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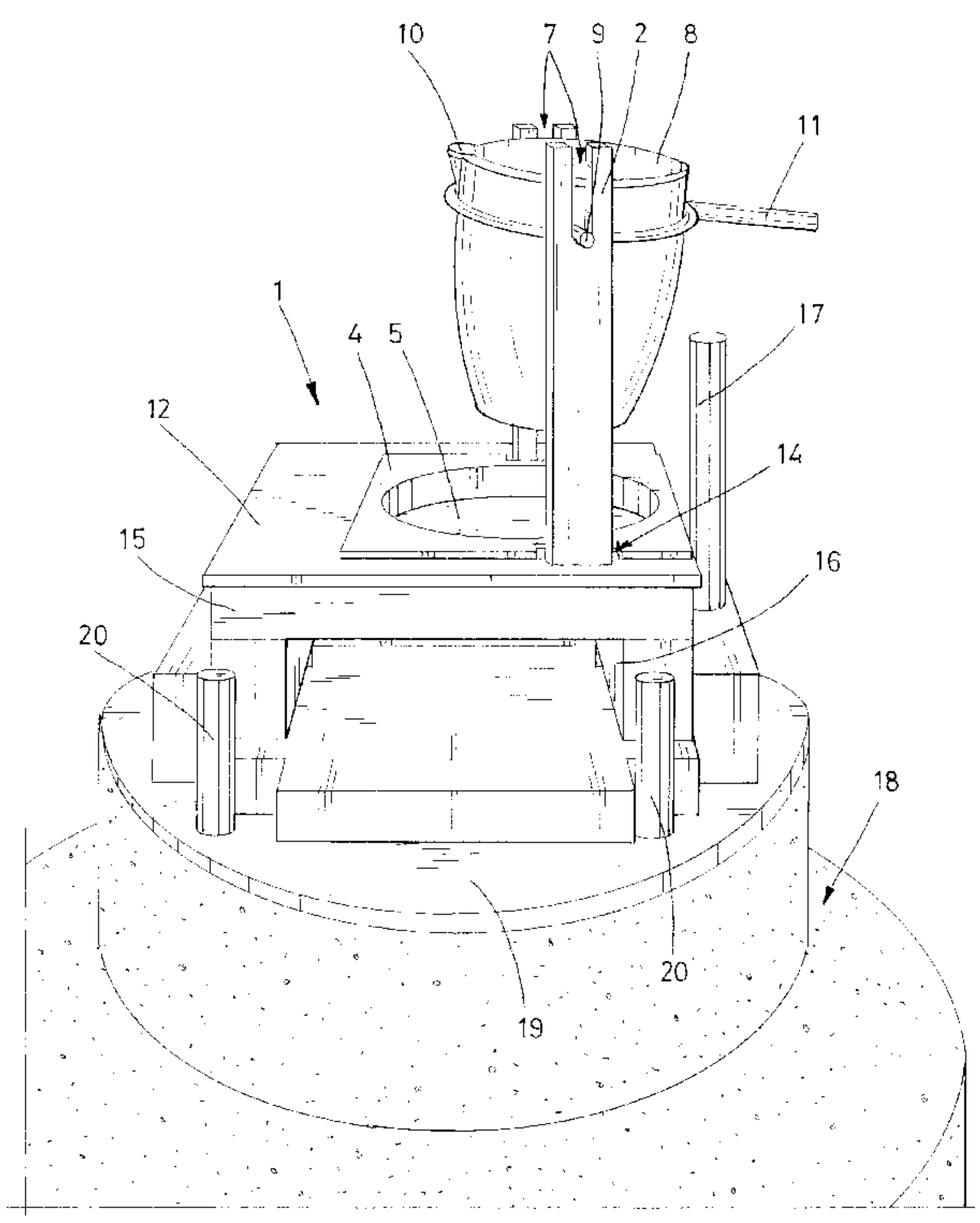
(54) **Titre : DISPOSITIF ET PROCEDE POUR LA PRODUCTION D'ECHANTILLONS POUR ANALYSE**
(54) **Title: ARRANGEMENT AND METHOD FOR PRODUCING ANALYSIS SAMPLES**

FIG. 3



(57) **Abrégé/Abstract:**
The invention relates to an arrangement for producing analysis samples for X-ray fluorescence analysis, with a crucible arranged in a furnace and receiving sample material to be melted, a crucible mount arranged in the furnace, and a collection dish, dimensioned

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(57) **Abrégé(suite)/Abstract(continued):**
for receiving the sample material present in the crucible, arranged underneath the crucible. The crucible is arranged in the furnace so as to be movable for mixing, in such a manner that the sample material present in the crucible can be intimately mixed by means of crucible movements. The crucible is arranged in the furnace so as to be movable for tilting, in such a manner that the collection dish can be filled with the sample material present in the crucible by means of the tilting movement of the crucible. According to the invention, the mounting is placed movably in the furnace. A mount suitable for such an arrangement is characterized in that the mount has a tilt bearing receiving the crucible. A crucible suitable for such an arrangement is characterized in that the crucible has two opposing protrusions, which form a tilting axis for the crucible. A furnace suitable for such an arrangement is characterized in that the furnace has a base on which the mount is positioned upright, and that the region of the base receiving the mount is designed as a turntable which is rotationally movable in an oscillating manner. The invention further relates to a procedure which is characterized in that the crucible and the mount are located outside the furnace prior to the beginning of the melting process, and that the mount is loaded with the crucible outside the furnace prior to the beginning of the melting process and is placed in the furnace together with the crucible.

