Vibrating sample magnetometer (vsm) with a sample holder

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(54) Title: VIBRATING SAMPLE MAGNETOMETER (VSM) WITH A SAMPLE HOLDER

(57) **Abstract:** The invention relates to a vibrating sample magnetometer (VSM) for measuring magnetic properties of a sample (S) using an elongated sample holder (SH, 10) with a controlled gas-atmosphere. The sample holder has an inlet (13) for receiving a first gas at the proximal end, an elongated first fluid channel (11) for conveying the first gas from the inlet to the sample. An elongated second fluid channel (12) conveys the first gas away from the sample, and an outlet (14) is arranged for conveying the first gas away from the elongated second fluid channel. Both the inlet and outlet are arranged at the proximal end of the sample holder near the head drive, and the sample holder facilitates vibrating sample magnetometry measurements of samples in gas-controlled environments at temperatures up to at least 1000 degrees C and in situ measurements of small sample masses.

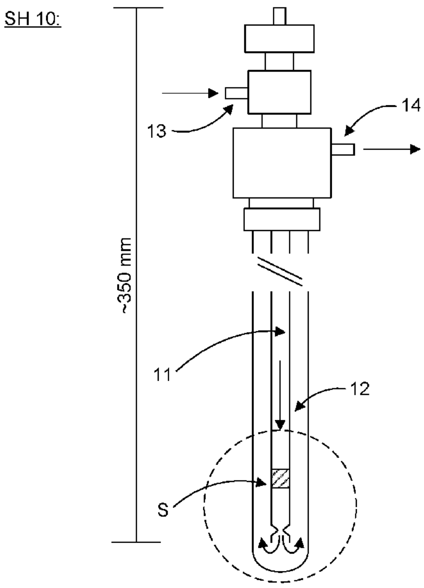

FIG. 4

[Continued on next page]

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VIBRATING SAMPLE MAGNETOMETER (VSM) WITH A SAMPLE HOLDER

FIELD OF THE INVENTION

The present invention relates to a vibrating sample magnetometer (VSM) with a sample holder, a corresponding sample holder for VSM, and a corresponding method for measuring a magnetic field.

BACKGROUND OF THE INVENTION

Vibrating sample magnetometry is one of the most commonly used techniques to measure hysteresis properties and Curie temperatures of magnetic samples and it was originally invented by Simon Foner, cf. US patent 2,946,948 filed 1957. The working principle of a vibrating sample magnetometer (VSM) is that the sample is physically vibrated, typically vertically, and the magnetic moment of sample is determined from the induced voltage in nearby pickup coils. Commercial available VSMs allow for measurements at temperatures up to 1000 degrees C from e.g. commercial providers like Lake Shore and MicroSense, and at magnetic fields up to >2 T.

However, at such elevated temperatures the sample may oxidize, sinter or otherwise change during measurements, depending on the conditions of the sample environment, in particular the gas atmosphere and humidity conditions surrounding the sample. Also, it is often relevant to be able to study samples at specific gas compositions. Furthermore, it may be of interest during measurements to analyze the composition of the gas being produced by or outgassed from the sample. Moreover, it may be of interest to collect the exit gas in order to protect equipment and people from unwanted exposure. Hence, control of the surrounding atmosphere, i.e. gas content, humidity, pressure, temperatures and other parameters of the sample environment is advantageous for such measurements. Nevertheless, commercially available VSMs do normally not allow for this kind of atmosphere or gas control. Rather, available options are e.g. only Argon gas surrounding a sample in a half- open containers in a VSM with a small cup holding the small sample (e.g. VSMs commercially available from Lakeshore), or vacuum surrounding the sample (e.g. VSM commercially available from Cryogenic Limited).

The lack of gas-control options for conventional VSMs may in part rely on the fact that in situ measurements at high temperatures come with several challenges. An in situ sample holder needs to:

- not influence the magnetic measurement
- be temperature-stable
- be able to work under the vibration of the VSM - and at the same time not hinder the vibrations – while simultaneously allowing gas flow and keeping the sample fixed in the holder
- be operational for relevant (user-chosen) gas compositions of interest
- prohibit chemical interaction between the gas composition and the VSM itself
- be compatible with the mass load constraints of the vibration head drive on the VSM, and
- be compatible with the spatial constraints of the particular oven option.

Recently, Claeys et al. in US patent application 2011/204884 has disclosed a VSM, which includes an elongate reactor in which a sample can be secured in a so-called sample support zone, and which is located within a magnetic field space of a magnetic field generator and one or more signal pickup coils like in a conventional VSM. Movement generating means is provided for generating relative movement in a linear direction between the reactor and at least one of the magnetic field and pickup coil, preferably by moving the reactor in its length. The magnetometer has a reactor being a metal tube having a length, which permits its ends to remain external of the signal pickup device during the relative movement.

The VSM suggested in US patent application 2011/204884 is primarily designed for studies of catalyst materials. The sample holder is accordingly a high-pressure chemical reactor tube (ca. 12 mm in diameter, ca. 30 cm long) made in stainless steel, which allows for pressures up to >50 bar, temperature up to >600 degrees C, and a large range of gas compositions and flow rates around the sample. The sample is situated in the tube as in a plug-flow reactor, and the forced gas-flow through, or around, the sample ensures a controlled gas atmosphere around and at the sample. The reactor tube vibrates with the sample. The reactor tube is magnetic (stainless steel), but because its ends extends beyond the zone of the pickup coils, it hardly affects the magnetic measurements of the sample. This VSM system works well for its specific purposes, but it also comes with drawbacks, which makes the system less suitable for other types of high temperature studies, where high pressures are not needed. Due to the relatively large mass of the reactor holder, it vibrates with a low frequency around 2 Hz, and a relatively large sample mass is therefore needed. Thus, the resulting measurement sensitivity is not very high.

Recently, another variant of a VSM with a controlled gas-atmosphere around the sample was disclosed by Chernavskii et al. in *Instruments and Experimental Techniques*, 2014, Vol. 57, No. 1, pp. 78–81. This scientific article shows an experimental setup for studying synthesis of ferromagnetic metal nanoparticles, where a quartz reactor tube is used instead of a stainless steel reactor tube, but it also suffers from some of the above-mentioned drawbacks, in particular complexity and the need for a substantial redesign of the VSM setup to include the suggested reactor tube. Similar Russian patent application RU 2 444 743 also from Chernavskii et al. discloses a VSM where the reaction gas is led through a flow-type microreactor containing the sample with a controlled temperature. However, the disclosed VSM does not effectively provide full control of the gas atmosphere around the sample because the gas is conducted to an outlet after passing the sample, and the outlet is directly into the surroundings.

US 7,582,222 B2 discloses in Figure 34 another VSM system but used for gas sensing purpose, preferably using iron-doped tin dioxide as sample sensor material. This VSM system is also open upwards to the surroundings, i.e., without full control of the gas atmosphere around the sample, and without possibility to collect and/or perform analysis of the reaction gas after passage of the sample.

US 7,836,752 B2 (to Univ. Boise State) discloses another VSM-like system used for gas sensing purpose, e.g. for hydrogen gas sensing by using nanoscale antiferromagnetic hematite. The gas sensing system does not have a well-controlled gas surrounding the hematite sample. Thus, this system is also not advantageous for using VSM for studying of gas-sample reactions.

Thus, these prior art systems are not advantageous for the study of gas-sample reactions or the prevention of non-wanted reactions during testing.

Hence, an improved vibrating sample magnetometer (VSM) would be advantageous, and in particular, a more efficient or simple vibrating sample magnetometer with a controlled gas atmosphere would be advantageous.

OBJECT OF THE INVENTION

It is a further object of the present invention to provide an alternative to the prior art.

In particular, it may be seen as an object of the present invention to provide a vibrating sample magnetometer (VSM) that solves the above mentioned problems of the prior art with high complexity for controlled gas atmosphere and/or lacking ease of use in, or together with, conventional VSMs.

SUMMARY OF THE INVENTION

Thus, the above-described object and several other objects are intended to be obtained in a first aspect of the invention by providing a vibrating sample magnetometer (VSM) for measuring magnetic properties of an associated sample, the VSM comprising:

- an electromagnet for providing a magnetic field at the sample,
- a receiver unit for receiving a magnetic response signal from the sample,
- a head drive (HD) arranged for vibrating motion of the sample, and

- an elongated sample holder (SH) for providing a controlled gas-atmosphere through and/or around the sample, a proximal end of the sample holder being mounted on, or at, the head drive, the sample holder comprising:

  - an inlet for receiving a first gas at the proximal end,
  - an elongated first fluid channel for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,
  - an elongated second fluid channel for conveying said first gas away from the sample, and

- an outlet arranged for conveying the first gas away from said elongated second fluid channel,

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD).

The invention is particularly, but not exclusively, advantageous for obtaining a VSM with an in situ sample holder (SH) capable of performing vibrating sample magnetometry measurements of samples in gas-controlled environments at temperatures up to at least 1000 degrees C in a simple and effective manner as compared to previous conventional solutions available for VSM.

The VSM with the improved sample holder works with gas flow under mechanical vibrations (e.g. around 60-100 Hz, such as around 80 Hz) as the inventors have convincingly demonstrated. Additionally, the sample holder allows for in situ measurements of small sample masses (e.g. down to <1 mg ferromagnetic material).

The sample holder ensures the sample is measured under controlled gas compositions, and the supplied first gas may be reactive e.g. oxidizing or reducing, and it flows in a closed fluid system comprising the first and the second fluid channel conveying the first gas to the sample and ensures that the first gas is exposed only to the sample and not to the VSM parts.
It is therefore advantageous for the present invention that the first gas is not in contact with the surrounding atmosphere because this may negatively influence the control of the first gas. Different prior art VSM setups for example like in the aforementioned Russian patent application RU 2 444 743, the gas outlet is directly into the surroundings, and there may be a back-flow of atmospheric gasses into the micro-reactor around the sample. This VSM setup with gas outlet directly into the surroundings also does not enable collection and analysis of the reaction gas after passage of the sample. The disclosed VSM in RU 2 444 743 therefore does effectively not provide full control of the gas atmosphere around the sample. It is also advantageous for the present invention that the first gas is not exposed to the VSM parts. For some conventional VSMs with a surrounding oven, or heater unit, without a controlled gas atmosphere, the exposure of the hot oven to a gas atmosphere may

possible damage or deteriorate the oven, or other parts, over time, and by applying the present invention this problem may be reduced or avoided.

The sample holder according to the present invention may be relatively inexpensive to fabricate, e.g. primarily in glass or a quartz material, and thereby the sample material can be disposable together with the used sample. Moreover, the sample holder is quite simple to use, replace, and/or retrofit in connection with existing VSMs, such as VSM equipment from Lakeshore or MicroSense, and thereby provides a cost-effective alternative to custom-build in-situ sample holder for a VSM suggested in US patent application 2011/204884 as a skilled person working with VSM equipment will readily understand. Also, the complexity of this reactor tube extending below the pick-up coil space in this VSM variant makes it difficult or complicated to use together with a conventional VSM, especially where the oven is closed immediately below the sample. Also, if the reactor tube in US patent application 2011/204884 is an integrated part of the VSM, the reactor tube should typically be discharged or intensively cleaned after each experiment or type of experiment.

Some definitions:

In the context of the present application, the term magnetometer, or the act of performing magnetometry, may be considered to include a device/instrument arranged or capable of measuring magnetic properties, such as magnetic field, magnetisation, permeability, susceptibility, coercivity, remanence, hysteresis, magnetic losses, and/or magnetic moment, of a sample.

In the context of the present application, the term ‘vibrating sample magnetometer’ (VSM) may be used in a broad meaning covering the principles originally developed by Simon Foner in 1955 for measuring magnetic properties of a sample. Sometimes the term ‘magnetometry’ is used to cover the step or process of performing a magnetic measurement with a magnetometer. Briefly, a sample may be magnetised in a homogenous magnetic field and linearly and relatively displaced, such as vibrated, and the magnetic moment of the sample is measured by neighbouring pick-up coils, preferably positioned in symmetrical setup around the sample. The induced voltage in the pickup coils is then proportional to the sample's magnetic moment, but does not depend on the strength of the applied magnetic field. Typically, a four-coil setup is used, but other configurations or setups may be applied within the context and teaching of the present invention as the skilled person will readily understand.

The term magnetometer includes, but is not limited to, a magnetometer for measuring DC- and/or AC-field properties, such as for the DC part the VSM or a SQUID (superconducting quantum interference device) magnetometer, and for the AC part the following: a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement.

In the context of the present application, the term 'sample holder' may be construed in a broad manner to cover an apparatus or device capable of receiving, holding and/or fixating a sample for subsequent measurement of magnetic properties of the sample. Because the sample holder according to the present invention comprises a closed fluid system for conveying a first gas to the sample, it may further be understood by the skilled person working with magnetometer, such as VSMs, and/or chemical reactions in magnetic samples that the sample holder may confine both the first gas and the sample to an interior part of the sample holder.

In the context of the present application, the term 'elongated' may be understood as being little in circumference or width in proportion to a length or a height of the sample holder. In some situations, it may be synonymous with stretched or thin. More specifically, the term elongated may be taken to mean that the height to width ratio (H/W) of the sample holder is at least 10:1, preferably at least 50:1, or more preferably at least 100:1.

In the context of the present application, the term 'sample' may be understood broadly as a sample in any phase (solid, liquid, or gas) confined within a volume that can be inserted into the sample holder. Furthermore, various solid compositions can be considered a sample within the context of the present application, thus, the sample may comprise a powder of one or more magnetic active materials, optionally a powder blended with a filler material or supported by another material for easier handling during the magnetic measurements in a VSM, particular if a small amount of magnetic active materials is to be measured. Particularly, the filler material may be selected as a material, such as shape, size, surface, etc., which is suitable for plug-flow reactions conditions. In some embodiments, the sample may be a piece of rock, a crystal, a piece of casted or sintered material, a substrate with thin films or particles deposited thereon.

