;

- Any ferromagnetic particles: Fe, CoFe, Ni;

- Any antiferromagnetic particles: any particles with multilayer structure Ti/Fe, Cr, NiO, Co₃O₄, a-Fe₂O₃, CuO, MnO, Cr₂O₃ nanoparticles;

- Any magnetic bead made of Fe₃O₄ in the polymer matrix with the sphere shape and any size ranging from 50 nm to 10 μ m.

20 12.- Micromagnetometry detection method for detecting the presence of very small quantities of magnetic particles carried out by a micromagnetometry system as defined by any of the claims 1 to 11, comprising the following steps of

25 firstly, calibrating in temperature under first known predetermined physical conditions the first magnetic sensor when the system comprises a single first magnetic sensor, or the set of the first and second magnetic sensor when the magnetometry system comprises a first magnetic sensor and a second magnetic sensor by providing a first calibration background thermal noise curve; then

deposit an unknown amount of magnetic particles upon the first magnetic sensor; then,

30 under the same first known predetermined physical conditions, by varying temperature on a predetermined range of temperature,

when the magnetometry system comprises a first single magnetic sensor, outputting a second curve as the evolution of differential voltage measurements carried out by the first sensor versus temperature, or

35 when the magnetometry system comprises a first magnetic sensor and a second magnetic sensor, outputting a first set of differential voltage measurements carried out by

the first sensor that has magnetic particles thereon and a second set of differential voltage measurements carried out by the second sensor that has no magnetic particles thereon, and determining a second curve as the evolution versus temperature of the difference between the first set of differential voltage measurements and the second set of differential voltage measurements;

5 determining a third curve as the difference versus temperature between the differential voltages of the second curve and the differential voltages of the first curve within the same range of temperature; and

10 detecting the presence of magnetic particles when the absolute value of voltage differences of the third curve remains stable above a predetermined detection threshold or the third curve exhibits a temperature interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

15 13.- Micromagnetometry detection method for detecting the presence of very small quantities of magnetic particles carried out by a micromagnetometry system as defined by any of the claims 1 to 11, comprising the following steps of

20 depositing (502) an unknown amount of magnetic particles upon the first magnetic sensor, the magnetic particles being switchable molecular nanoparticles by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command, then

25 in a next step (504), under known predetermined physical conditions, by varying the physical property magnitude over a predetermined range of the physical property,

when the magnetometry system comprises a first single magnetic sensor, outputting a first curve as the evolution of differential voltage measurements carried out by the first sensor versus the magnitude of the physical property, or

30 when the magnetometry system comprises a first magnetic sensor and a second magnetic sensor, outputting a first set of differential voltage measurements carried out by the first sensor that has magnetic particles thereon and a second set of differential voltage measurements carried out by the second sensor that has no magnetic particles thereon, and determining a first curve as the evolution versus the physical property of the difference between the first set of differential voltage measurements and the second set of differential voltage measurements; then

35 determining (506) over the predetermined range of the physical property a second curve as a fitting curve from a lower portion of the first curve, this lower portion of the first curve corresponding to a lower interval included within the predetermined range of the

physical property having its upper bound lower than the predetermined switching threshold;

5 determining (508) a third curve as the difference versus the magnitude of the switching physical property between the differential voltages of the first curve and the differential voltages of the second curve within the same range of magnitude of the physical property; and

10 detecting (510) the presence of magnetic particles when the third curve exhibits a switching physical property interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT.

14.- Micromagnetometry detection method according to claim 13, wherein the switching physical property is temperature, pressure, optical irradiation, electrical field, magnetic field, chemical guest molecules.

15 15.- Micromagnetometry detection method for detecting the presence of very small quantities of magnetic particles down to a single magnetic particle or a single magnetic object in nano or micro scale carried out by a micromagnetometry system as defined in the claims 9 or 10, comprising the following steps of

20 depositing (502) an unknown amount of magnetic particles or a single magnetic object upon the first magnetic sensor (4), then

either

under known predetermined physical conditions,

25 outputting a first voltage measurement carried out by the first sensor (4) that has magnetic particles thereon and a second voltage measurement carried out by the second sensor (404) that has no magnetic particles thereon, and determining a first difference between the first voltage measurement and the second voltage measurement; then

detecting the presence of magnetic particles or a magnetic object when a second difference as the difference between the first difference and a reference difference has an amplitude greater than a predetermined detection threshold,