ABSTRACT

This invention relates to apparatus for producing analysis samples for X-ray fluorescence spectroscopy, with a crucible arranged in an oven and receiving sample material to be melted, a crucible holder placed in the oven, and a casting dish, dimensioned for receiving the sample material present in the crucible, provided underneath the crucible. The crucible is arranged in the oven so as to be movable for mixing, in such a manner that the sample material present in the crucible can be thoroughly mixed by means of the motion of the crucible. The crucible is arranged in the oven so as to be movable for tilting, in such a manner that the casting dish can be filled with the sample material present in the crucible by means of the tiling movement of the crucible. According to the invention, the crucible holder is placed movably in the oven. A holder suitable for such an arrangement is characterized in that the holder has a tilt bearing that receives the crucible. A crucible suitable for such an arrangement is characterized in that the crucible has two opposing protrusions, which form a tilting axis for the crucible. An oven suitable for such apparatus is characterized in that the oven has a base on which the crucible holder is positioned upright, and that the region of the base receiving the crucible holder is designed as a turntable which is rotationally movable in an oscillating manner. The invention further relates to a procedure which is characterized in that the crucible and the crucible holder are located outside the oven prior to the beginning of the melting process, and that the crucible holder is loaded with the crucible outside the oven prior to the beginning of the melting process and is placed in the oven together with the crucible.

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ARRANGEMENT AND METHOD FOR PRODUCING ANALYSIS SAMPLES

The invention relates to apparatus according to the preamble of Claim 1, as well as to a method of producing analysis samples for X-ray fluorescence spectroscopy.

In X-ray fluorescence spectroscopy, the material to be analyzed is first melted. The melting temperatures can range from 900 degrees C to 1400 degrees C, for example, which means that the equipment used for the process is exposed to high temperature loads. The melting crucibles typically have a height of just a few centimeters, for example, approximately 3 to 5 cm, and are similar in diameter. Hence, the amount of the material to be melted is in the range of several grams and at most several cubic centimeters. The crucibles can thus be designated as analysis sample crucibles. Despite substantial differences to crucibles of the type used in steel mills, foundries, and similar production facilities, the shorter term “crucible” is also used for the analysis sample crucibles used in the laboratory.

The analysis samples for X-ray fluorescence spectroscopy are relatively small amounts, and the equipment used for the analysis is also small in its dimensions. This is in contrast to the equipment that is not used in laboratory work, such as, for example, the industrial productions of objects, whereby the amount of material to be melted in these cases is measured in the range of several, possibly several hundred, kilograms and the volume is measured in many liters or possibly cubic meters.

The crucibles used for industrial production, for example, are typically so large, that they are not put into the melting oven, but rather, the molten liquid material that is in the oven is poured outside the oven into crucibles or is melted directly in crucibles that are heatable, without the use of an oven. Because the crucibles are not placed in an oven, they are not as a whole resistant to the high temperatures used in melting operations,

but instead, the surface that comes into contact with the melt is coated with a heat-resistant material, such as a ceramic material. An external sheath of metal, for example, does not, however, have sufficient resistance to the temperature of the molten material that is in the crucible, and particularly, not to the temperatures that exist in a melting oven that is used to produce the samples for X-ray fluorescence spectroscopy. Foundry apparatus that is used in the industrial processing of large volumes of material is, thus, non-conventional or non-related to apparatus for producing the samples for X-ray fluorescence spectroscopy.

The following are some brief examples from the non-related field of industrial production.

German publication DE 589,569 A provides an example of a non-related tilt apparatus for melting crucibles, melting ovens, or other types of containers that are used to hold molten material. In these cases, it is not intended that a crucible be placed in an oven and that heat be applied externally to the crucible.

EP 0 775 906 A1 discloses a crucible that is intended for use in the production of analysis samples for X-ray fluorescence spectroscopy. The crucible has a hole in its floor. The sample material initially forms a bridge, which prevents the material from trickling downward out through the hole. When the sample material has melted, however, then it can flow in liquid form through the hole, so that it automatically reaches the casting dish already placed beneath the crucible. The publication does not mention that the sample material is mixed with the help of motion applied to the crucible and/or the crucible holder.

German publication DE 25 04 918 A1 discloses a crucible for melting, keeping warm, and pouring metals. With this crucible, a heat source is provided within the melt, so that

the heat develops inside the crucible. Here, too, it is not intended that the crucible be placed in an oven and that the necessary heat be applied externally to the crucible.

German publication DE 28 06 335 A1 shows apparatus for tiltable crucible ovens. The purpose of this type of oven is to enable disposal of a used-up crucible in a simple and environmentally friendly manner. Hydraulic tilt cylinders, which are normally used to tilt and empty the crucible oven, can also be used to lift the entire used-up crucible oven, so that it can then be torn down or partially renewed, by stamping a new stamped mass into the crucible oven.