In the context of the present application, the term ‘distal’ may be understood as being opposite to the word ‘proximal’ when defining a position at the elongated sample holder according to the present invention, such as a position of the sample. However, the word distal does not necessarily imply that the position is the extreme distal end of the sample holder, unless explicitly mentioned. It may also imply that the position is away and close to, or beyond, a central position of the sample holder. More specifically, the sample may be positioned in the sample holder by having a relative longitudinal position along the sample holder being, but not limited to, maximum 20%, more preferably maximum 10%, most preferably maximum 5% of the total length of the sample holder away from the distal end point of the sample holder.

In the context of the present application, the term ‘closed fluid system’ may be practically understood as a system working under gas tight or gas impermeable conditions i.e. the system is effectively impervious to gas, at least substantially or approximately gas tight conditions in the sense that a skilled person in gas and vacuum technology will of course understand that no gas system or vacuum system is in reality completely gas tight, because there will always be an insignificant or minute gas leakage over time, even for state of the art gas tight system. On the other hand, the skilled person will appreciate that under practical conditions the concept of a ‘closed’ fluid system is still operationally understandable.
It is to be understood that the closed fluid system according to the present invention is closely connected to the sample holder providing a controlled gas-atmosphere through and/or around the sample, in particular that the sample holder facilitates that a VSM with the sample holder according to the invention further makes it possible to have a controlled gas flow through the sample holder and around the sample. Thus, unlike some prior art VSM setups, the present invention makes it possible to have effectively complete separation between the VSM parts and first gas, often being a reactive gas.

Furthermore, the present invention enables improved control of gas input and output relative to the VSM. Thus, there may be very little leakage in, or out of the sample holder and the connected fluid or gas conducting parts. Also, there is effectively no back flow into the sample and the region around the sample, which enables full control of any gas reactions. The gas can through the outlet be conveyed away and collected.

As mentioned previously, this also enables measurements of the resulting gas from chemical reactions between the sample and first gas as well as safe handling of reactive outlet gasses compared to previous open air outlets. Additionally, the skilled person working with vacuum and gas technologies will understand that various standard levels are available, e.g. for gas purity, gas pressure and gas handling systems, and the present invention may be applied at various levels depending on the sample, the first gas and/or the chemical reactions being studied.

In one embodiment, the elongated sample holder (SH) including the inlet for receiving a first gas, and including the outlet arranged for conveying the first gas away, may be arranged for vibrating by, or together with, the head drive (HD) during one or more magnetic measurements with the VSM, and is contributing to the advantages of the present invention by providing a simple and more effective VSM as compared to previous conventional solutions available for VSM.

Advantageously, the elongated sample holder (SH) may be arranged for fixating a sample (S), preferably at a distal end, in the elongated first fluid channel to stay in this position during the vibration of the VSM.

In other embodiments, the elongated first fluid channel, where the sample is positioned, may have an inner geometry facilitating plug-flow reaction conditions between the sample and the first gas. In plug-flow, the velocity of the fluid is assumed to be constant across any cross-section of the pipe perpendicular to the axis of the pipe. The concept of plug-flow reaction conditions will be well-known to the skilled person in chemistry and is explained in more detail below in the paragraph 'Detailed description of an embodiment'. For flows in pipes, if flow is turbulent then the laminar sublayer caused by the pipe wall is so thin that it is negligible. Plug-flow conditions will be achieved if the sub-layer thickness is much less than the inner pipe diameter, and it will be discussed in more detail below.

Advantageous, the sample holder may facilitate sample masses below 100 milligram, preferably below 50 milligram, or most preferably below 10 milligram being measured in the VSM, which always enables much small masses than possible with the controlled gas-atmosphere in the VSM suggested in US patent application 2011/204884.

Preferably, the elongated first fluid channel and the elongated second fluid channel may be arranged in – at least partly - a coaxially configuration to each other in the sample holder, with one fluid channel surrounding the other fluid channel while said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD), which provides a relatively compact and strong design of the sample holder.

Preferably - but not always - the sample may be positioned near, or at, the distal end of the sample holder during measurement of magnetic properties. As defined above, the term 'distal' is to be interpreted in a broad way.

Advantageously, a temperature regulating unit, preferably a heater unit, e.g. an oven, may be arranged for thermally controlling the sample during measurement of magnetic properties, which enables control of both temperature and gas atmosphere around the sample. Preferably, the temperature regulating unit, preferably a heater unit, may form a substantially closed receptacle with an opening at one end, said opening being capable of receiving the elongated sample holder (SH) at said one end, which may enable a quite stable and effective way of controlling the temperature at the sample.

In some embodiments, the first and the second fluid channel may be arranged so that the sample holder forms a closed fluid system for the first gas through and/or around the sample, which allows for very efficient and reliable control of the gas atmosphere around the sample. Preferably, the sample holder may be arranged for the first gas being a reactive gas, an inert gas, or a gas at equilibrium with the sample for studying various kind of reactions of the sample with the first gas.

In a second aspect, the invention relates to an elongated sample holder (SH) arranged for cooperating with a vibrating sample magnetometer (VSM), a SQUID magnetometer, a magnetometer for measuring AC susceptibility, or a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, a proximal end of the sample holder being mounted on, or at, a head drive, alternatively a holding position, of the magnetometer, and the sample being receivable in the sample holder, the elongated sample holder (SH) providing a controlled gas-atmosphere through and/or around the sample during measurements, the sample holder comprising:

- an inlet for receiving a first gas at the proximal end,
- an elongated first fluid channel for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,
- an elongated second fluid channel for conveying said first gas away from the sample, and
- an outlet arranged for conveying the first gas away from said elongated second fluid channel

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD).

Advantageously, the sample holder according to this aspect is that the sample holder is retrofitable into an existing vibrating sample magnetometer (VSM), an existing SQUID magnetometer, an existing magnetometer for measuring AC susceptibility, an existing magnetometer for measuring dynamic hysteresis loops, or an existing calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement. The skilled person will readily understand - once the teaching and general principle of the invention is understood - that even though the invention is explained and demonstrated in connection with VSM, the teaching may be adapted in various other areas of magnetic measurements with minor adaption and/or modification of the sample holder, e.g. in connection with the positioning and/or fixation to the remaining measurement setup of the sample holder.

In a third aspect, the present invention relates to a method for measuring magnetic properties of a sample using a vibrating sample magnetometer (VSM), or a SQUID magnetometer, a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, the method comprising:

- providing an electromagnet for providing a magnetic field at the sample,
- providing a receiver unit for receiving a magnetic response signal from the sample, and

- providing an elongated sample holder (SH) for providing a controlled gas-atmosphere through and/or around the sample, a proximal end of the sample holder being mounted on, or at, a head drive, the sample holder comprising:

- an inlet for receiving a first gas at the proximal end,
- an elongated first fluid channel for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,
- an elongated second fluid channel for conveying said first gas away from the sample, and
- an outlet arranged for conveying the first gas away from said elongated second fluid channel,

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD).

In a fourth aspect, the present invention relates to a magnetometer for measuring magnetic properties of an associated sample, the magnetometer comprising:

- an electromagnet for providing a magnetic field at the sample,
- a receiver unit for receiving a magnetic response signal from the sample,

- an elongated sample holder (SH) for providing a controlled gas-atmosphere around the sample, a proximal end of the sample holder being mounted on, or at, a holding position on the magnetometer, the sample holder comprising:

- an inlet for receiving a first gas at the proximal end,
- an elongated first fluid channel for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,
- an elongated second fluid channel for conveying said first gas away from the sample, and
- an outlet arranged for conveying the first gas away from said elongated second fluid channel,

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near said holding position.

Advantageously, the magnetometer may be a vibrating sample magnetometer (VSM), but the skilled person will readily understand - even though the invention is explained and experimentally demonstrated in connection with VSM – that for a SQUID magnetometer, a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, the sample holder may be adapted in various other areas of magnetic measurements with minor adaptions and/or modifications, and the application of the invention may therefore advantageously have a broader application than VSM.

The first, second, third, and/or fourth aspect of the present invention may each be combined with any of the other aspects, in particular that the first and the second fluid channel are arranged so that the sample holder forms a closed fluid system for the first gas through and/or around the sample (S) may be found in all aspects of the invention. These and other aspects of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.

BRIEF DESCRIPTION OF THE FIGURES

The invention according to the invention will now be described in more detail with regard to the accompanying figures. The figures show one way of implementing the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

Figure 1 is a schematic drawing of a vibrating sample magnetometer (VSM) according to the present invention,

Figure 2 is a schematic drawing of the gas flow in a prior art vibrating sample magnetometer (VSM),

Figure 3 is a schematic drawing of the gas flow in a sample holder for a vibrating sample magnetometer (VSM) according to the present invention,

Figure 4 is another schematic drawing of the gas flow around, and/or through, the sample in the sample holder for a vibrating sample magnetometer (VSM) according to the present invention,

Figure 5 is close-up schematic drawing of Figure 4 showing again the gas flow around, and/or through, the sample in the sample holder for a vibrating sample magnetometer (VSM) according to the present invention,

Figure 6 is a schematic diagram of gas system supplying the first gas to the in situ sample holder according to the present invention,
Figure 7 is an annotated picture of the gas system supplying the first gas to the in situ sample holder mounted underneath a conventional VSM head drive together with the VSM oven,

Figure 8 shows a technical drawing and two pictures of the sample holder according to the present invention,

Figures 9-11 show some measured magnetization (σ) results using the in situ sample holder in a VSM according to the present invention,

Figure 12 is a flow-chart of a method according to the invention,

Figure 13 is a schematic drawing of the in-situ sample holder adapted to AC-calorimetry,

Figure 14 show annotated pictures of the sample holder adapted to a commercial AC-calorimeter, and

Figure 15 show examples of AC-calorimetry measurements with the adapted sample holder.

DETAILED DESCRIPTION OF AN EMBODIMENT

Figure 1 is a schematic drawing of a vibrating sample magnetometer VSM 100 according to the present invention with a sample holder 10 with a sample S. On the left part a), an electromagnet (solid grey) produces a homogeneous magnetic field (indicated with dashed lines) in the area of the sample S. Pickup coils, A, B, C and D, are symmetrically arranged around the sample S and measures the change in magnetic flux. On the right part b), a sketch is shown of how the vibration of sample holder - indicated with a double arrow in black - with the sample changes the magnetic flux in the pickup coils, which induces a voltage proportional to the magnetization of the sample.

Generally, a VSM 100 comprises an electromagnet for providing a magnetic field at the sample S and a receiver unit, preferably a set of pick-up coils, more preferably a set of four coils symmetrically positioned around the sample, for receiving a magnetic response signal from the sample. In some embodiments, the receiver unit could be one or more super-conducting devices capable of measuring a magnetic field, such as those used in SQUID-magnetometers, but other magnetic sensors available to the skilled person are contemplated within the teaching and principle of the present invention.

Figure 2 is a schematic drawing of the gas flow in a PRIOR ART vibrating sample magnetometer VSM from LakeShore, model 7404-S. In this option, gas, e.g. Ar gas, is let into the VSM oven, where the Ar gas "falls by gravity" (by being heavier than air) to the sample holder area. Excess gas exits into open air via the gap between the vibrating sample tail and the stationary oven, just below the VSM head drive HD 20. The Ar gas is supplied to enhance heat exchange between oven and sample, as well as to protect the sample and VSM oven from oxidization at high temperatures. This "gravity-controlled" gas flow combined with the fact that the VSM oven, head drive HD and surroundings are exposed to the gas, essentially precludes the use of other gasses than Ar, i.e. light gasses and reactive gasses cannot be used.

On top of this, it is uncertain to which extent the supplied gas (Ar or other) can actually control the gas environment in the sample holder. For powder samples, the Lake Shore sample holder option consists of boron nitride (BN) cup and lid screwed together around the sample (exploded view in the insert). Any gas exchange (of e.g. Ar, air, and/or water vapor desorbed from the sample) in/out of the sample happens by diffusion through narrow, undefined paths of small gaps in the threading and sample (schematically indicated with the small arrow through the sample cup in the exploded view).

Without a forced flow, it will take a long time before the gas in the sample cup is in equilibrium with its surroundings (tests by the inventors show >20 hours). Consequently, the gas composition at the sample during measurements is unknown and most likely also uneven across the sample, i.e. this is not a true in situ option. Moreover, even at equilibrium not all samples will be prevented from oxidation in Ar gas due to gas impurities. Another problem with the semi-closed BN sample holder, without forced gas flow, is that, with increasing temperature, water desorbing from the sample surface can remain as vapour in the holder, for unknown time and temperature ranges, and hence provide an uncontrolled chemical environment, which e.g. enhances sample oxidation and sintering.

Thus, the way of controlling the gas around a sample for VSM measurement need improvements. Generally, it is desired that the present invention may be combined, use or retrofitted with the VSM setup schematically indicated in Figure 2 with an oven 30, i.e. a heater unit surrounding the sample in the sample holder and a head drive HD 20 arranged for vibrating motion of the sample. In the context of the present application, the supplied gas around the sample holder, e.g. Ar gas, may be considered a second gas i.e. different from the first gas.

Figure 3 is a schematic drawing of the gas flow in a sample holder SH 10 for a vibrating sample magnetometer VSM according to the present invention. The elongated sample holder SH provides a controlled gas-atmosphere through and/or around the sample S, a proximal end of the sample holder being mounted on, or at, the head drive. A first and a second fluid channel are arranged along the elongated sample holder, and an inlet for receiving the first gas (to the left in this view, named 'sample gas inlet') and an outlet for letting the first gas out (to the right in this view) are both arranged at the proximal end of the sample holder SH 10 near the head drive HD in the top of Figure 3. The head drive HD is of course connected, mechanically, electronically and/or operationally, to the remaining part of the VSM, but this is not shown for clarity.

For VSM measurements, it is to understood that the head drive will be vibrating, for but other kinds of measurements; for example some types of SQUID magnetometry, a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, for measuring magnetic properties, such as magnetic field, magnetisation, permeability, susceptibility, coercivity, remanence, hysteresis, magnetic losses, and/or magnetic moment, of a sample, the head drive may be fixated. In these aspects of the invention, the magnetometer may have a holding position for the sample holder, upon which the sample holder may be mechanically, electronically and/or operationally connected to remaining part of the magnetometer.