30 the reference difference being the difference between a first voltage measurement carried out by the first sensor (4) that has no magnetic particles thereon and a second voltage measurement carried out by the second sensor (404) that has no magnetic particles thereon under the same known predetermined physical conditions, and the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT,

35 or

when the magnetic particles are molecular nanoparticles or a single object switchable by overstepping a predetermined switching threshold in terms of a switching physical property that operates as a switching command ,

under known predetermined physical conditions, by varying the physical property magnitude over a predetermined range of the physical property, then

5 outputting a first set of voltage measurements carried out by the first sensor (4) that has magnetic particles thereon and a second set of voltage measurements carried out by the second sensor (404) that has no magnetic particles thereon, and determining a curve as the evolution versus the physical property magnitude of the difference between the first 10 set of differential voltage measurements and the second set of voltage measurements; then

15 detecting the presence of magnetic particles or magnetic object when the curve exhibits a switching physical property interval over which a transition occurs having an amplitude greater than the predetermined detection threshold, the predetermined detection threshold corresponding to a minimal magnetization field shift detectable of 10nT,

16.- Humidity or gas sensing measurement system comprising a micromagnetometry system as defined in any of the claims 1 to 11, wherein the particles are molecular nanoparticles are switchable by overstepping a predetermined temperature 20 switching threshold, the predetermined temperature switching threshold depending on the humidity of the degree environment, or on the environment concentration of any vapour of external molecules,

and wherein

25 the processing unit is configured to determine the humidity degree or the environment concentration of the vapour of external molecules from magnetic field change measurements of magnetic particles that are sensitive to the humidity degree or the environment concentration of the vapour of external molecules, and from a previously determined mapping curve between a calibrated humidity degree or a calibrated environment concentration of the vapour of external molecules measured by another 30 method and a corresponding parameter such as a temperature threshold, a transition temperature, or a width of an hysteresis loop determined through the magnetic property change of the magnetic particles detected by the micromagnetometry method of any of claims 12 to 14.

35 17.- Humidity or gas sensing measurement system according to claim 16, wherein the vapour of external molecules that can be detected are amongst the external molecules of the family consisting of N₂, He, I₂, CO₂, ethanol, methanol, 2-propanol, acetone, D₂O,

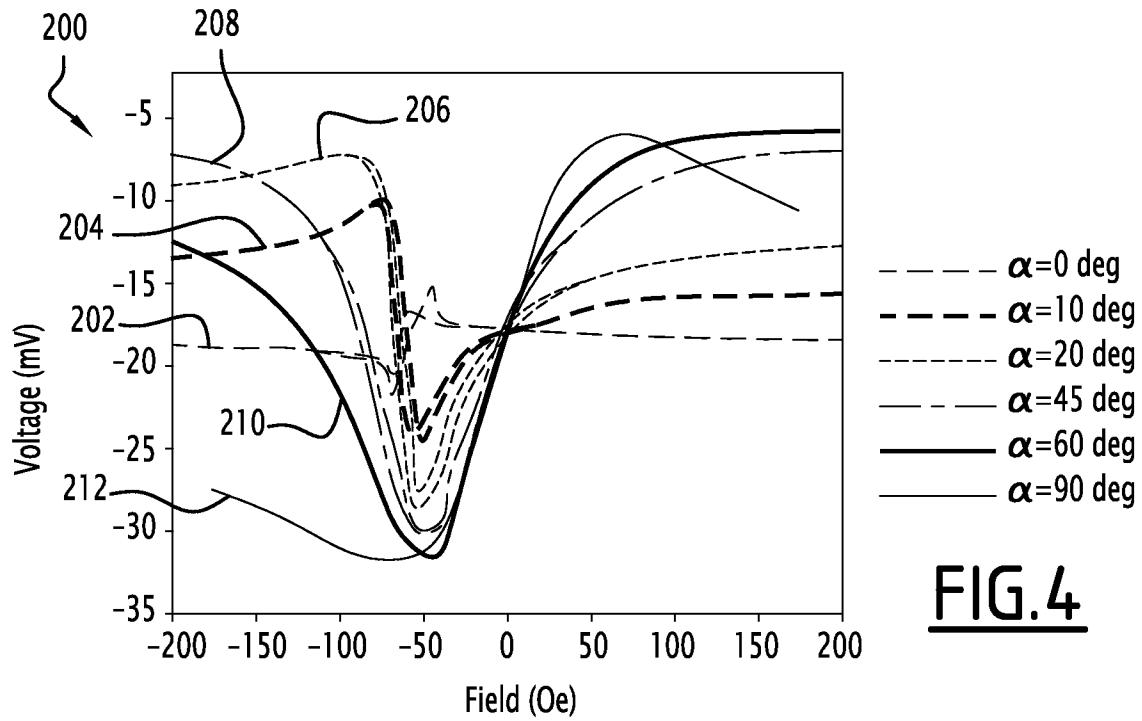
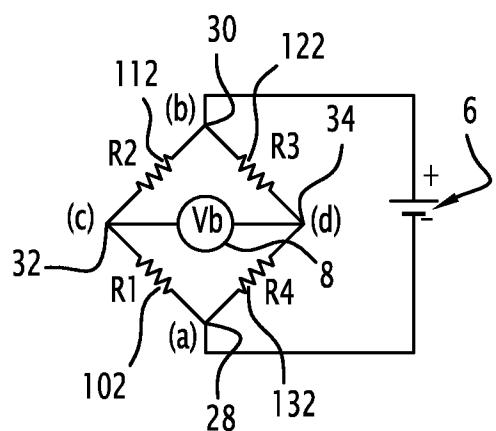
CS₂ , CO, Iode (I), brome (Br), chlore (Cl), benzene, toluene, chlorobenzene, bromobenzene, iodobenzene, dichlorobenzene, trichlorobenzene, pyrazine, pyridine, pyrrole, thiophene, furane, thf.