PCT Publication WO 97/06060 A1 discloses a crucible that is supported, so as to be movable about two axes, in order, in the pour step, to very precisely pour the molten metal or metal alloys into a form The crucible holder for the crucible can be provided with a hydraulic motor. It is not intended to place the crucible along with its crucible holder into the oven.

German publication DE 10 2010 037 866 A1 discloses an electric stove for wood panels.

German publication DE 906 428 B discloses a periodically working burn oven, which is used particularly for firing ceramic goods that cannot tolerate any vibrations. The goods are supported in a fixed position and parts of the oven are formed as a hood that is movable on wheels.

German publication DE 1 596 729 A does not relate to the production of analysis samples, but to glass objects, their ability to last a long time being strongly influenced by the surface hardness of the glass. This publication relates to a method of increasing the strength of the glass objects.

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In the production of analysis samples for X-ray fluorescence spectroscopy, by contrast, the crucible is not setup outside the oven and filled outside the oven with the molten sample material, and the crucible is also not a crucible oven that can be heated directly. Rather, the crucible is placed in the oven and is passively heated by the temperature that exists in the oven. It is essential for a crucible used for analysis samples, that not only the fire-resistant coating on the inside of the crucible is exposed to the temperature of the molten material, but that it is in its entirety exposed to the temperature that exists inside the oven. For this reason, crucibles for analysis samples don't have an inner coating, but are made entirely of a material that is thermally resistant to the temperatures in the oven and chemically resistant to the sample material. An example of material for such crucibles is platinum or a platinum alloy.

Often, several crucibles, for example, two, four, or six crucibles, are placed together in one oven. Due to the small dimensions, the ovens used for this are often referred to as tabletop devices that can be placed on a lab table, for example. But even if the ovens are set up on the floor, or are placed on a rack or cabinet that is set on the floor, they are still referred to as so-called tabletop devices within the context of the present proposal, because of their small dimensions.

German publication DE 16 48 994 C3 teaches cooling the sample material in the crucible. Electrical current is passed through the glass-like body of the sample material during the cooling, in order to prevent the sample material from sticking to the crucible and to enable the hardened sample to be easily removed later from the crucible.

The sample material that is melted in the oven is processed into a flat, round sample that is referred to as a "tablet," and that has a comparatively small volume, for example, has approximately the dimensions of a one-Euro or two-Euro coin. In order to produce the tablet, the molten sample material in the crucible is cast from the crucible into a casting dish. It is known to carry out this casting operation inside the oven, in order to

prevent the sample material from cooling prematurely. For this reason, the casting dish, which is sometimes referred to as a mold, is placed in the oven beneath the crucible. The casting dish has a hollow that determines the shape of the tablet being produced. It is the tablet that is the object of the actual analysis procedure.

Besides the material to be examined, the tablet also contains a flux as filler, whereby this flux is frequently in the form of glass. The crucible is set in motion, in order to achieve a thorough mixing of the actual sample material and the additives within the crucible. The use of stirrers in the crucible hasn't proven useful, for a variety of reasons. For that reason, the conventional method is to set the complete crucible including its crucible holder and the contents of the crucible in motion.

It is often problematic in practice, that the crucible holder that is placed in the oven is subject to undesirably high wear. If such a crucible holder breaks and has to be replaced, then the particular oven for two, four, or six crucibles, for example, cannot be used for the duration of the repair, which means a significant economic loss. The sensitivity of the crucible holder is based, among other things, in the fact that the entire crucible holder with all the crucibles contained in it, is moved, in order to mix the samples, and is thereby exposed to high temperatures. Furthermore, the crucible holder with all the crucibles is tiltably supported, in order to be able to empty all the crucibles simultaneously into the casting dishes that are beneath the crucibles. This simultaneous emptying is done to avoid a premature and undesired cooling of the samples, and, for this reason, the crucibles cannot be emptied one after the other.

German publication DE 103 38 886 A1 discloses non-related apparatus. With this apparatus, the oven does not have an enclosed inner chamber. The oven chamber is open at the top and a gas burner is used to provide sufficient heat to the oven chamber to melt the material for the samples. The crucible holder for the multiple crucibles is referred to as a changeable frame: it can be removed from the oven, turned 180

degrees and put back into the oven. Because this non-related apparatus can be operated with two different functionalities, it is referred to as a bi-functional expansion device (Aufschlußgerät). In order to arranged the crucible holder in a different functionality, the oven must first be cooled down.

Depending on the orientation of the crucible holder, the two different functions of the oven are either to empty the crucibles into molds by tilting the entire crucible holder, along with all the crucibles, or to empty the crucibles into Teflon or ceramic crucibles with a magnetic stirrer. The two different modes of operation entail automatically switched operation of the main and auxiliary gas burners, so that, depending on the different arrangement of the crucible holder, two different functionalities of the apparatus are made possible, and this eliminates the need to acquire two separate devices for preparing samples.