The sample holder SH 10 is inserted into the oven in the open top part of the oven, the sample holder having an narrow and elongated shape for fitting into the oven from above because the oven has an open top and a closed lower portion (as shown in this view).

In Figure 3, a flow of Ar gas is also schematically indicated but this is an optional feature of the present invention, the Ar gas being an example of a second gas, which does not mix with the first gas, at least not around the sample S. The sample gas i.e. the first gas can thus be controlled to have no, or limited, contact with the main parts of the VSM, in particular the oven and vibrating head drive (HD), and therefore make it possible to use reactive gasses for the sample gas by having a controlled gas-atmosphere through, near and/or around the sample, thus the first gas i.e. the sample gas is conveyed in a closed gas/fluid system.

In Figure 3, the elongated sample holder (SH) including the inlet for receiving a first gas, and the outlet arranged for conveying the first gas away, is seen as being arranged for vibrating together with the head drive during a magnetic measurement with the VSM. This is quite different from the conventional VSM shown for example in Figure 2, where the gas supply system does not vibrate with the sample holder. Of course, the gas supply of the present invention should be adapted for this displacement with the sample holder, e.g. by providing flexible tubing systems for providing the first (sample) gas.

Figure 4 is another schematic drawing of the gas flow around, and/or through, the sample S in the sample holder SH 10 for a vibrating sample magnetometer (VSM, not shown in this view for clarity) according to the present invention. The sample holder comprises an inlet 13 for receiving a first gas at the proximal end near the head drive, cf. Figure 3, and an elongated first fluid channel 11 for conveying said first gas from said inlet to the sample S as indicated by the downwards pointing solid arrow in black, the first gas being arranged for flowing through and/or around the sample S. After the gas flows through or around, such as near, next to or along, the sample, possibly causing a chemical reaction between the first gas and sample but not necessarily always, the gas is guided at the end of the first fluid channel towards an elongated second fluid channel 12 (as indicated by the U-shaped arrows) for conveying the first gas away from the sample S, and towards an outlet 14 arranged for conveying the first gas away from said elongated second fluid channel 12.

As indicated in Figure 4 but not limiting in any way, the length of the sample holder may be around 350 mm, but sample holder may more generally have a total length in an interval of approximately 100-500 mm, preferably in an interval of approximately 200-400 mm, most preferably in an interval of approximately 250-350 mm.

Figure 5 is close-up schematic drawing of Figure 4 showing again the gas flow around, and/or through, the sample S in the sample holder SH 10 for a vibrating sample magnetometer (VSM) according to the present invention. The elongated sample holder SH is arranged for fixating a sample S, preferably at the distal end of, in said elongated first fluid channel. This may be done by inserting quartz wool above and below the sample S as shown in this embodiment, but generally various other kind of fixation may be considered by the skilled person. For example a grid may support the sample from below. Alternatively, other kind of wool like glass wool may be considered, and other kind of fixation and support including gluing etc. Of course, the fixation should be considered to be sufficiently robust to withstand the vibrating during VSM measurements. Possibly a protrusion or an indention may be provided below and/or above the sample. In Figure 5, a protrusion is provided at the lower part of the first fluid channel for supporting the quartz wool from below during measurements.

Generally, the first fluid channel (or alternatively the second fluid channel, if the sample is positioned in the second channel instead) may have an inner geometry facilitating plug-flow reaction conditions between the sample and the first gas. Plug-flow reaction conditions will be well-known to the skilled person in chemistry, but briefly for plug-flow conditions, the velocity of the fluid, here the first gas, is assumed to be constant across any cross-section of the pipe, here the first fluid channel 12, perpendicular to the axis of the pipe. For flows in pipes, if a flow is turbulent then the laminar sublayer caused by the pipe wall is so thin that it is negligible. Plug-flow conditions will then be achieved, if the sublayer thickness is much less than the pipe diameter. With respect to plug-flow conditions, the reactor diameter may, as a rule of thumb, be at least 10 times larger than the particles/granules of the sample. This is explained in more detail in *Concepts of Modern Catalysis and Kinetics* by I. Chorkendorff, J. W. Niemantsverdriet WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, and from "Characterization of Catalyst Development: An Iterative Approach" – Bradley, Gattuso, and Bertolacini (ACS Symposium Series Vol 411, 1989). This is part of a set of guidelines for catalyst testing, so the reactor width to sample size may be considered a fairly well-established condition. For more details, the skilled person is also referred to Bradley et al.; *Characterization and Catalyst Development*, ACS Symposium Series; American Chemical Society: Washington, DC, 1989, especially Chapter 11 by Dautzenberg. Both the flow rate of the first gas, the sample size and shape, and the inner geometry of the first fluid channel may accordingly be adapted to provide plug-flow, or near plug-flow, conditions in the sample holder.

In another embodiment, the sample may be positioned in, near or between the transition from the first to the second fluid channel, for example in a U-shaped fluid section between the first and the second channel.

In one embodiment, the sample is situated in the inner quartz tube, in a plug-flow reactor style, sandwiched between two layers of Insulfrax quartz wool, cf. Figure 5. The inner tube is approximately 300 mm long, with an outer diameter of 3 mm, and an inner diameter of 2 mm. Two indents were made approx. 10 mm from the bottom of the inner tube. These are used to anchor the bottom layer of quartz wool that the sample rests on. The inner tube is considered disposable and is loaded with approximately 10 mm^3 (5-10 mg) sample material. The outer tube is approx. 300 mm long with an inner diameter of 4 mm and an outer diameter of 5 mm. The outer tube is closed at the bottom end. The support used in this study (PURALOX MG 2818) has particle sizes of 30 µm, which is approx. 65 times smaller than the width of the inner quartz tube (2 mm, see Fig. 2), and 100 times smaller than the bed height (approx. 3 mm), which fulfils the rules of thumb for establishing plug-flow conditions. Plug-flow conditions will ensure that the material in the inner quartz tube will be uniformly exposed to the gas flowing through the quartz tube. In this case the gas will only have to diffuse through the porous support particles to achieve uniform exposure to the gas, while in the conventional BN cup, cf. Figure 2, the gas has to diffuse through the threading of the BN cup, and then through the porous support, in order to uniformly expose the sample.

Typically, the sample holder SH 10 facilitates sample masses below 100 milligram, preferably below 50 milligram, or most preferably below 10 milligram being measured in the VSM, and sample may have various corresponding volumes ranges to physical properties and/or surface properties during VSM measurement with a flow of the first gas. In one embodiment, the magnetic properties of a thin film on a substrate may be measured with the present invention.

In Figure 5, the elongated first fluid channel 11 for conveying said first gas from said inlet 13 and arranged for flowing through, or around, along, near, etc., the sample with the sample S positioned at the end of the first fluid channel 11. However, the sample S may in principle be positioned in any other position in the sample holder. It may for example be positioned in the second fluid channel. In one embodiment, the sample may be positioned where the first and the second fluid channel are interfaced.

In one embodiment, the disposable inner quartz-tube is roughly 350 mm long with an inner diameter of 2 mm, as shown and explained in Figure 8 below. The tube has two indents approximately 1 cm from the end of the tube to act as a shelf for the quartz wool to sit on. All of the loading of the tube was performed in a fume hood. A thin 400 mm long steel rod is used to load the quartz tube with Insulfrax LT quartz wool from Unifrax. This wool is stamped thoroughly before the sample powder is poured into the quartz tube. As powder tend to stick to the side of the tube, it is tapped against the table surface. When all of the powder has settled on top of the quartz wool, another layer of wool is stamped down on top of the sample to secure it in place as shown in Figure 5. The in situ holder is then assembled inside a fume-hood, and transported to the VSM to be saddled and measured.

Figure 6 is a schematic diagram of the gas system supplying the first gas to the in situ sample holder SH 10 according to the present invention. The gas tubing outside the VSM is 1/8″ stainless steel, and mass flow controllers of type MKS GM50A supply gasses (i.e., hydrogen and argon, in tests of this invention). Synthetic air (20 vol. % O_2 in N_2) was supplied at the variable gas line via a gas flow meter. Pneumatic valves open for the flow of gas that can either be led through the in situ holder, or through the bypass. In Figure 6, it is also shown how the first and the second fluid channel are arranged along the elongated sample holder SH 10 having a sample (black square inside the SH). The inlet 13 and outlet 14 are both arranged at the proximal end of the sample holder near the head drive (not shown for clarity in this figure) i.e. in the upper part in this view. The first and the second fluid channel, and their respective inlet 13 and outlet 14, are arranged so that the sample holder SH forms a closed fluid system for the first gas when being supplied to the inlet 13 and further through and/or around the sample (S) and again when leaving the sample holder via the outlet 14, symbolically indicated 'out'. Preferably the first gas leaving the sample holder can be analysed in dedicated gas analysis equipment (not shown in this figure).

Figure 7 is an annotated picture of the gas system supplying the first gas to the in situ sample holder mounted underneath a conventional VSM head drive together with the VSM oven. It is advantageous that the tubes from the gas system to the sprouts on the sample holder are flexible enough that the vibration of the sample holder is minimally affected. For this the inventors chose tubes of ISO-VERSINIC (a fluoroelastomer) seen as black tubes in Fig. 7. The ISO-VERSINIC is connected to the 1/8" steel tubing and the spouts of the in situ sample holder by simply sliding the tubes over the steel tubing and the plastic sprouts. The system might be optimized by more leak-tight solutions. However, no leakage was detected from these tubes, or anywhere else in the system, when searching for leaks with a Testo 316-EX leak detector. Even after several days of running experiments, and multiple exposures of the tip of the sample holder SH to 950 deg. C, no leaks were detected. The inlet 13 and outlet 14 ensures that the VSM system including the sample holder forms a closed fluid system for the first gas, in particular before and after being exposed to the sample.

Figure 8 shows a technical drawing and two pictures of the sample holder according to the present invention. Part a) shows a technical drawing of in situ VSM sample holder comprising an inner and an outer quartz tubes, which together form two concentric fluid channels, the first and inner fluid channel surrounded by the second and outer fluid channel. The drawings also shows an upper assembly for further fluid connection to a gas system and mechanical connection with the head drive at the upper part of the sample holder. The first and the second fluid channel are arranged along, e.g. co-axially, the elongated sample holder, and inlet 13 and outlet 14 are arranged at the proximal end (in this view upper part) of the sample holder whereby conveying of the first gas takes place so that the sample holder and the inlet and outlet (and their further fluid connections, e.g. gas tubes) forms a closed fluid system for the first gas through and/or around the sample S. Depending on the gas type, the connections, e.g. treadings, tubes, intermediate parts, rings, joints, valves, etc. should of course be chosen in suitable materials and qualities appropriate for the task, e.g. plastic, metal (copper), rubber, for vacuum applications as the skilled person in vacuum and gas technology will readily understand. Part (b) shows a picture of fabricated in situ sample holder, whereas part (c) shows a close-up picture of the inner quartz tube with sample (black powder) loaded.

Results:

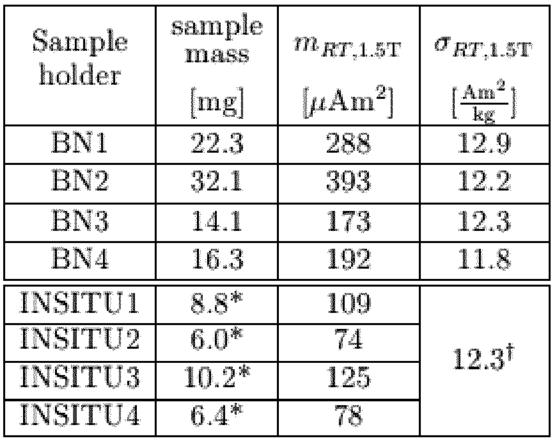
The inventors prepared a material of partially oxidized Co nanoparticles on porous $MgAl_2O_4$ spinel support. This material allowed to follow the oxidation and reduction via change of the magnetic moment and thereby test the functionality of the in situ sample holder according to the present invention.

A batch of 2 g of $MgAl_2O_4$ with 10 wt.% cobalt was made by incipient wetness impregnation of cobalt-nitride salt ($Co(NO_3)_2$) on PURALOX MG 28 ($MgAl_2O_4$) from Sasol. The impregnated sample was then dried at 80 deg. C on a hot plate overnight followed by calcination of the cobalt-nitride salt to cobalt oxide (CoO/Co_3O_4) nanoparticles at 450 deg. C in air for 1 hour. Afterwards, the particles were partially reduced (to Co/CoO /Co_3O_4).

Metallic Co is ferromagnetic up to 1121 deg. C, whereas a fully oxidized cobalt sample (CoO/Co_3O_4) possesses a close-to-zero magnetic moment. The moment of Co enables magnetic centering of the sample for VSM measurements. The partial reduction was carried out by heating the sample in an atmosphere of 2.4% H_2 in Ar, first to 110 deg. C for 2 h to remove any moisture in the sample, and then to 850 deg. C where it was left for 45 min. Afterwards the sample was cooled to room temperature.

Four of the samples were measured on a Lake Shore 7407 model VSM in commercial boron-nitride (BN) cups as the sample holder. The other four samples were measured in the in situ sample holder according to the present invention on a 7404-S model Lake Shore VSM to facilitate comparison of the invention with convention methods and experimental setups.

Table 1:



Sample holder	sample mass [mg]	$m_{RT,1.5\mathrm{T}}$ [$\mu\mathrm{Am}^2$]	$\sigma_{RT,1.5\mathrm{T}}$ [$\frac{\mathrm{Am}^2}{\mathrm{kg}}$]
BN1	22.3	288	12.9
BN2	32.1	393	12.2
BN3	14.1	173	12.3
BN4	16.3	192	11.8
INSITU1	8.8*	109	12.3†
INSITU2	6.0*	74	
INSITU3	10.2*	125	
INSITU4	6.4*	78	

Sample masses for the as-prepared samples together with their sample magnetic moments $m_{RT,1.5T}$ at RT and 1.5 T, and the mass-specific magnetizations $\sigma_{RT,1.5T}$ for the samples in BN holders at RT and 1.5 T are shown in Table 1 above.
The masses for the samples in the in situ sample holder according to the invention (marked with * above) have been calculated as $m_{RT,1.5T}$ divided by the average $\sigma_{RT,1.5T}$ obtained for the samples in BN cups (12.3 Am^2/kg, in the table).