1/7

DC field H_{DC} current

FIG.2

FIG.3



3/7

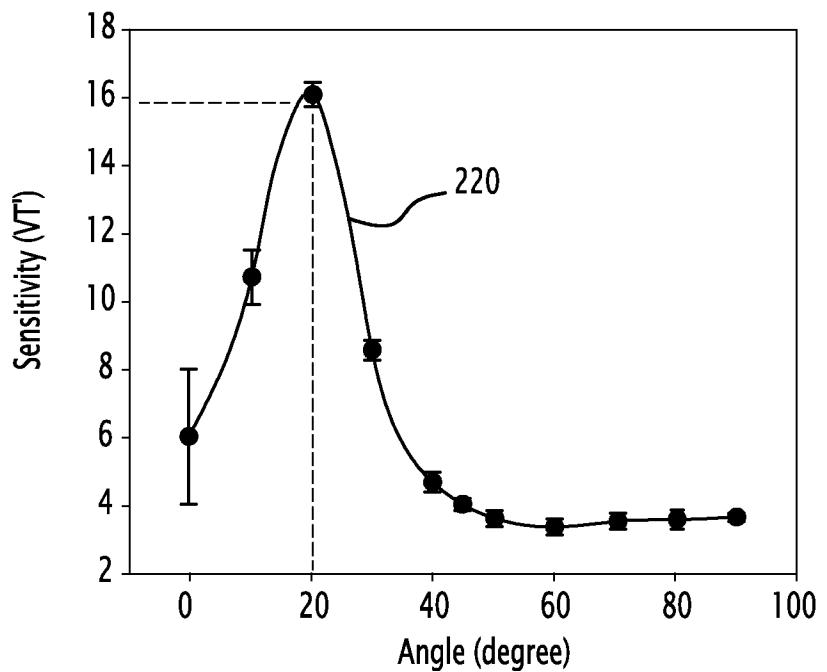