In the non-related apparatus just described, a mixing device is provided, so that the sample material can be mixed within the crucible. This mixing device includes a changeable frame and the crucibles that are held in it, as well as a drive that has a drive belt and drive discs. This comparatively complex drive, as well as the fact that the entire changeable frame with all the crucibles is set in motion, leads to a negatively high susceptibility to interruptions of the entire apparatus. If, for example, the changeable frame fails because of the vibration loading on it, i.e., it breaks, then the entire changeable frame has to be removed and replaced. This interrupts operation of the apparatus for all of the crucibles that are held in the crucible holder for the duration of the repair.

By contrast, conventional apparatus that is known in the applicable field includes an enclosed inner chamber. Because of that, the conventional apparatus has lower temperature losses than the non-conventional apparatus with the open oven that is described above. Consequently, the conventional apparatus can be operated more

economically and furthermore, can be operated with heaters that have a lower heat output than a gas burner, namely, for example, with an electric heater, and that can be viewed as advantageous for safety reasons. In the described non-conventional apparatus, the heating effect of the gas burner is concentrated on a small area, for example, on the crucibles. With the conventional apparatus, a significantly more even temperature is provided in the entire closed inner chamber of the oven. The crucible holders for the crucibles in conventional apparatus are thus subjected to higher thermal loading. The same applies also for the drive elements of the crucible holder that are also inside the inner chamber of the oven. These drive elements serve to set the crucible holder along with all its crucibles in motion for mixing, the purpose of which is to thoroughly mix the sample materials in the crucibles. Having to repair the crucible holders is a relatively complex task and takes a correspondingly long time, because the oven has to be first cooled down before the crucible holder can be removed.

The publications US 5,315,091 A and EP 2 270410 B1 each disclose conventional apparatus, and the publication DE 35 07 493 A1 discloses apparatus to producing analysis samples for X-ray fluorescence spectroscopy, in which the casting dish is open toward the bottom and placed above the crucible. To produce the tablets, the crucibles and the casting dishes are rotated.

EP 0 501 835 A2 discloses a conventional arrangement, that includes several holders placed in the ofen, each holding one crucible. The holders together with the crucibles held in them can be rotated around two tilt axes. Certain different curved paths along which the sample material can be mixed in the crucibles can be defined, by programming the drive and by superpositioning the two tilt axes. In order to secure the holders in the tilt arrangement, each is held in a slotted clamping block, whereby the width of the slot can be changed by means of a setscrew. The holder placed into the clamping block is basically fixed, but can be removed from the clamping block by actuating the setscrew and thereby increasing the width of the slot.

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The object of the invention is to improve the conventional apparatus such, that the apparatus may be operated at the highest possible productivity level and with the shortest possible down times, as well as suitable components for the apparatus and also to provide a method to producing analysis samples for X-ray fluorescence spectroscopy.

This object is solved by providing apparatus having the characteristics of Claim 1, as well as a method according to Claim 23. An advantageous embodiment of the apparatus can be achieved particularly by means of a crucible holder according to Claim 5, a crucible according to Claim 12, an oven according to Claim 16, and/or a casting dish according to Claim 21. Further advantageous embodiments of the present proposal are described in the dependent claims.

The improvement suggests in other words, that the crucible holder be constructed as a component separate from the oven, which can be handled separately from the oven, and is loosely set inside the oven during the melting process, i.e., is not fixed in the ofen. Should the crucible holder become damaged, then it can be replaced within a short period of time with a spare crucible holder. For example, the oven is regularly opened to withdraw the crucibles and replace them with new crucibles filled with non-molten material for samples. At the same time, the samples that have been poured into the casting dishes are also removed from the oven. The casting dishes are either emptied and placed back in the oven, or new, empty casting dishes are placed in the oven. While carrying out these steps that would be done anyway, the crucible holder that has just been loosely placed within the oven may be easily removed, so that the interruption in the oven operations is extended by only a few seconds and the oven operations can proceed with very little change, by which charges of one or several crucibles with sample material, one after the other, are heated to the point of melting the sample material.

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According to the proposal, the apparatus according to the proposal is handled such, that both the crucible as well as the crucible holder are outside the oven before the melting step begins, and that the crucible is loaded into the crucible holder before the start of the melting step, outside the oven, and crucible and crucible holder are then placed in the oven.

After the melting step, the crucible holder along with the crucible can also be removed from the oven, loaded with a new crucible and placed back in the oven, along with the new crucible, for another melting step. This saves time, because the previously used equipment, such as the crucible and the casting dish, do not have to cool down and be cleaned, before they can be put back in use.

The common handling of the crucible and possibly also the casting dish together with the crucible holder saves time loading and unloading the oven, because the two components don't have to be removed from the crucible holder first, and then be handled, but rather, they can be handled together in a single step.

The embodiment of the crucible holder as a component separate from the oven makes possible an almost continuous melting process: advantageously, a second crucible holder can be prepared, while the first crucible holder along with the first crucible is in the oven and the sample material in the first crucible is being melted. The preparation of the second crucible holder entails loading it with a second crucible that contains unmelted sample material and that this second crucible holder may perhaps also be loaded with a second, empty casting dish. When the oven is opened, the second crucible holder can immediately be placed in the oven as soon as the first crucible holder has been removed. Temperature losses in the opened oven are kept to a minimum in this way and the cycle time for the subsequent melting steps for the individual samples can be kept as short as possible.