Figures 9-11 show some measured magnetization (σ) results using the in situ sample holder in a VSM according to the present invention,

Figure 9 shows magnetization curves showing the reduction of samples of $Co/CoO/Co_3O_4$ particles on porous MgAl-spinel as a function of time. The measurements are taken at 850 deg. C in an applied magnetic field of 1 T. INSITU samples are as such, with the oxidised INSITU sample named INSITU4-oxi. BN samples are named BN1 to BN4. This shows that the in situ holder performs very well, i.e. that the invention provides a stable and durable sample holder for in situ high-temperature VSM studies.

Figure 10 shows magnetization σ and temperature as a function of time for a Co nanoparticle sample on porous MgAl-spinel support during oxidation in the in situ VSM sample holder according to the invention. In this experiment, the sample was exposed to a flow of synthetic air and an applied field of 1 Tesla.

From figure 10, it is clearly seen, that as the temperature in the VSM oven option is raised, σ drops, as a result of the oxidation of the sample. Full oxidation is reached at

300 deg. C. Hereafter, only a magnetization of around 0.3Am^2/kg remains. This kind of investigation is not possible in conventional high temperature VSM using a conventional BN sample cup, as the oven cannot handle exposure to oxidizing atmospheres at elevated temperatures.

Figure 11 shows magnetization σ as a function of temperature while heating to 850 deg. C, in an atmosphere of 2.4 vol.% H_2 in Ar. The measurements were performed in an applied field of 1 Tesla. Samples measured in the in situ quartz holder according to the invention are named INSITU3 and INSITU4. Samples measured in a BN cup are named BN3 and BN4. The INSITU4-oxi curve is from the sample that had also been oxidized in the in situ sample holder prior to this measurement.

For all these samples, the reduction starts at around 300 deg. C. Upon increasing temperature, the magnetization in all five cases rises to a peak, after which the magnetization decays. The decay is caused by the drop in magnetization as temperature approaches the Curie temperature of the samples. Again, the behaviour of the similar samples (i.e. those that were partly reduced before the measurement) is almost identical in the in situ holders but less consistently reproduced in the BN cups probably due to the less optimal gas flow. The inventors also performed measurements at 950 deg. C (not shown). The in situ system showed stability also at this high temperature. Measurements at 950 deg. C took approx. 2 hrs and were done twice or more per sample. No changes of the sample holder were observed, neither to the assembly, nor to the inner disposable quartz tubes and the re-used outer quartz tube.

The results presented here showed, that the in situ sample holder according to the invention can measure just as well as the conventional BN system in these sorts of experiments where a sample is reduced, and the magnetic properties investigated in a weakly reducing atmosphere. Additionally, the in situ sample holder according to the invention also works for studies in an oxidizing atmosphere of synthetic air. As presented in Table 1 above, the masses of the INSITU samples varied between 6-10 mg. With the loading of 10 % cobalt, this meant that the samples contained about 0.6-1 mg of Co. This is a reduction of magnetic material of 90-94 % when comparing to the approx. 0.1 g of magnetic material typically used in the in situ reactor in US patent application 2011/204884.

The advantages of the sample holder according to the present invention lies inter alia in the freedom to expose the sample to various gas-mixtures, which is not a possibility in the conventional VSM where the gas will interact with the oven. Here, the inventors limited the investigations to a hydrogen-argon mix and synthetic air, but these investigations can be expanded to many different gas mixtures. The gas flow of 10 mL/min, and the estimated sample volume of 10 mm^3, makes for an exchange of sample volume in gas approximately 17 times per second. If pure H_2 gas had been chosen instead of H_2 in Ar, it is likely that the samples in the in situ sample holders would reduce even faster. The use of pure H_2 is a possibility only in the in situ sample holder, as pure hydrogen would be a safety hazard in the open air system used for the BN sample cups. Other advantages of the in situ sample holder according to the present invention include the possibility to analyze the exit gas, and/or that this sample holder is made of relatively inexpensive materials, that can be easily manufactured.

Other aspects contemplated within the teaching and principle of the present invention could include an improved estimation of the mass in the quartz tube, and an improvement on the design, allowing for higher-risk gasses to be sent through the system, such as CO.

Figure 12 is a flow-chart of a method according to the invention i.e. a method for measuring magnetic properties of a sample using a vibrating sample magnetometer VSM 100, or a SQUID magnetometer, a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, for measuring magnetic properties, such as magnetic field, magnetisation, permeability, susceptibility, coercivity, remanence, hysteresis, magnetic losses, and/or magnetic moment, of a sample, the method generally comprising:

- **S1** providing an electromagnet for providing a magnetic field at the sample,
- **S2** providing a receiver unit for receiving a magnetic response signal from the sample, and

- **S3** providing an elongated sample holder SH 10 for providing a controlled gas-atmosphere through and/or around the sample, a proximal end of the sample holder being mounted on, or at, a head drive, the sample holder comprising:

- an inlet 13 for receiving a first gas at the proximal end,
- an elongated first fluid channel 11 for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,
- an elongated second fluid channel 12 for conveying said first gas away from the sample, and
- an outlet 14 arranged for conveying the first gas away from said elongated second fluid channel, as shown Figures 3-6,

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive HD 20.

Figure 13 is a schematic drawing of the sample holder adapted to AC-calorimetry. The left panel shows the sample holder on its' own, the right panel shows the sample holder placed in the AC-coil of the calorimeter. The principles of the sample holder are similar to those of the VSM sample holder, comprising a gas inlet, 13, a first fluid channel, 11, a second fluid channel, 12, and an outlet, 14, for achieving a closed fluid system with a controlled gas atmosphere through and/or around the sample, S. Additionally, in order to adapt the sample holder to calorimetric measurements, a temperature sensor is introduced to the holder, here it is a thin non-magnetic thermocouple, 15, fed from the top of the sample holder to the sample (with the probe position at the sample shown by the black dot in the drawing). The sample holder is positioned in the AC-coil (right panel) such that its' centre axis coincides with the centre axis of the coil and such that the sample vertically is in the middle of the coil. The holder is held in position by a holding fixture (not shown in the drawing).

Figure 14 shows annotated photos of said sample holder adapted to an AC-calorimeter. In the specific example, the sample holder is fitted to a commercial AC-calorimeter of type magneTherm from the company nanoTherics. The left panel of Figure 14 is a picture of the sample holder. The top part of the sample holder, here made with Swagelok Fittings in metal, has gas inlet 13 and gas outlet 14 connected to

the first and second fluid channels, here made in quartz. For AC-calorimetry measurements, the sample holder is kept at a holding position (i.e. it is not vibrating) and therefore it has been possible to build a heavier sample holder with larger sample volume (here ca. 0.5 cubic centimeter). The sample S (here an iron-based catalyst material) rests on a layer of quartz wool at the distal end of the first fluid channel as shown in the middle panel in Figure 14. A thin non-magnetic thermocouple (not shown) is fed through a ceramic tube from the top of the sample holder to the sample. The middle panel shows an enlarged version of the sample S and the quartz tubes used for the first fluid channel 11 and the second fluid channel 12.
The right panel of Figure 14 shows a picture of the sample holder inserted into a water-cooled coil in the AC-calorimeter. When turned on, the current in the coil can provide an alternating magnetic field to the sample with field amplitudes and frequencies in the ranges of ca. 0-25 mT and ca. 100-1000 kHz. The white material between the sample holder and the coil is insulation material. In the displayed case, the sample holder is placed in the AC-coil at the front panel of the magneTherm box. It is also possible to place the sample holder in the other AC-coil located inside the box (in the picture, this coil is hidden under the top lid and pointed toward by the white arrow). A main advantage of said sample holder is that it can readily be implemented into magnetometry systems with an open top but a closed lower part.

Figure 15 shows AC-calorimetry measurements obtained on the sample in the adapted sample holder. The temperature of the sample is measured as a function of time for different magnetic field amplitudes (7 mT, 14 mT, 22 mT) and frequencies (567 kHz, 916 kHz) in a gas flow of 2.4 vol.% H_2 in Ar (100 mL/min). The measurements show that the sample holder is adaptable to AC-calorimetry. Specifically, the data shows that after 60 s, where the AC-coil is turned on, the sample is heated by induction heating and temperature increases. After 120 s, the AC-coil is turned off, and the sample cools. From such curves, power losses can be determined. As it is the case for all calorimetry, also in this setup, power losses in the sample and to the surroundings need careful evaluation. In connection to this, is noteworthy that the gas in the second fluid channel both conveys heat away from the sample and provides a heated region around the first fluid channel and the sample.

In short, the invention relates to a vibrating sample magnetometer VSM 100 for measuring magnetic properties of a sample S using an elongated sample holder SH 10 with a controlled gas-atmosphere as shown Figures 3-6. The sample holder has an inlet 13 for receiving a first gas at the proximal end, an elongated first fluid channel 11 for conveying said first gas from the inlet to the sample. An elongated second fluid channel 12 conveys the first gas away from the sample, and an outlet 14 is arranged for conveying the first gas away from the elongated second fluid channel. Both the inlet and the outlet are arranged at the proximal end of the sample holder near the head drive, the sample holder facilitates vibrating sample magnetometry measurements of samples in gas-controlled environments at temperatures up to at least 1000 degrees C and in situ measurements of small sample masses.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the numbered items and/or claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different numbered items and/or claims, may possibly be advantageously combined, and the mentioning of these features in different numbered items and/or claims does not exclude that a combination of features is not possible and advantageous.

ANNEX OF NUMBERED ITEMS:

1. A vibrating sample magnetometer (VSM, 100) for measuring magnetic properties of an associated sample (S), the VSM comprising:

- an electromagnet for providing a magnetic field at the sample,
- a receiver unit for receiving a magnetic response signal from the sample,
- a head drive (HD, 20) arranged for vibrating motion of the sample, and

- an elongated sample holder (SH, 10) for providing a controlled gas-atmosphere through and/or around the sample, a proximal end of the sample holder being mounted on, or at, the head drive, the sample holder comprising:

  - an inlet (13) for receiving a first gas at the proximal end,

  - an elongated first fluid channel (11) for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,

  - an elongated second fluid channel (12) for conveying said first gas away from the sample, and

  - an outlet (14) arranged for conveying the first gas away from said elongated second fluid channel

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD, 20).

2. The VSM according to item 1, wherein the elongated sample holder (SH, 10) including the inlet (13) for receiving a first gas, and the outlet (14) arranged for conveying the first gas away, is arranged for vibrating by the head drive (HD) during a magnetic measurement with the VSM.

3. The VSM according to item 1 or 2, wherein the elongated sample holder (SH, 10) is arranged for fixating a sample (S) in said elongated first fluid channel,

preferably at the distal end, preferably fixating by a grid, glass wool, and/or an indent/protrusion, etc.

4. The VSM according to any of items 1-3, wherein the elongated first fluid channel has an inner geometry facilitating plug-flow reaction conditions between the sample and the first gas. This is very different from a conventional BN cup VSM from e.g. LakeShore.

5. The VSM according to any of items 1-4, wherein the sample holder facilitates sample masses below 100 milligram, preferably below 50 milligram, or most preferably below 10 milligram being measured in the VSM.

6. The VSM according to any of items 1-5, wherein the elongated first fluid channel for conveying said first gas from said inlet and arranged for flowing through, or around, along, nearby etc., the sample at the end of the first fluid channel, preferably the first gas interacts with the sample.

7. The VSM according to any of the preceding items, wherein the elongated first fluid channel and the elongated second fluid channel are arranged in a coaxially configuration to each other in the sample holder, with one fluid channel surrounding the other fluid channel while said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD).

8. The VSM according to any of the preceding items, wherein the first and second fluid channel are arranged in a parallel configuration to each other, while said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD).

9. The VSM according to item 1, wherein the sample is positioned near, or at, the distal end of the sample holder during measurement of magnetic properties.

10. The VSM according to item 9, wherein the sample is positioned near, or at, the distal end of the sample holder by having a relative longitudinal position along the sample holder being maximum 20%, more preferably maximum 10%, most preferably maximum 5% of the total length of the sample holder away from the distal end point of the sample holder.

11. The VSM according to item 1, wherein a temperature regulating unit, preferably a heater unit, is arranged for thermally controlling the sample during measurement of magnetic properties.

12. The VSM according to item 11, wherein temperature regulating unit is surrounding the sample.

13. The VSM according to any of items 11 or 12, wherein the temperature regulating unit, preferably a heater unit, forms a substantially closed receptacle with an opening at one end, said opening being capable of receiving the elongated sample holder (SH) at said one end.

14. The VSM according to item 1 or 13, wherein gas supply means are arranged for providing a second gas around the sample holder and between the sample holder and the temperature regulating unit, preferably a heater unit, more preferably said second gas being a substantially inert gas, alternatively a vacuum could also used instead of the second gas.

15. The VSM according to item 1, wherein first and the second fluid channel are arranged so that the sample holder forms a closed fluid system for the first gas through and/or around the sample.

16. The VSM according to item 1, wherein the sample holder is arranged for the first gas being a reactive gas, an inert gas, or a gas at equilibrium with the sample. The first gas can be collected after the outlet, for analysis, for reuse, and/or safety reasons.

17. The VSM according to any of the preceding items, wherein the sample holder is manufactured substantially in glass, or a glass-like material, preferably quartz, steel, metal alloy, or ceramic or any combination thereof.

18. The VSM according to any of the preceding items, wherein the sample holder has total length in an interval of approximately 100-500 mm, preferably in an interval of approximately 200-400 mm, most preferably in an interval of

approximately 250-350 mm, but other intervals or ranges may be considered and applied in the context of the present invention by the skilled person.

19. An elongated sample holder (SH) arranged for cooperating with a magnetometer, such as a vibrating sample magnetometer (VSM) for measuring magnetic properties, or a SQUID magnetometer for measuring magnetic properties, a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, such as magnetic field, magnetisation, permeability, susceptibility, coercivity, remanence, hysteresis, magnetic losses, and/or magnetic moment, of a sample, a proximal end of the sample holder being mounted on, or at, a head drive, alternatively a holding position, of the magnetometer, and the sample being receivable in the sample holder, the elongated sample holder (SH) providing a controlled gas-atmosphere through and/or around the sample during measurements, the sample holder comprising:

- an inlet (13) for receiving a first gas at the proximal end,

- an elongated first fluid channel (11) for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,

- an elongated second fluid channel (12) for conveying said first gas away from the sample, and

- an outlet (14) arranged for conveying the first gas away from said elongated second fluid channel

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD).