FIG.5

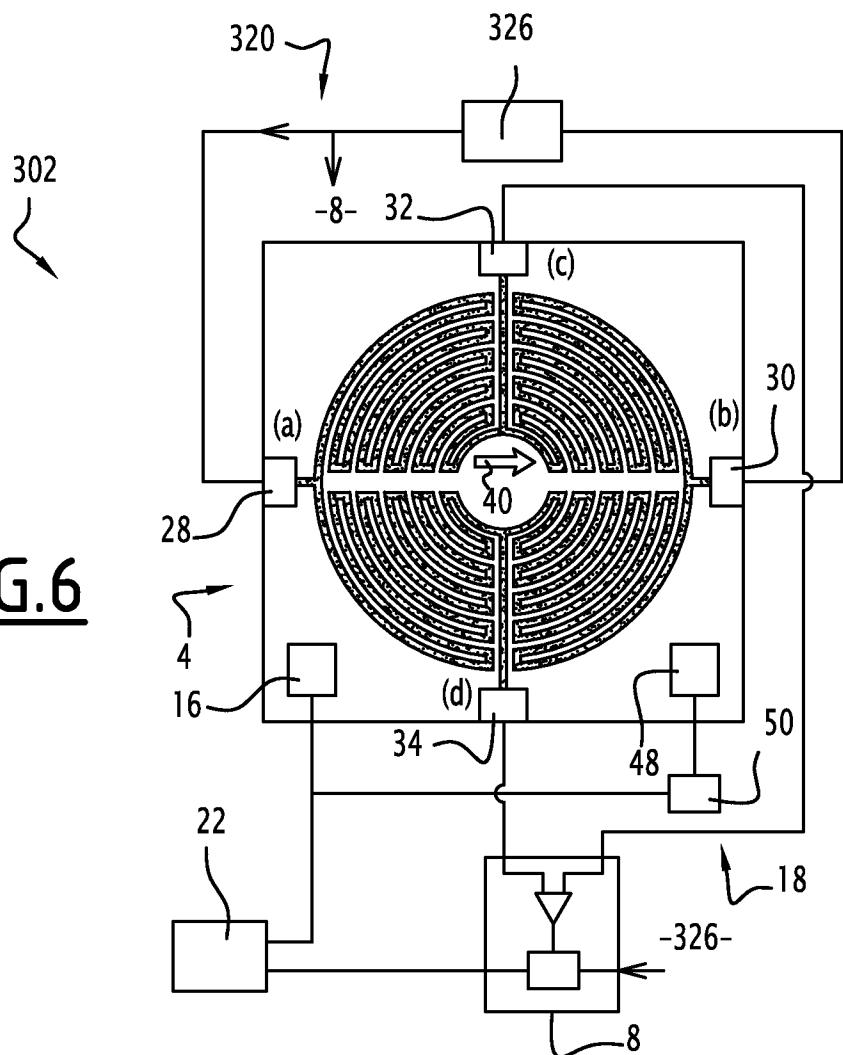
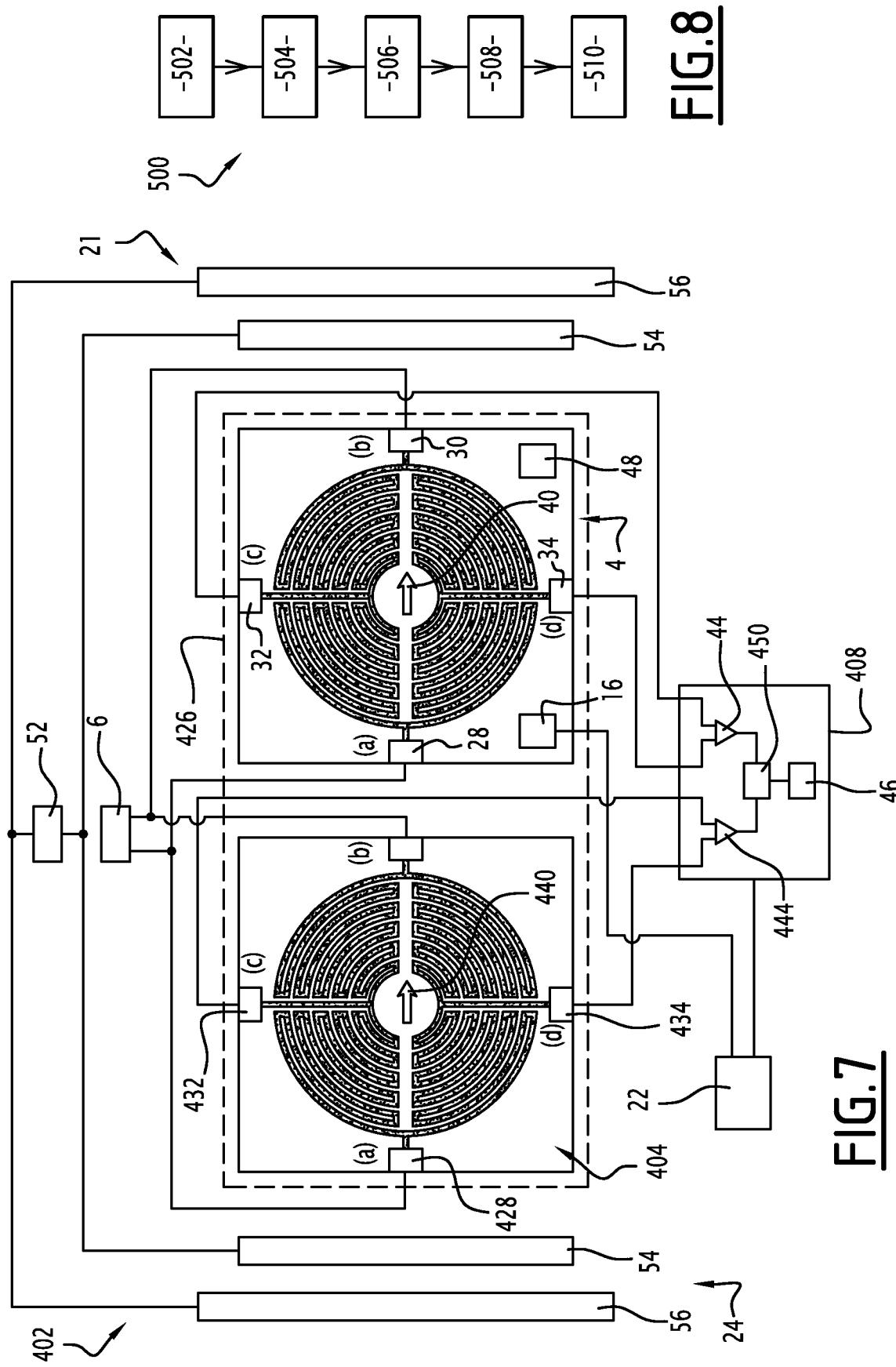