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According to the proposal, it is intended that the crucible holder be placed loosely in the oven. "Loosely" within the context of this proposal means that the crucible holder is placed easily and quickly in the oven and can be removed from the oven again, without, for example, as the first step in the process, and possibly even with the use of tools, having to release latches or actuate fixing elements, which are used to secure the crucible holder in the oven, because the holder is not fixed in the oven. For example, the crucible holder, due to its own weight and/or geometry may be so stable, that even with a filled crucible, will be reliably secure against lifting forces or against falling over in the oven. In this case, no additional measures are required, to arranged the crucible holder securely in the oven. The assessment of the mentioned stability is particularly related to the intended motions that are applied on the crucible and also the crucible holder for mixing, when the oven is used according to its intended purpose.

It is possible, however, to secure the crucible holder additionally in the oven, whereby in this case the crucible holder is "loosely" arranged in the oven in the sense of the present proposal: for example, the crucible holder may be slid along guide tracks or something similar, so that it, together with the crucible, securely stands in place within the oven when the mixing motions are applied to the crucible. It is also possible, that when placing the crucible holder in the oven, automatically latches that are pivotable or otherwise movable are actuated. For example, a latch may be provided that is pivotably mounted and extends from the pivotable mount in a first direction. The latch has an actuating pin that extends in a second direction from the pivotable bearing. When the crucible holder is shoved into the oven, it is pushed against the actuating pin. Without having to actually handle the actuating pin or the latch, the latch is automatically swung about by the wide movement of the crucible holder and extends over or extends around, for example, a portion of the crucible holder, so that it is secured against lifting forces or against falling over within the oven. When removing the crucible holder from the oven in the reverse direction of movement, the latch is automatically swung back by the

crucible holder, so that it is just as uncomplicated to remove the crucible holder from the oven as if it had actually stood entirely unsecured within the oven.

Advantageously, an arrangement of several crucibles within the same oven may be provided, in which each crucible is placed in its own crucible holder. Should a crucible holder fail, then it can be easily and within the shortest possible time be replaced, as described above. Replacement of the crucible holder is simplified by the fact that a comparatively small crucible holder has to be handled, one that is not constructed to carry several crucibles. If, however, there is no replacement crucible holder available, then the operation of the oven is not completely impossible, but rather, all the other crucible holders that are not defective and accordingly don't have to be removed from the oven, can be loaded with crucibles, just as before, so that according to the number of the crucibles and crucible holders used, operation of the oven is reduced by only a small percentage that corresponds to the defective crucible holder and the corresponding crucible that is no longer in use.

The separate placement of each individual crucible in its own crucible holder according to the proposal brings an additional advantage: Variously constructed crucibles can be used without problem in the same oven, because each one is arranged in the oven in its own crucible holder, in contrast to a crucible holder that is set up for several crucibles, which means then that only certain crucibles that are adapted to the particular crucible holder may be used.

Alternatively to the above described embodiment of the crucible holder, in which only a single crucible is loaded into the crucible holder, it may also be advantageous, to place two or more crucibles in the same crucible holder. Removing the crucible holder from the oven makes it possible in this case to remove several crucibles at the same time and, when using a tilt mechanism that works on all crucibles simultaneously, it is also possible to simultaneously empty these several crucibles into their respective casting

dishes. Also, removing the crucibles and then loading a new charge into the oven is simplified by the fact that only a single crucible holder need be handled, so that a crucible holder that is already placed in the oven is not in the way when handling the next separate crucible holder.

Finally, the fact that only a single crucible holder need be handled reduces the amount of time during which the oven is open for loading in a new charge of crucibles or removing crucibles, so that the heat loss is reduced. This is not only ecologically and economically advantageous, because of the reduced need to heat up and, thus, reduced energy requirements, but is also reduces the cycle time that is necessary to produce the samples.

It may be advantageous that the entire crucible holder is not tilted when emptying the crucible. Rather, it may be more advantageous that the crucible be tiltably mounted within the crucible holder, so that a relative motion of crucible to crucible holder is possible and that just the crucible has to be tilted, while the crucible holder itself remains unchanged in its position. In this way, the embodiment of the crucible holder may be kept particularly simple, because this crucible holder does not have to be connected to a drive mechanism inside the oven, because the crucible holder along with the crucibles does not have to be tilted. Particularly when, as described above, the apparatus is such, that each crucible is placed in its own crucible holder, then various tilt mechanisms can be used, so that variously constructed crucibles, which are possibly variously constructed with regard to their tilt movement, are each held in a crucible holder adapted to the particular construction.

It may be advantageous in the apparatus according to the present proposal, that the crucible holder have a tilt bearing or mount that supports the crucible. This can, for example, be a construction in which the crucible holder has recesses or grooves, which together create a tilt axis and that the crucible then has protrusions that together also

create a tilt axis, so that the crucible with its protrusions can be suspended in the recesses in the crucible holder and in this way, can be tilted about the common tilt axis of the crucible and the crucible holder. The principles of this type of support may be exactly reversed, such that the crucible holder has protrusions that can be suspended in recesses that are formed in the crucible, so that then the coextensive tilt axes of the crucible on the one hand and the crucible holder on the other hand create a tilt bearing about which the crucible may be rotated, in order to pour the molten sample material into a casting dish, which is also referred to as a mold.