20. The sample holder according item 19, wherein the SH is retrofitable into an existing vibrating sample magnetometer (VSM), or an existing SQUID magnetometer, an existing magnetometer for measuring AC susceptibility, an

existing magnetometer for measuring dynamic hysteresis loops, or an existing calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement.

21. A method for measuring magnetic properties of a sample using a vibrating sample magnetometer (VSM), a SQUID magnetometer, a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, the method comprising:

- providing an electromagnet for providing a magnetic field at the sample,
- providing a receiver unit for receiving a magnetic response signal from the sample, providing an elongated sample holder (SH, 10) for providing a controlled gas-atmosphere through and/or around the sample, a proximal end of the sample holder being mounted on, or at, a head drive, the sample holder comprising:

  - an inlet (13) for receiving a first gas at the proximal end,
  - an elongated first fluid channel (11) for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,
  - an elongated second fluid channel (12) for conveying said first gas away from the sample, and
  - an outlet (14) arranged for conveying the first gas away from said elongated second fluid channel

  wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD, 20).

22. A magnetometer for measuring magnetic properties of an associated sample, the magnetometer comprising:

- an electromagnet for providing a magnetic field at the sample,
- a receiver unit for receiving a magnetic response signal from the sample,

- an elongated sample holder (SH) for providing a controlled gas-atmosphere around the sample, a proximal end of the sample holder being mounted on, or at, a holding position on the magnetometer, the sample holder comprising:

- an inlet for receiving a first gas at the proximal end,

- an elongated first fluid channel for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,

- an elongated second fluid channel for conveying said first gas away from the sample, and

- an outlet arranged for conveying the first gas away from said elongated second fluid channel

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near said holding position (HP).

23. The magnetometer according to item 22, the magnetometer being a vibrating sample magnetometer (VSM), or a SQUID magnetometer, a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, for measuring magnetic properties, such as magnetic field, magnetisation, permeability, susceptibility, coercivity, remanence, hysteresis, magnetic losses, and/or magnetic moment, of a sample.

CLAIMS

1. A vibrating sample magnetometer (VSM, 100) for measuring magnetic properties of an associated sample (S), the VSM comprising:

- an electromagnet for providing a magnetic field at the sample,
- a receiver unit for receiving a magnetic response signal from the sample,
- a head drive (HD, 20) arranged for vibrating motion of the sample, and

- an elongated sample holder (SH, 10) for providing a controlled gas-atmosphere through and/or around the sample, a proximal end of the sample holder being mounted on, or at, the head drive, the sample holder comprising:

  - an inlet (13) for receiving a first gas at the proximal end,

  - an elongated first fluid channel (11) for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,

  - an elongated second fluid channel (12) for conveying said first gas away from the sample, and

  - an outlet (14) arranged for conveying the first gas away from said elongated second fluid channel

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD, 20),
wherein the first (11) and the second (12) fluid channel are arranged so that the sample holder forms a closed fluid system for the first gas through and/or around the sample (S).

2. The VSM according to claim 1, wherein the elongated sample holder (SH, 10) including the inlet (13) for receiving a first gas, and the outlet (14) arranged for

conveying the first gas away, is arranged for vibrating by the head drive (HD) during a magnetic measurement with the VSM.

3. The VSM according to claim 1 or 2, wherein the elongated sample holder (SH, 10) is arranged for fixating a sample (S) in said elongated first fluid channel (11), preferably at a distal end.

4. The VSM according to any of claims 1-3, wherein the elongated first fluid channel (11) has an inner geometry facilitating plug-flow reaction conditions between the sample (S) and the first gas.

5. The VSM according to any of claims 1-4, wherein the sample holder (SH, 10) facilitates sample masses below 100 milligram, preferably below 50 milligram, or most preferably below 10 milligram, being measured in the VSM.

6. The VSM according to any of the preceding claims, wherein the elongated first fluid channel (11) and the elongated second fluid channel (12) are arranged in a coaxially configuration to each other in the sample holder, with one fluid channel surrounding the other fluid channel, while said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD, 20).

7. The VSM according to claim 1, wherein the sample (S) is positioned near, or at, the distal end of the sample holder (SH, 10) during measurement of magnetic properties.

8. The VSM according to claim 1, wherein a temperature regulating unit, preferably a heater unit, is arranged for thermally controlling the sample during measurement of magnetic properties.

9. The VSM according to claim 8, wherein the temperature regulating unit, preferably a heater unit, forms a substantially closed receptacle with an opening at one end, said opening being capable of receiving the elongated sample holder (SH) at said one end.

10. The VSM according to claim 1, wherein the first gas is collected after said outlet (14) for analysis, for reuse, and/or safety reasons.

11. The VSM according to claim 1, wherein the sample holder (SH, 10) is arranged for the first gas being a reactive gas, an inert gas, or a gas at equilibrium with the sample.

12. An elongated sample holder (SH, 10) arranged for cooperating with a vibrating sample magnetometer (VSM, 100) for measuring magnetic properties, or a SQUID magnetometer for measuring magnetic properties, a magnetometer for measuring AC susceptibility, or a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, of a sample, a proximal end of the sample holder being mounted on, or at, a head drive, alternatively a holding position, of the magnetometer, and the sample being receivable in the sample holder, the elongated sample holder (SH) providing a controlled gas-atmosphere through and/or around the sample during measurements, the sample holder comprising:

- an inlet (13) for receiving a first gas at the proximal end,

- an elongated first fluid channel (11) for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,

- an elongated second fluid channel (12) for conveying said first gas away from the sample, and

- an outlet (14) arranged for conveying the first gas away from said elongated second fluid channel

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD),
wherein the first (11) and the second (12) fluid channel are arranged so that the sample holder forms a closed fluid system for the first gas through and/or around the sample (S).

13. The sample holder according claim 12, wherein the sample holder is retrofitable into an existing vibrating sample magnetometer (VSM), an existing SQUID

magnetometer, an existing magnetometer for measuring AC susceptibility, an existing magnetometer for measuring dynamic hysteresis loops, or an existing calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, preferably a magnetometer, or calorimeter, where a heater unit is surrounding the sample in the sample holder.

14. A method for measuring magnetic properties of a sample using a vibrating sample magnetometer (VSM), a SQUID magnetometer, a magnetometer for measuring AC susceptibility, a magnetometer for measuring dynamic hysteresis loops, or a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement, the method comprising:

- providing an electromagnet for providing a magnetic field at the sample,
- providing a receiver unit for receiving a magnetic response signal from the sample, and
- providing an elongated sample holder (SH, 10) for providing a controlled gas-atmosphere through and/or around the sample, a proximal end of the sample holder being mounted on, or at, a head drive, the sample holder comprising:
  - an inlet (13) for receiving a first gas at the proximal end,
  - an elongated first fluid channel (11) for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,
  - an elongated second fluid channel (12) for conveying said first gas away from the sample, and
  - an outlet (14) arranged for conveying the first gas away from said elongated second fluid channel

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near the head drive (HD, 20),
wherein the first (11) and the second (12) fluid channel are arranged so that the sample holder forms a closed fluid system for the first gas through and/or around the sample (S).

15. A magnetometer for measuring magnetic properties of an associated sample, the magnetometer comprising:

- an electromagnet for providing a magnetic field at the sample,
- a receiver unit for receiving a magnetic response signal from the sample,

- an elongated sample holder (SH, 10) for providing a controlled gas-atmosphere around the sample, a proximal end of the sample holder being mounted on, or at, a holding position on the magnetometer, the sample holder comprising:

- an inlet (13) for receiving a first gas at the proximal end,

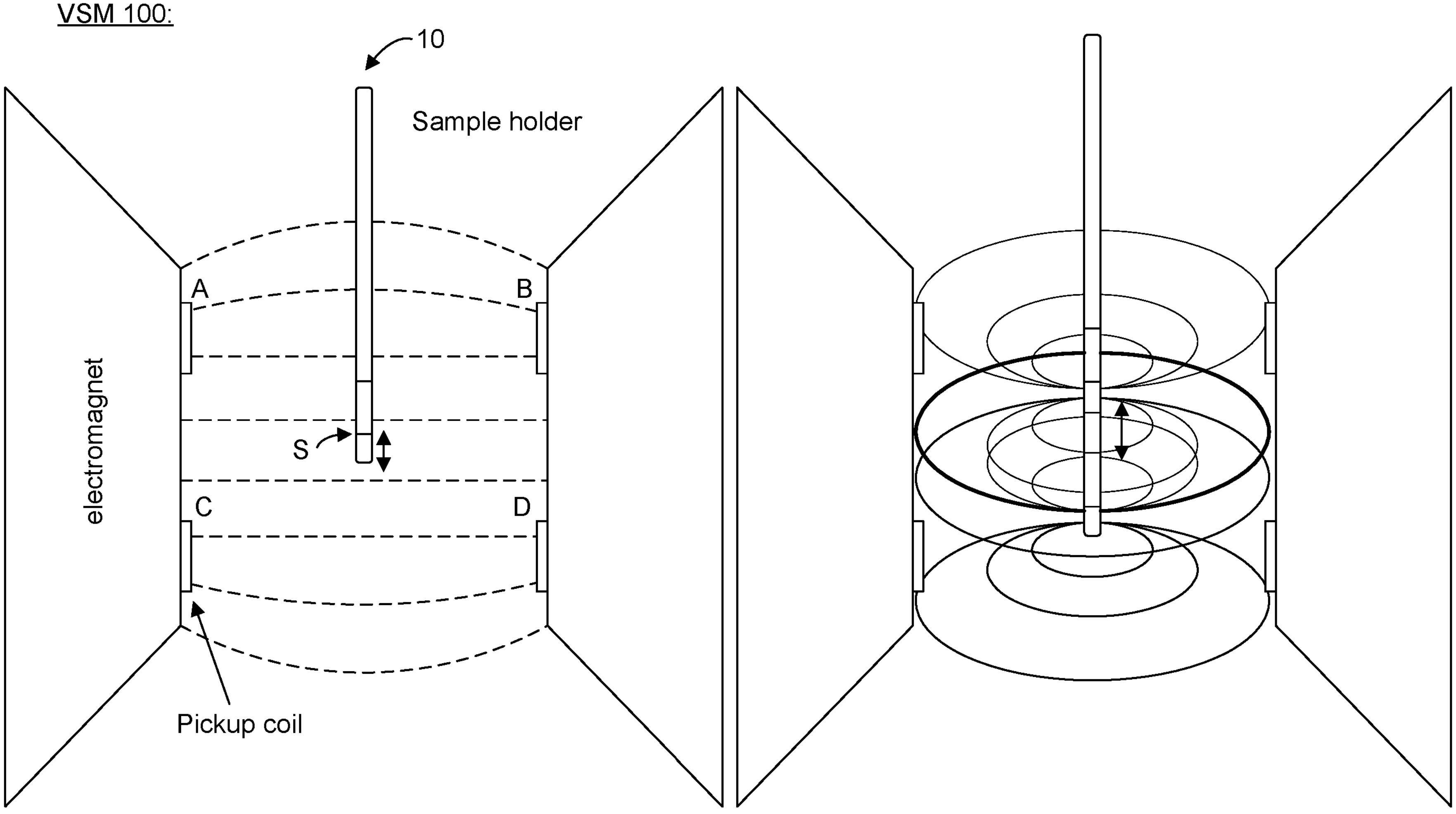
- an elongated first fluid channel (11) for conveying said first gas from said inlet to the sample, the first gas being arranged for flowing through and/or around the sample,

- an elongated second fluid channel (12) for conveying said first gas away from the sample, and

- an outlet (14) arranged for conveying the first gas away from said elongated second fluid channel

wherein the first and the second fluid channel are arranged, at least partly, along the elongated sample holder, and wherein said inlet and said outlet are both arranged at the proximal end of the sample holder near said holding position, wherein the first (11) and the second (12) fluid channel are arranged so that the sample holder forms a closed fluid system for the first gas through and/or around the sample (S).

16. The magnetometer according to claim 15, the magnetometer being:
- a vibrating sample magnetometer (VSM, 100),
- a SQUID magnetometer
- a magnetometer for measuring AC susceptibility,
- a magnetometer for measuring dynamic hysteresis loops, or
- a calorimeter for measuring AC-field-induced power losses in magnetic materials by temperature measurement.