FIG.6

4/7

FIG.8**FIG.7**

5/7

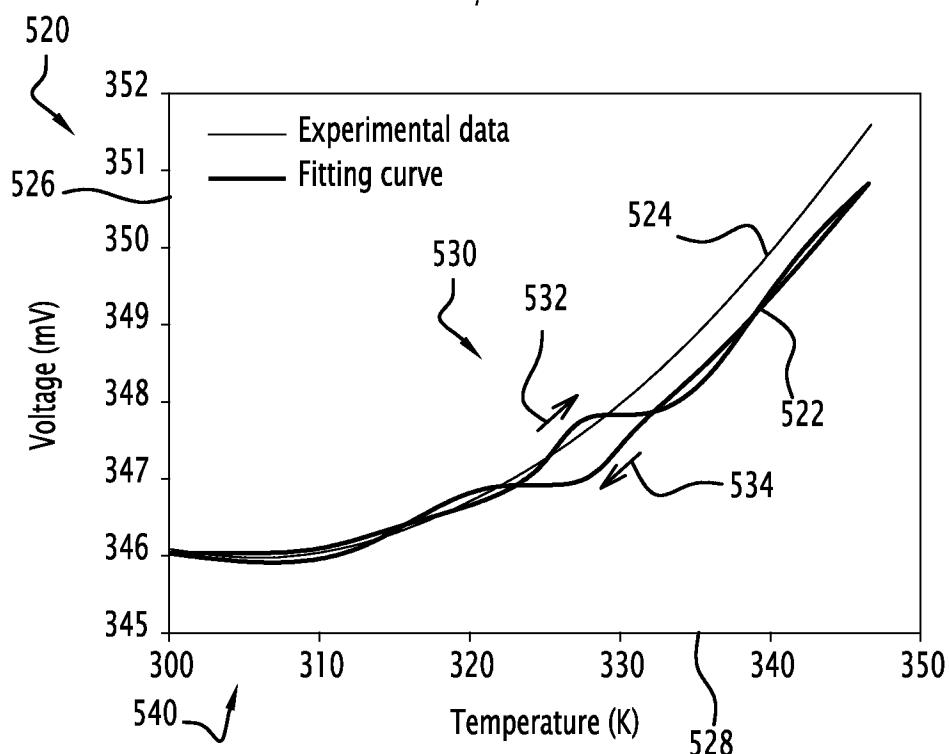


FIG.9

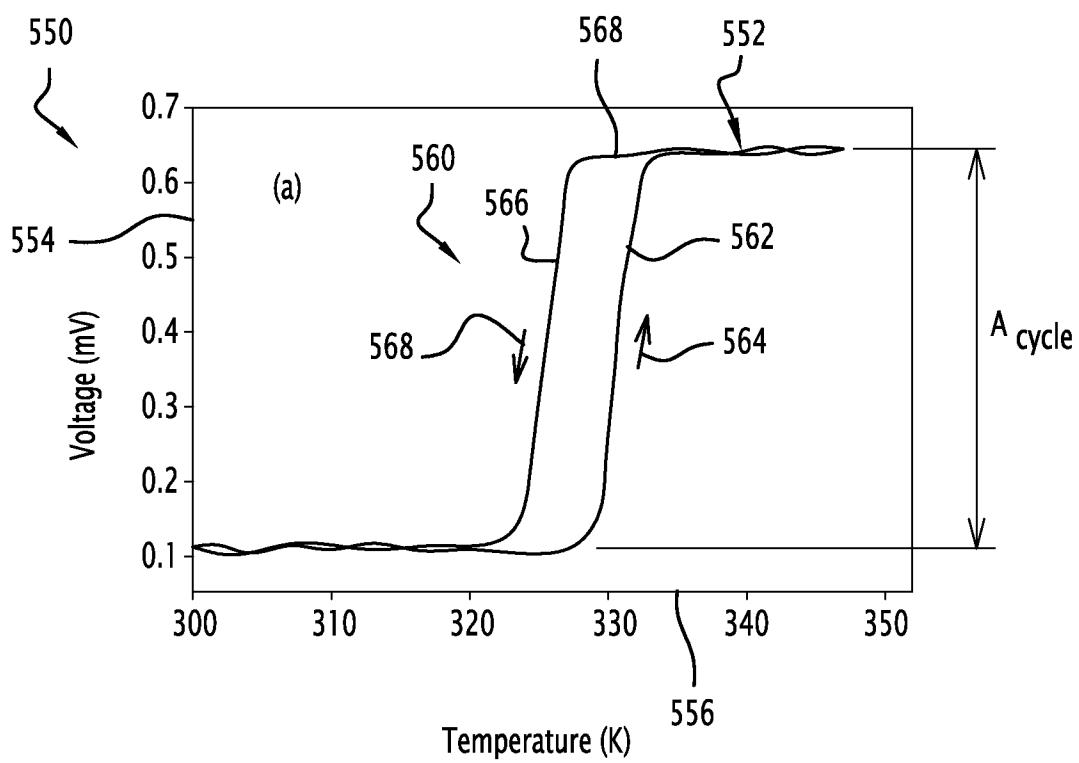