Advantageously, the crucible holder may not only serve to support the crucible, but also advantageously support the casting dish, and so, in this manner, ensure a defined location for the casting dish. This ensures that, when the crucible is tilted, the crucible contents flow safely into the casting dish.

In order to ensure the desired position of the casting dish in the crucible holder, the casting dish may advantageously have a cut-out and/or a protrusion that extends along its circumferential edge, so that the shape or geometry of the crucible holder provides a positive locking fit between the casting dish and the crucible holder. The positive locking fit secures the casting dish against certain movements relative the crucible holder, namely, shifts in position in horizontal directions.

The positive locking fit mentioned above may advantageously be achieved by providing two notches along the circumferential edge of the casting dish, for example, two notches opposite each other, so that two elements of the crucible holder can extend into these notches. This ensures that the casting dish is secured in all direction in the horizontal plane in the crucible holder. The casting dish may be removed from the crucible holder easily by moving it upward. A positive locking fit can also be created, however, by providing the casting dish with a trough or hollow that extends into a corresponding recess or cut-out in the crucible holder.

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Advantageously several such positive locking fit locators may be provided between the casting dish and the crucible holder. By doing that, the casting dish may be secured in a particularly reliable manner in the desired position in the crucible holder. On the other hand, easy movability of the casting dish relative the crucible holder may be possible, when the casting dish is placed into the crucible holder or removed from it. In particular, if the materials that are used on the casting dish and the crucible holder have different thermal expansion coefficients, the two or more locking fits may be constructed with relatively large tolerances, so that it is ensured, that the casting dish doesn't get stuck in the crucible holder and thereby interfere with its handling.

Advantageously and surprisingly, the crucible holder may be made of a high temperature resistant, high carbon content nickel-chrome-iron-alloy. Such an alloy is commercially available under the trade name NICROFER from the company Krupp VDM GmbH. This alloy is easily longlasting at the temperatures that prevail in the oven. Surprisingly it has been found that, in conjunction with the material for the crucible, which, for example, in a conventional embodiment of a crucible is platinum, the alloy has no negative effects on the crucible or on the crucible holder, so that the crucible may be used with this crucible holder over an extended period time, i.e., for a number of trials, without a problem. The spatial weight of this metallic material is so high, that the crucible holder along with the crucible placed in it is stable when both are moved together in the oven to mix the sample materials.

As an alternative to this material, the crucible holder may be created from a different material, one that has a suitable resistance for the intended temperature loads. For example, ceramic materials may be used, particularly silicon nitride. The ceramic materials, namely, can possibly have a higher chemical resistance compared to metallic materials, when they come into contact with the sample material under the temperatures that exist in the oven, for example, when splashes of the sample material splash out of the crucible, due to the movement of the crucible.

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It may able be advantageous that the crucible holder is made of a combination of different materials. Thus, the lower portion of the crucible holder may be constructed of a heavy material, to enhance stability, and above that, in the direction of the crucible, of a more chemically resistant material, one which is on the one hand resistant to the splashes from the crucible and, on the other hand, can protect the material used in the lower portions of the crucible holder from the splashes.

It may be advantageous that the tilt support is placed as close to the edge in the crucible holder as possible. This enables an intensive mixing of the sample material, by exerting the strongest possible centrifugal forces on the sample material, when the crucible holder is oscillated back and forth by a rotational motion. If the crucible holder, for example, is placed on a rotationally oscillating plate, it can be arranged as close as possible to the edge, i.e., as far as possible from the center or rotational axis of the plate. This close-to-the-edge placement of the crucible tilt mounting ensures that the crucible, too, within the crucible holder is placed as far as possible out on the rotationally oscillating plate.

A crucible that may be used advantageously within the context of the apparatus according to the proposal can advantageously have two juxtaposed protrusions that form a tilt axis of the crucible, as this was described above. In an exact reversal of the embodiment of the mounting it is possible that the crucible also have two juxtaposed recesses or grooves, to create the tilt axis of the crucible, when the crucible holder has two juxtaposed protrusions, rather than the grooves for the protrusions of the crucible.

Advantageously the crucible may have a pour spout, that enables a precise emptying of the molten sample material.

Advantageously the crucible may have a handle that is used to tilt the crucible about its tilt axis. Thus, it is not necessary, that the crucible be taken completely out of the

crucible holder, but rather, this handle just needs to be grabbed and moved, in order to empty the crucible. A simple and robustly constructed mechanism may be provided, for example, a horizontally extending beam. The tilt mechanism doesn't have to move the relatively high weight of the crucible and the crucible holder, and because of that, a small and inexpensive tilt mechanism with a low drive performance may also be oversized and appropriately robust.

If one or more crucible holders loaded with crucibles are arranged in the oven, or when one crucible holder loaded with several crucibles is arranged in the oven, they can be so aligned, that the protrusions of the crucibles are above the just mentioned beam. When the samples in the crucibles are molten, only the mentioned beam has to be raised, in order to simultaneously empty all the crucibles in a time-saving manner.