(a)

(b)

FIG. 1

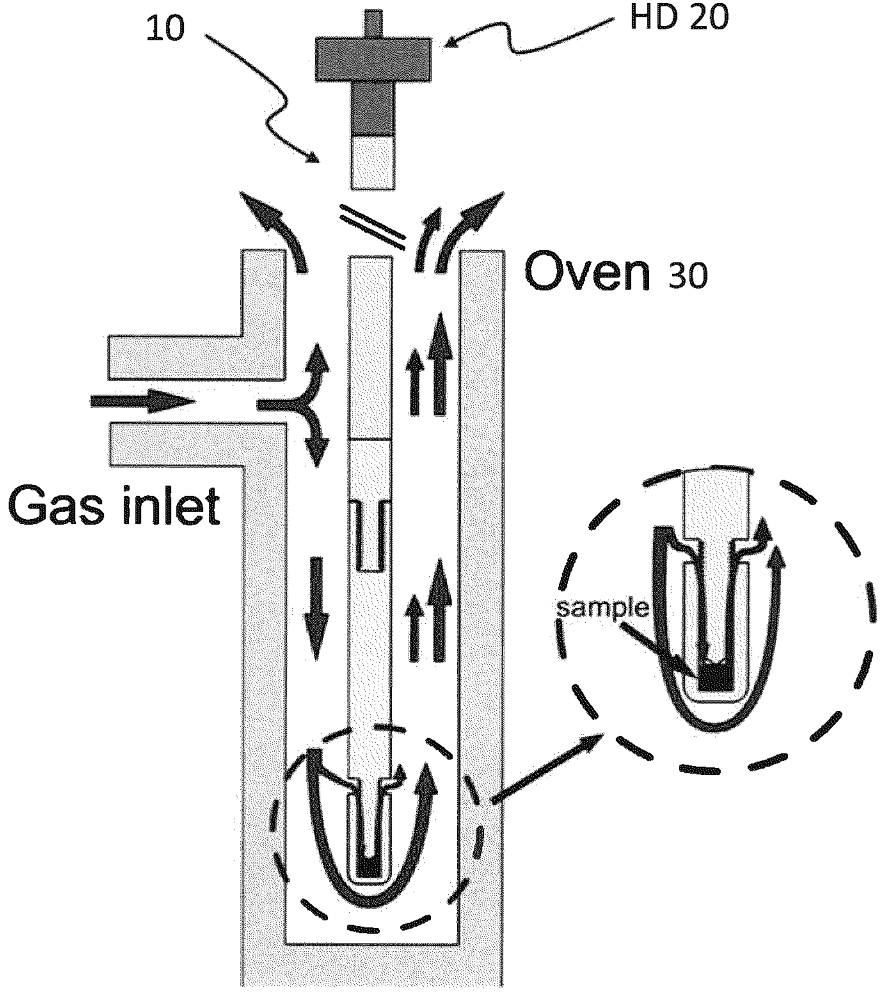


FIG. 2 (PRIOR ART)

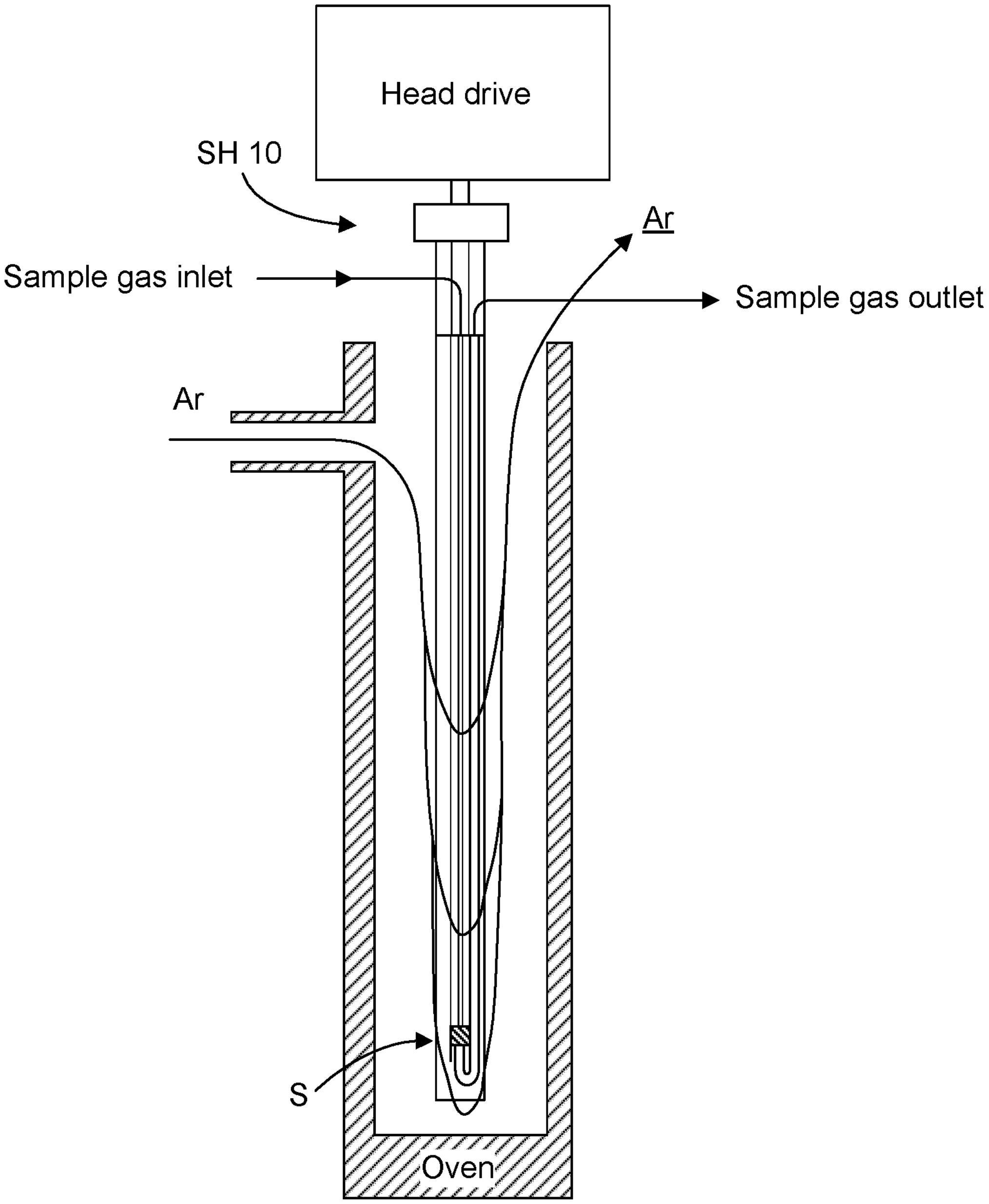

Head drive
SH 10
Ar
Sample gas inlet
Sample gas outlet
Ar
S
Oven

FIG. 3

SH 10:

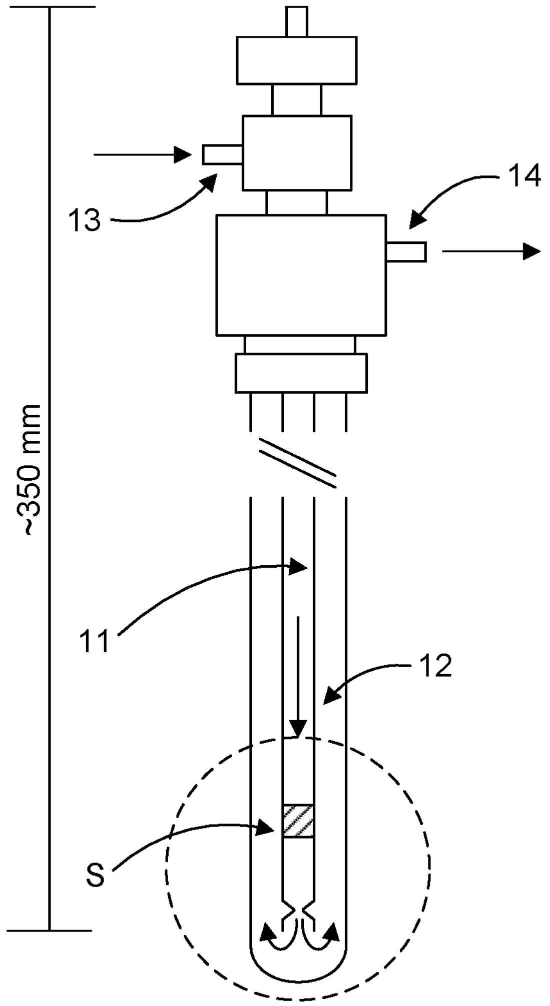


FIG. 4

SH 10:

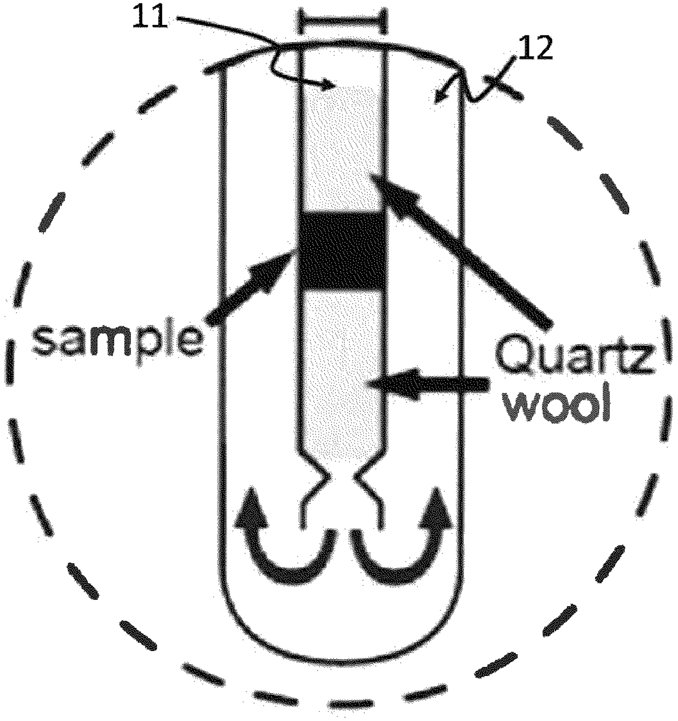


FIG. 5

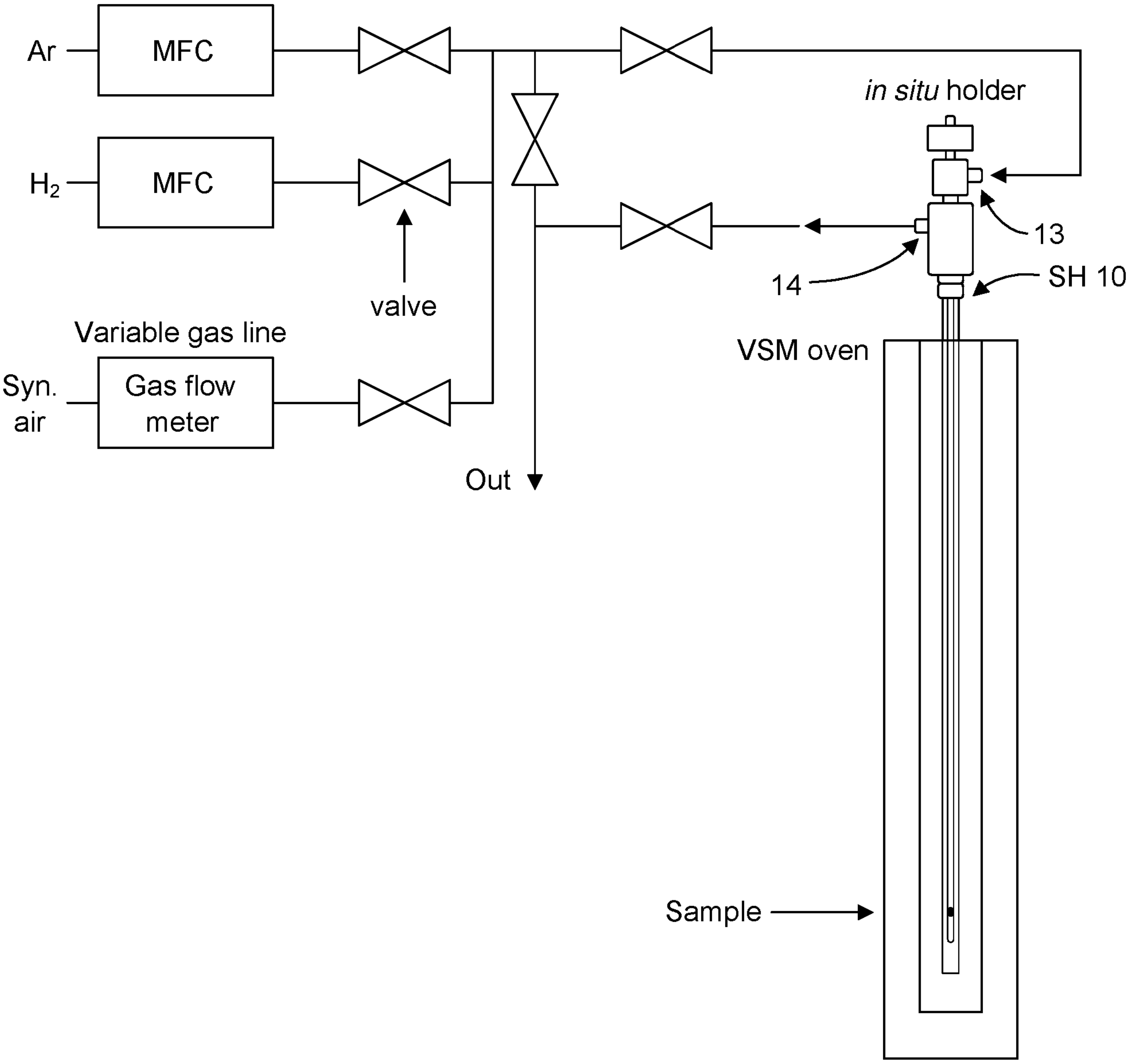

Ar
MFC
H_2
MFC
valve
Variable gas line
Syn. air
Gas flow meter
Out
in situ holder
13
14
SH 10
VSM oven
Sample