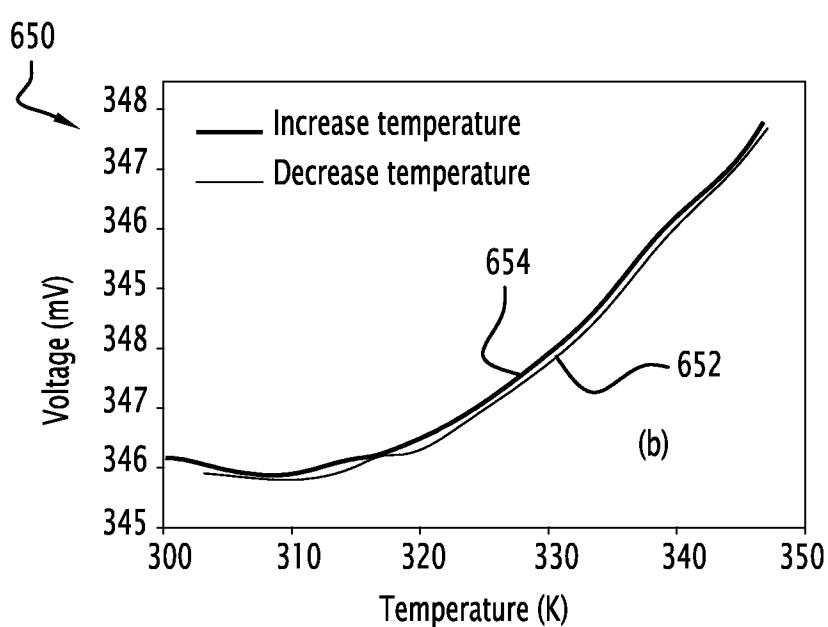
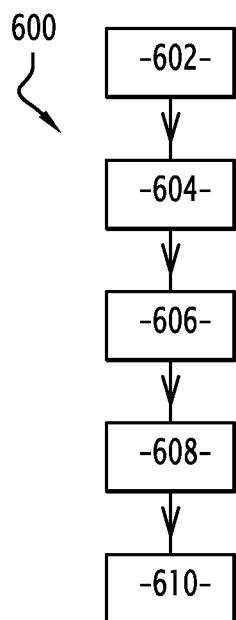
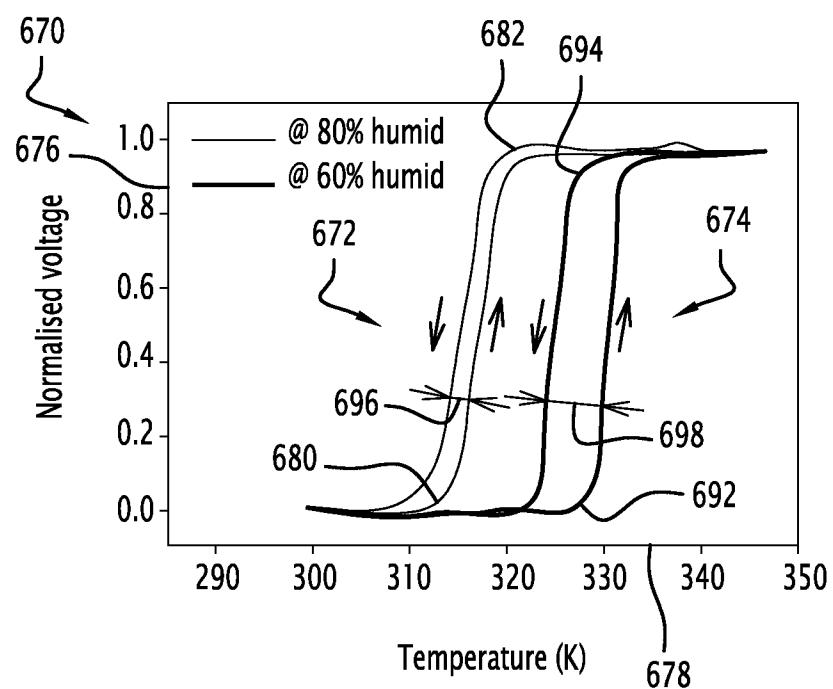