It may be advantageous thereby that the mentioned protrusion is placed horizontally opposite the aforementioned pour spout of the crucible. Raising the protrusion lowers the pour spout, so that the liquid molten sample material may flow precisely out of the crucible.

A first alternative to an embodiment of the tilt mechanism may be to place the mechanism inside the oven, so that the molten sample material may be filled immediately into the casting dish, without any temperature loss. Temperature losses in the oven are minimized in this way, because the oven is only opened for loading and unloading. As mentioned above, the tilt mechanism may have a simple and robust construction, and because of that, be able to withstand the high temperature loads, despite being placed inside the oven.

A second possible alternative is to place the tilt mechanism outside the oven and to take the crucible holder, loaded with the crucible and the casting dish therebelow, out of the oven and to tilt the crucible outside the oven and empty the sample material into the

casting dish. The tilt mechanism is thereby almost completely free from temperature loads, with the exception of the contact with the crucible.

A third alternative, one that combines the advantages of the first two solutions, provides the tilt mechanism outside the oven, but the crucible is tilted and emptied into the casting dish while the crucible is still inside the oven. To achieve this, the oven is opened and the tilt mechanism moved into the oven. For example, the above-mentioned beam may be pushed into the oven, while the drive unit moving the beam remains outside the oven. The temperature losses of the sample material are kept low, because the sample remains in the oven. The temperature load on the tilt mechanism is also low, because it is only briefly inside the oven during the tilt operation and not during the entire duration of the melting process, so exposure to the high temperatures in the oven is brief. Also, it is possible that only certain parts of the tilt mechanism are in the oven.

A fourth alternative of an embodiment of the tilt mechanism provides a two-part construction of the mechanism. For example, the above-mentioned beam may be movably supported inside the oven and may always remain in the oven. The relatively more complicated and more temperature-sensitive drive unit for the tilt mechanism is arranged outside the oven and remains there for the duration of the melting process. An actuating connection between the drive unit and the beam is created only when the crucible is ready for tilting, so that the mechanism may be moved and the crucible tilted. A small opening in the oven may be sufficient, to create the connection, so that the temperature losses in the oven and on the sample material may be kept particularly low.

In order to be resistant to the high temperatures and to avoid unacceptable contamination of the sample, the crucible is constructed of a particularly suitable material, such as, for example, graphite, nickel, zirconium, or a ceramic material, or possibly graphite. As previously mentioned, the crucible may advantageously be

constructed of a platinum alloy. In practice, an alloy that is 95% platinum and 5% gold has proven useful; other platinum alloys with admixtures of gold (in a different ratio than 5%), rhodium, iridium, palladium, etc, have also proven useful. With regard to the materials processed and the high temperatures, the platinum alloy, in doing X-ray fluorescence spectroscopy, has proven itself by its long service life and, despite the high costs for the materials, in view of the small dimensions of a crucible, has made the analysis affordable.

An oven that is advantageous to use with the apparatus according to the present proposal is one that has a floor on which the crucible holder is placed. The mixing motion, that is applied to the crucible and its sample material is done advantageously with a back-and-forth oscillating rotational motion, whereby each change in direction brings about a particularly intensive mixing effect. For that reason, the floor where the crucible holder is placed, is advantageously constructed as a turntable that is rotationally movable in an oscillating manner. In this way, a robust design can be used that is placed outside the heated inner chamber of the oven and provides the oscillating rotational drive for the turntable. Also, a mechanically robust construction of the entire apparatus with the use of such an oven is possible, in that no mechanical linking of the crucible holder to a drive means in the oven is required in order to set the crucible holder in motion and thereby achieve the desired mixing motion of the crucible. For example, no crank apparatus has to be connected to the crucible holder, in order to apply a motion to the crucible holder that is then transmitted to the crucible, thereby effecting a mixing of the sample material inside the crucible.

As an alternative, instead of a movable part in the oven, the entire oven may be set in motion, thereby setting the crucible holder in the inner chamber of the oven in motion and, thus, the crucible that is held in the crucible holder, to obtain the desired mixing of the sample material. In so far as the oven has the appropriate vibration resistant heating elements, such an oven that is set in motion from the outside is a mechanically

very simple construction. In this connection, the housing that surrounds the inner chamber of the oven and the heater that brings the inner chamber to the desired temperature is designated as "oven." The external drive of such an oven is optimally protected from the temperatures that exist in the oven. When a crucible holder is provided that carries several crucibles, or when several crucible holders are provided, each loaded with just one crucible, the crucibles are preferably placed on the turntable such, that they are all in the same circular path, so that the same mixing conditions are ensured for all crucibles.

Advantageously the turntable may be lowered, in order to provide free access to an opening in the oven, that can be used as a loading opening. The raised position, in which the turntable forms a part of the oven floor, is referred to as the operation position of the turntable. In contrast to this operation position, the turntable may be lowered to a so-called loading position, in which it is possible to load and unload the oven. In doing so, the lowering can be done to a limited extent, so that possibly the entire crucible holder is not able to be removed from the oven, but that it is still possible to remove the crucible as well as the casting dish from the crucible holder. In that way, when the turntable is in its lowered position, it is possible to load the crucible holder with a fresh crucible and a fresh casting dish. The turntable is subsequently moved to its operating position.