FIG. 6

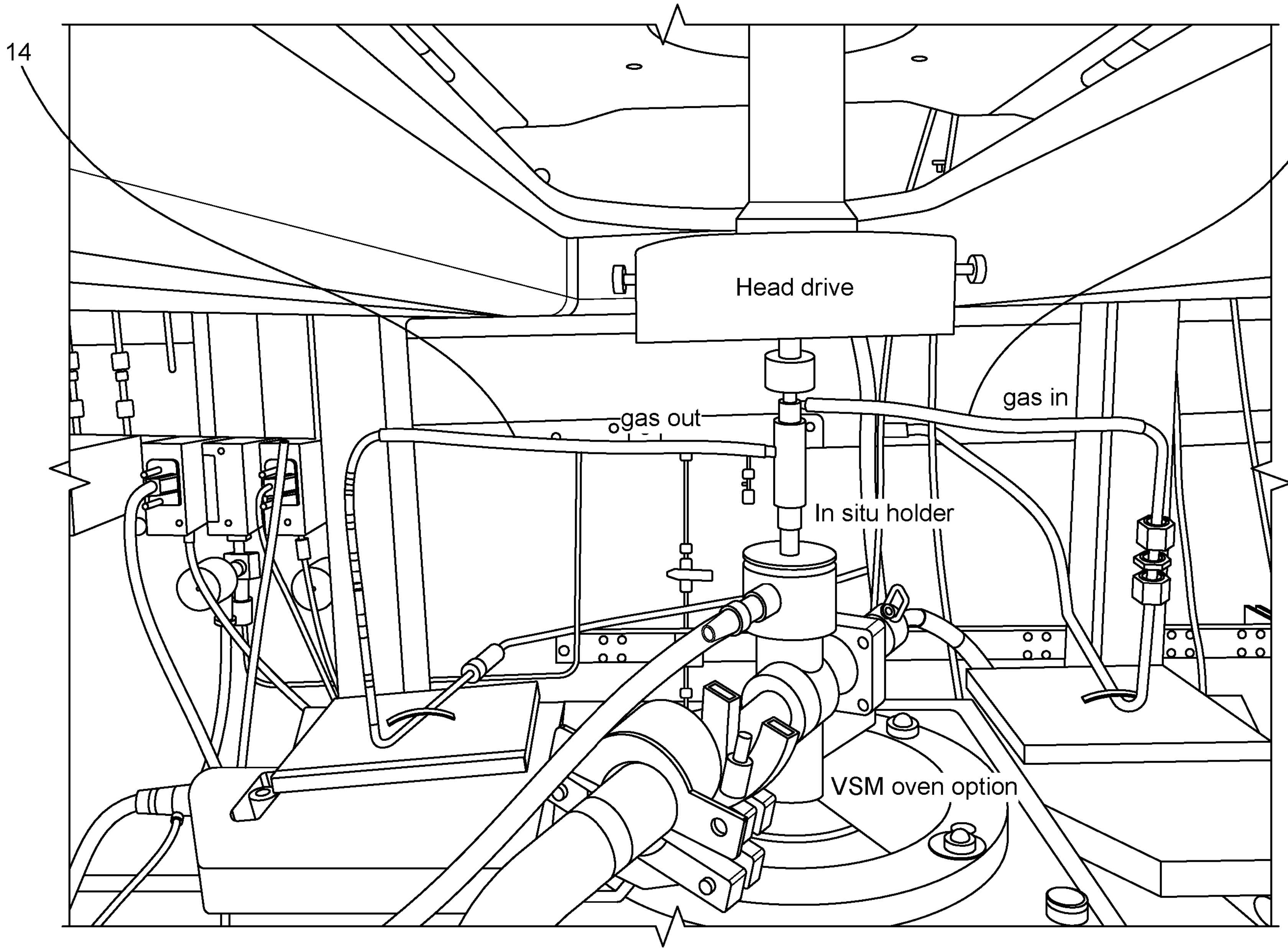


FIG. 7

SH 10:

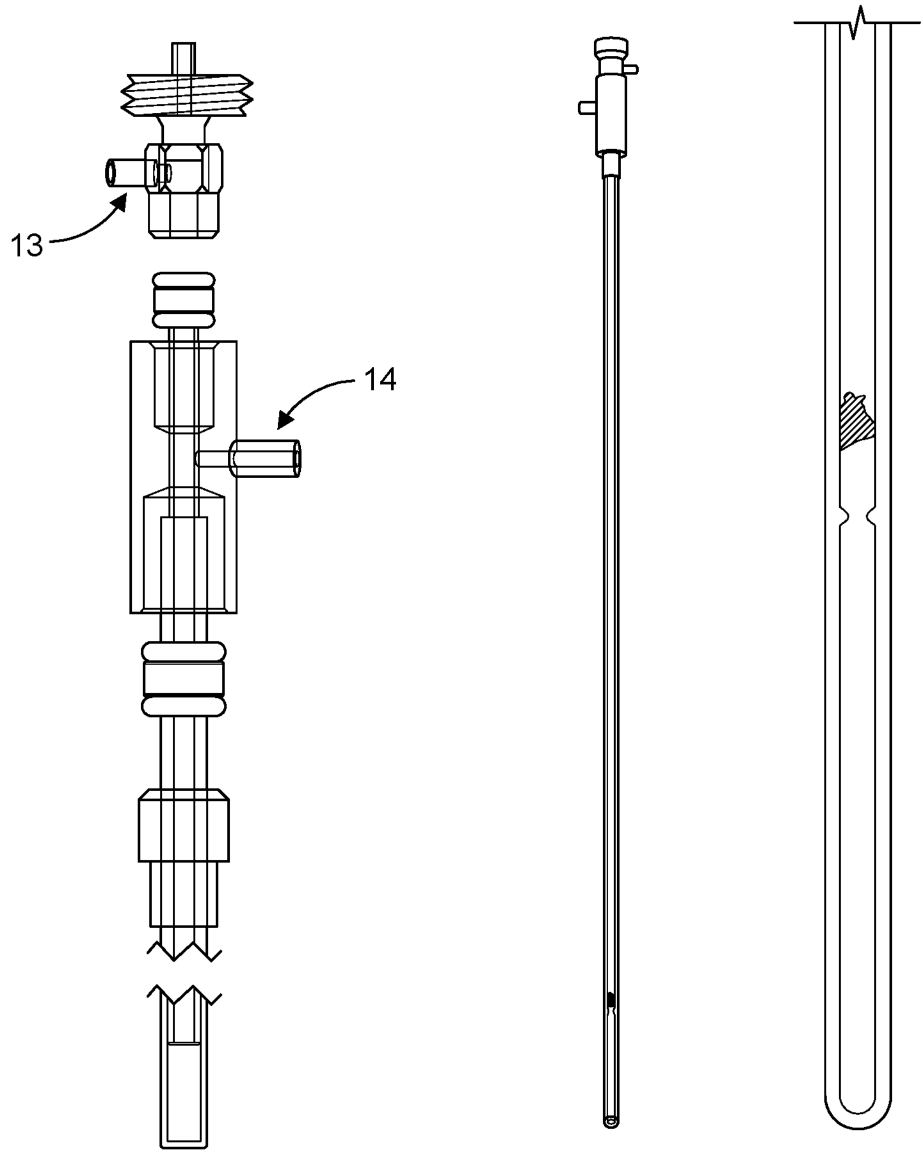


FIG. 8

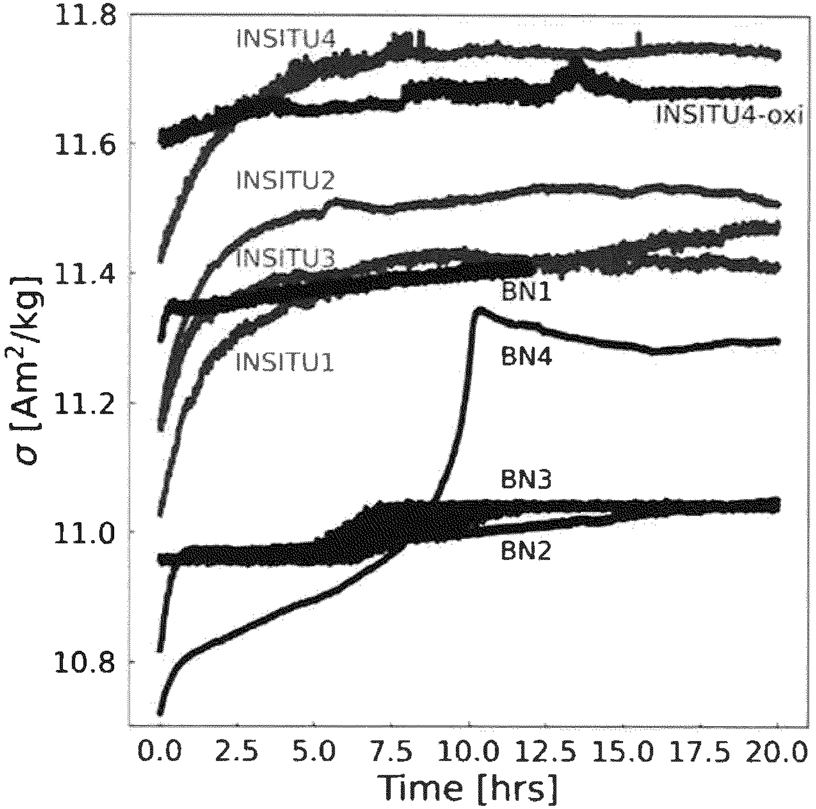

INSITU4
INSITU4-oxi
INSITU2
INSITU3
BN1
INSITU1
BN4
BN3
BN2
11.8
11.6
11.4
11.2
11.0
10.8
σ [Am²/kg]
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Time [hrs]

FIG. 9

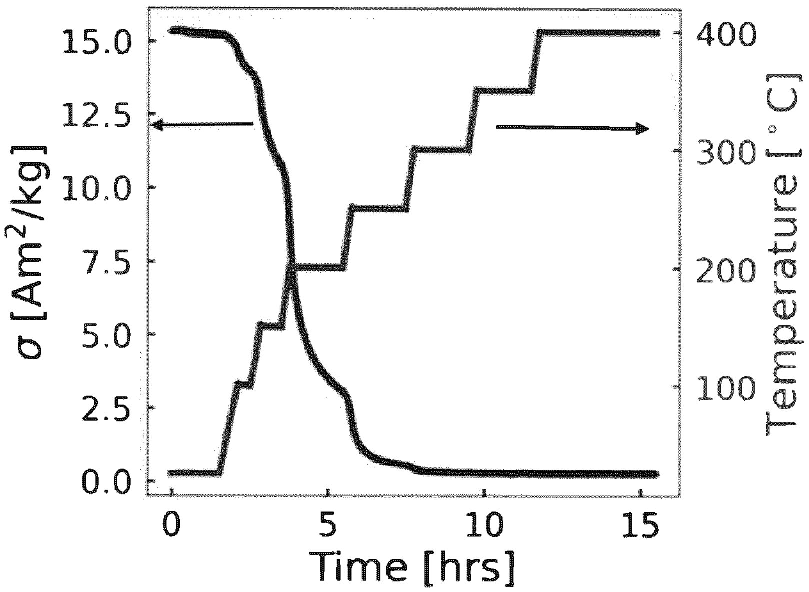

15.0
12.5
10.0
7.5
5.0
2.5
0.0
σ [Am²/kg]
400
300
200
100
Temperature [°C]
0
5
10
15
Time [hrs]

FIG. 10

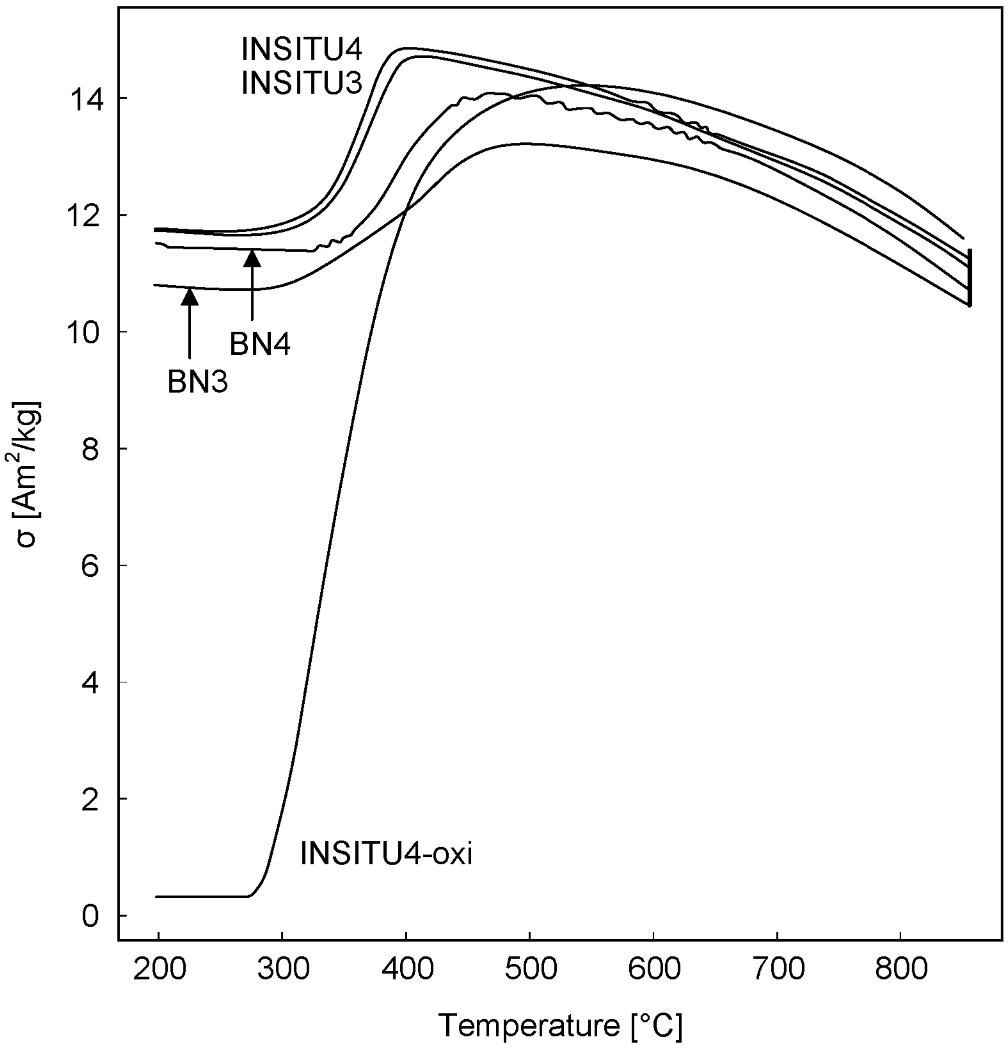

INSITU4
INSITU3
BN4
BN3
INSITU4-oxi
σ [Am²/kg]
0
2
4
6
8
10
12
14
Temperature [°C]
200
300
400
500
600
700
800