FIG.10

6/7

FIG.11FIG.12FIG.13

7/7

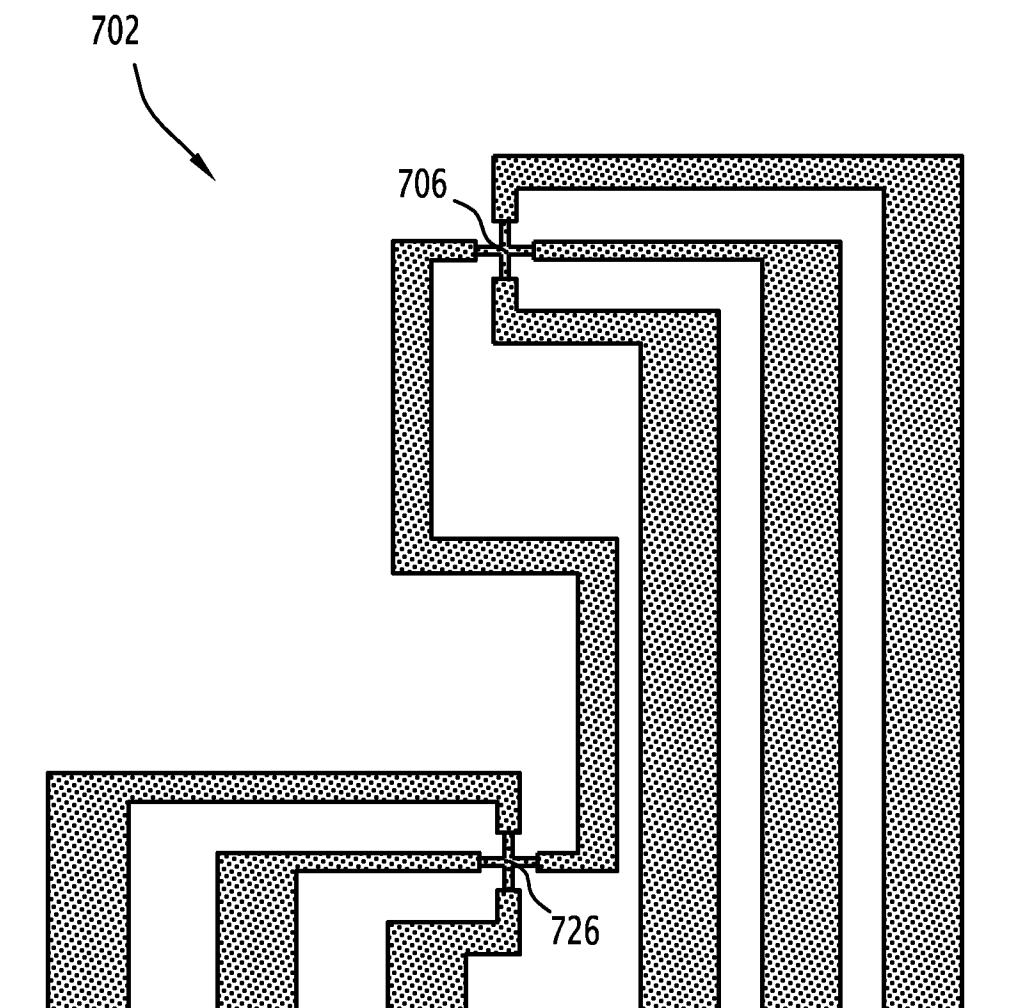


FIG.14

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/064775

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01R33/12
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)
G01R

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, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>SUNJONG OH ET AL: "Analytes kinetics in lateral flow membrane analyzed by cTnI monitoring using magnetic method", SENSORS AND ACTUATORS B: CHEMICAL: INTERNATIONAL JOURNAL DEVOTED TO RESEARCH AND DEVELOPMENT OF PHYSICAL AND CHEMICAL TRANSDUCERS, ELSEVIER S.A, SWITZERLAND, vol. 160, no. 1, 19 August 2011 (2011-08-19), pages 747-752, XP028110965, ISSN: 0925-4005, DOI: 10.1016/J.SNB.2011.08.058 [retrieved on 2011-09-08] the whole document</p> <p>-----</p> <p style="text-align: center;">-/-</p>	1-17

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	Date of mailing of the international search report
6 August 2013	12/08/2013

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Böhm-Pélissier, A

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2013/064775

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SUNJONG OH ET AL: "Hybrid AMR/PHR ring sensor", SOLID STATE COMMUNICATIONS, PERGAMON, GB, vol. 151, no. 18, 29 May 2011 (2011-05-29), pages 1248-1251, XP028251303, ISSN: 0038-1098, DOI: 10.1016/J.SSC.2011.05.049 [retrieved on 2011-06-12] the whole document -----	1-17
A	US 2006/194327 A1 (KAHLAN JOSEPHUS ARNOLDUS H M [NL] ET AL) 31 August 2006 (2006-08-31) abstract; claim 19 -----	1,9
A	US 2010/231213 A1 (NIEUWENHUIS JEROEN HANS [NL] ET AL) 16 September 2010 (2010-09-16) abstract; claim 1; figures 1-3 -----	1,9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/064775

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 2006194327	A1 31-08-2006	CN	1829922 A	06-09-2006
		EP	1685418 A2	02-08-2006
		JP	2007500347 A	11-01-2007
		KR	20060054351 A	22-05-2006
		US	2006194327 A1	31-08-2006
		WO	2005010542 A2	03-02-2005
<hr/>				
US 2010231213	A1 16-09-2010	BR	PI0709233 A2	28-06-2011
		CN	101416040 A	22-04-2009
		EP	2005139 A2	24-12-2008
		JP	2009531706 A	03-09-2009
		RU	2008142996 A	10-05-2010
		US	2010231213 A1	16-09-2010
		WO	2007113724 A2	11-10-2007
<hr/>				