FIG. 11

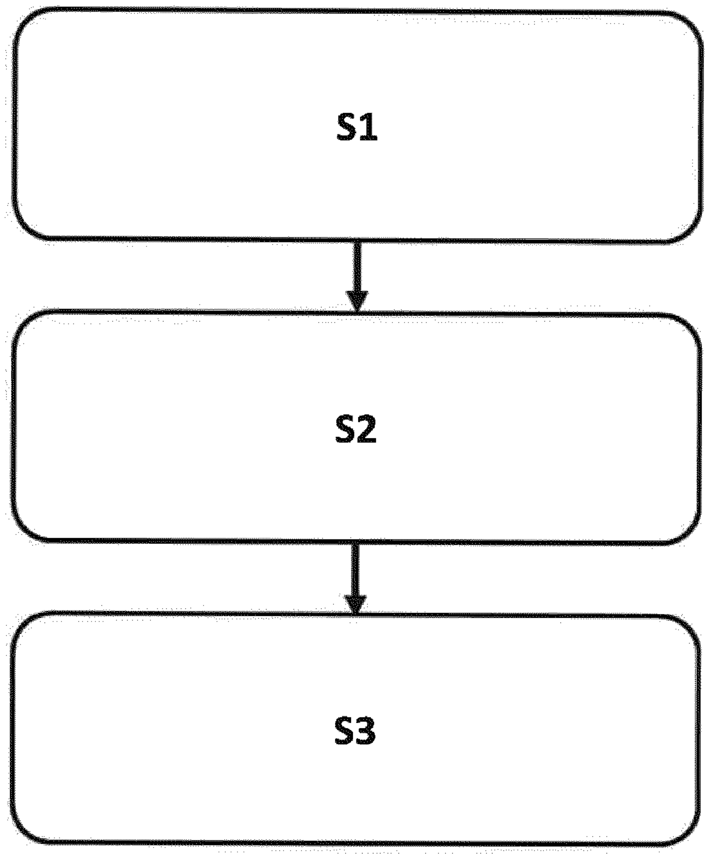

S1
S2
S3

FIG. 12

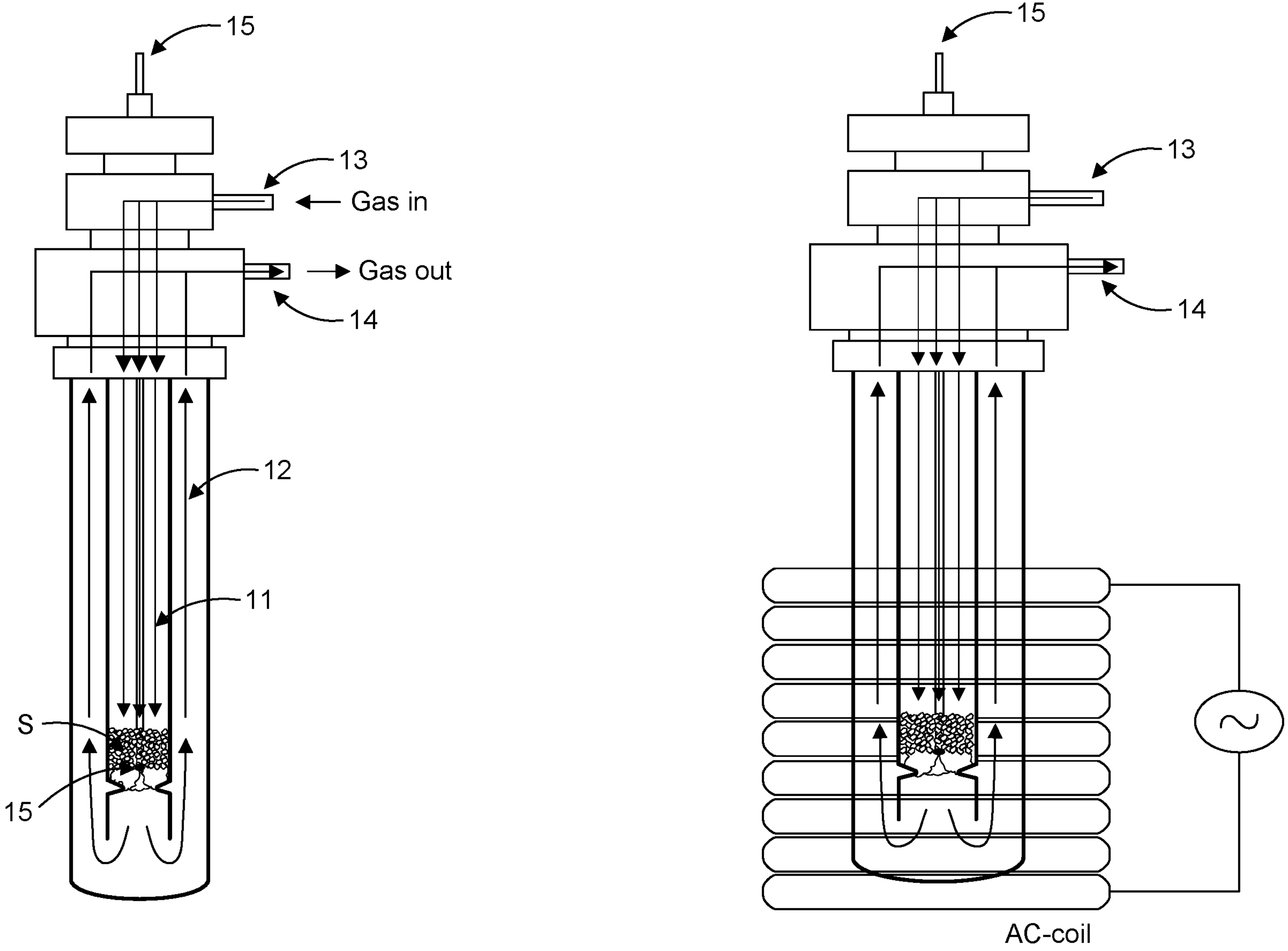


FIG. 13

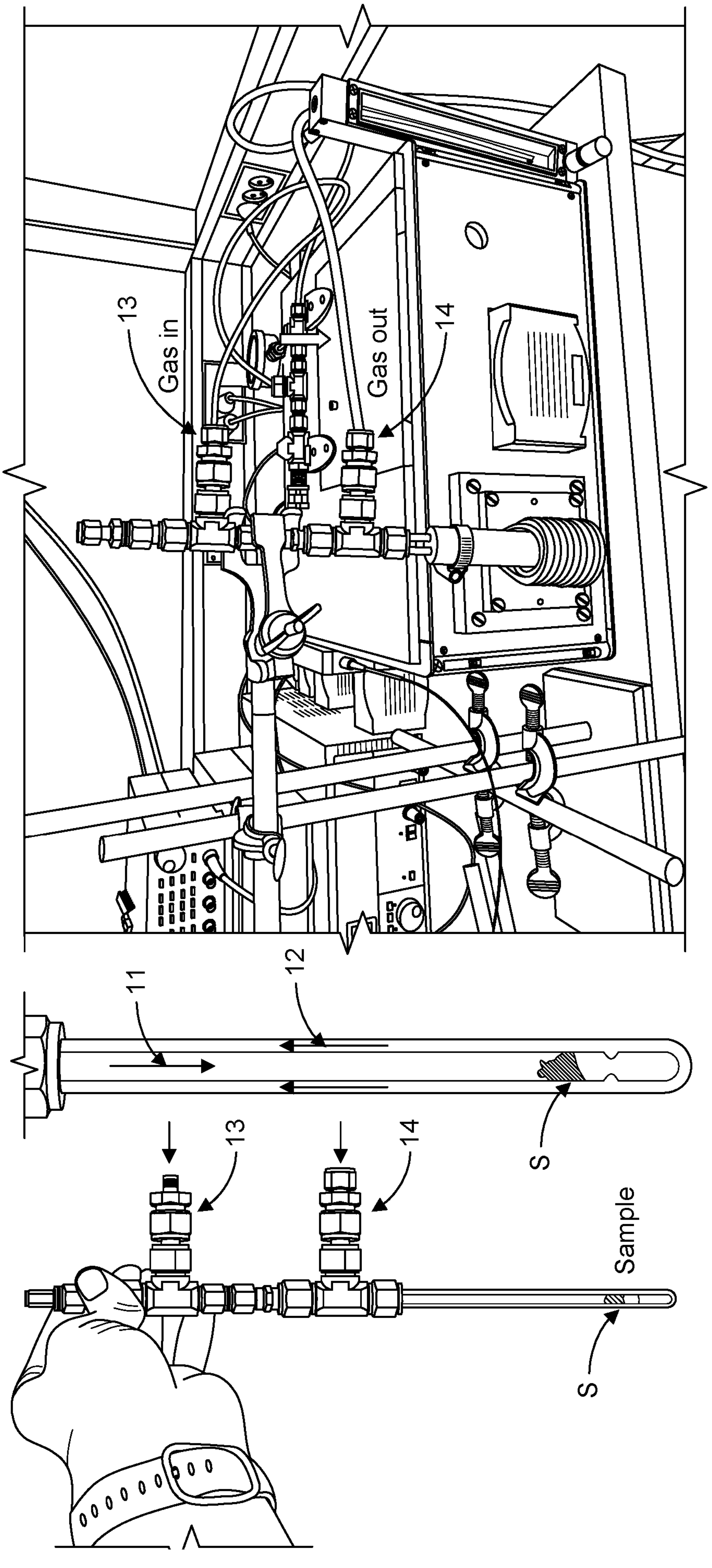


FIG. 14

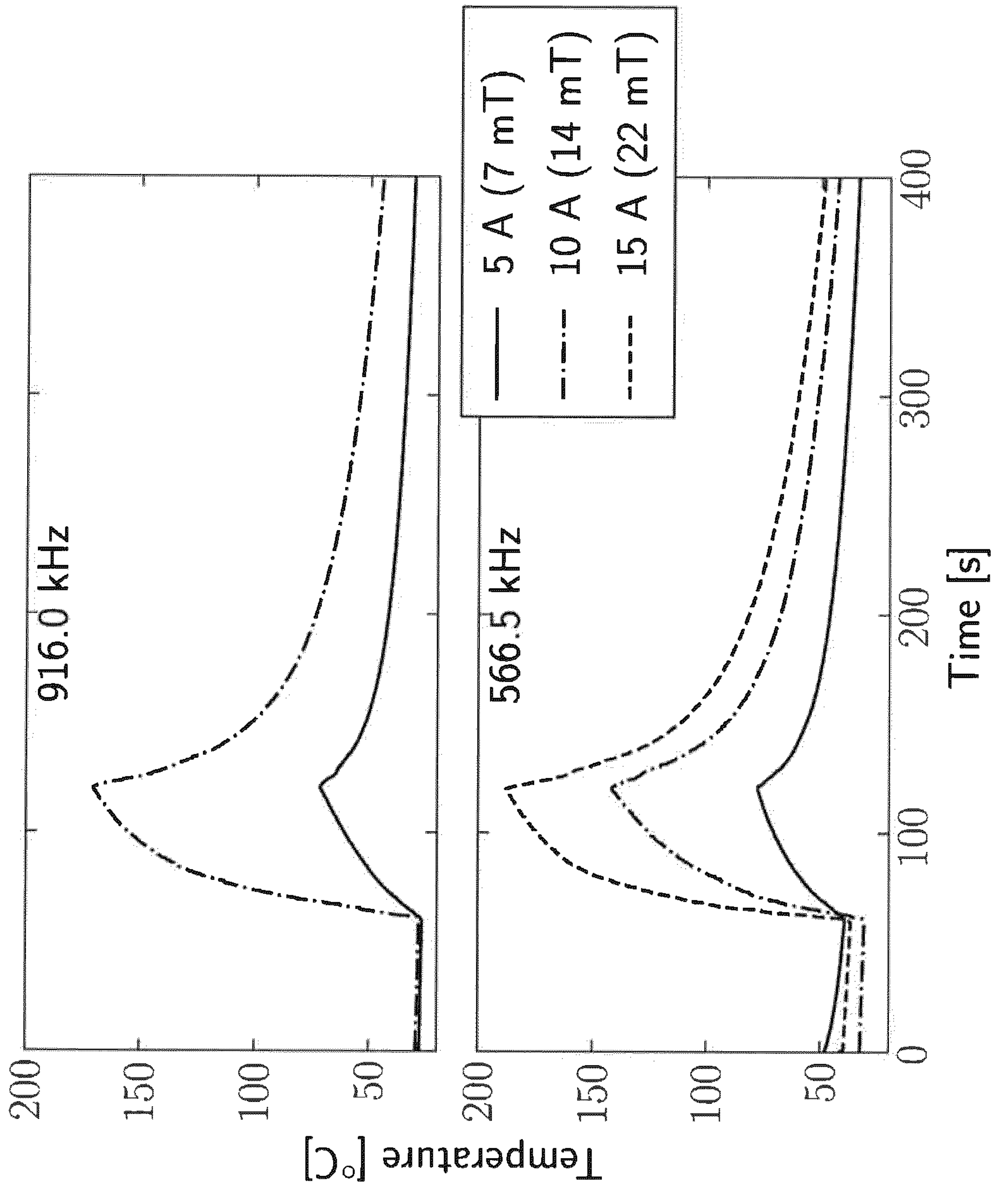

916.0 kHz
566.5 kHz
Temperature [°C]
200
150
100
50
0
100
200
300
400
Time [s]
5 A (7 mT)
10 A (14 mT)
15 A (22 mT)

FIG. 15

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/056031

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01R33/028 G01N27/00 G01R33/00 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 G01N

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RU 2 444 743 C2 (G UCHEBNO NAUCHNOE UCHREZHDENIE KHIM FAKUL TET MO G UNI IM M V LOMONOS) 10 March 2012 (2012-03-10)	1-3,5-16
A	the whole document -----	4
X	US 7 836 752 B2 (UNIV BOISE STATE [US]) 23 November 2010 (2010-11-23) Section "Experimental Details"; figure 1 -----	1,5-16
X	US 7 582 222 B2 (UNIV BOISE STATE [US]) 1 September 2009 (2009-09-01) figure 34 -----	1,5-16

☐ 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 9 June 2022	Date of mailing of the international search report 22/06/2022
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 Philipp, Peter

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2022/056031

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
RU 2444743 C2	10-03-2012	NONE	
US 7836752 B2	23-11-2010	US 2009133473 A1	28-05-2009
		WO 2008153603 A1	18-12-2008
US 7582222 B2	01-09-2009	US 2006060776 A1	23-03-2006
		US 2006060815 A1	23-03-2006
		US 2010064771 A1	18-03-2010
		WO 2006015321 A2	09-02-2006