Because the loading of the oven occurs from below, and, as is known, because the heated air in the oven moves upward, the heat generated in the oven will be held for the most part in the oven, when the oven is opened from below in order to load the crucible holder. Operating the oven is not only economically more advantageous, because cooling losses are reduced when the oven is opened, but it also supports an economically more advantageous operation of the oven, because the times for heating up the oven can be correspondingly reduced, because during the loading/unloading times of the oven, the temperature losses are kept as low as possible, so that, in the

end, heating the oven to its desired temperature can be done in the shortest time possible.

Advantageously the turntable can be lowered not only so far that the it is possible to load the crucible holder, that is, removing a crucible and a casting dish and a renewed loading with a new crucible and a new casting dish, but advantageously the turntable can be lowered far enough that the complete crucible holder can be removed from the turntable, so that, if necessary, the crucible holder can be exchanged for another one in the shortest possible time.

The present invention is described below, with reference to the purely schematic figures, whereby

FIG. 1 illustrates in a perspective view a first embodiment of a crucible holder with the crucible and the casting dish placed within it,

FIG. 2 also in a perspective view, shows the crucible of FIG. 1 in a tilted emptying position, and

FIG. 3 is a second example of an embodiment of a crucible holder, in which a crucible and a casting dish are placed, whereby the crucible holder is standing on a movable part of an oven floor.

FIG. 1 shows a crucible holder **1** that is constructed from a high temperature resistant, high carbon content nickel-chrome-iron alloy. The crucible holder **1** has two side walls **2**, the lower portions of which form narrow support profiles **3** that face each other. A casting dish **4** has a square contour with a circular dish **5** formed in the center that forms a corresponding circular tablet. Two of the side edges of the casting dish **4** are supported on the two support profiles **3** of the sides **2**. The casting dish **4** is unable to

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shift horizontally in any direction, due to the two sides **2** and also to the retaining noses **6**, that extend upward at each end of the support profile **3**.

Notches **7** in the form of slits or grooves are formed in the sidewalls **3** above the support profiles **3**, in which a crucible **8** is suspended. Just as with the casting dish **4**, the crucible **8** is also made of a platinum alloy.

The crucible **8** has two juxtaposed protrusions, which together form a hinge axis or tilt axis of the crucible **8** and which extend into each of the two notches **7**.

Furthermore, the crucible **8** has an pour spout **10**, and opposite that an extension **11** that serves as a handle.

FIG. 1 shows the crucible **8** suspended in the crucible holder **1** in an orientation what would be used during the melting process when the sample material contained in the crucible **8** is being melted.

The crucible holder **1**, along with the crucible **8** suspended therein, is loosely placed in a melting oven that is not shown in the figures. The oven has an enclosed inner chamber, whereby the floor has a movable portion, that is constructed, for example, as a rotationally oscillating turntable. By moving this portion of the floor, the crucible holder **1** along with the crucible **8** and, particularly, the contents of the crucible, may be rotationally moved back and forth, and, in this manner, a thorough mixing of the contents of the crucible is achieved.

When the sample is melted and is to be poured into the casting dish **4**, the handle **11** is raised, which causes the crucible **8** to tilt about the axis formed by the two extensions **9**, so that the pour spout **10** is lowered, as is shown in **FIG. 2**. The crucible contents flow out of the spout **10** and into the mold **5** in the casting dish **4**.

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No organ or body for actuating the handle **11** is arranged in the oven and, for that reason, as with the oven, is not shown in the drawings. The actuating body may be a robust construction with simple kinematics, such as, for example, a beam connected to the underside of the handle **11**, that is raised in a circular arc motion, so that the handle **11** for example, is guided from the horizontal orientation shown in **FIG. 1**, to the approximately vertical orientation shown in **FIG. 2**. It is preferable that the beam be pushed into the oven when the sample material is melted, so that the crucible **8**, which remains in the oven, can be tilted and emptied into the casting dish **4**.

The crucible holder **1** is shown only schematically, as a way to illustrate the essential components and surfaces that provide its functionality, for example, how the tilted orientation of the crucible holder **1** together with the crucible **8**, with the crucible suspended in the crucible holder, as well as the placement of the casting dish **4** in a defined position, ensures that the crucible properly empties when tilted. The comparatively clunky or cumbersome embodiment of the crucible holder **1** results in a comparatively heavy weight, which ensures a high degree of stability of the crucible holder on, for example, a turntable in the oven. In deviation from the embodiment shown, the crucible holder **1** may, for example, be embodied in a more filigree construction, with a substantially lesser amount of material, so that the time needed for the heating up and cooling down processes may be substantially shortened.

Furthermore, deviating from the embodiment shown, the suspension means of the crucible **8**, for example, in the form of the notches **7**, may be positioned farther outward to the edge of the crucible holder **1**, in order to utilize the strongest possible centrifugal forces for the mixing of the sample material when the crucible holder **1** is rotated back and forth on a turntable.

FIG. 3 shows a second embodiment of the crucible holder **1** with a crucible **8** arranged therewithin, as well as a casting dish **4**. The sidewalls **2** of this crucible holder **1** are

made of silicon nitride, as is a platform **12**, that has a cut-out to receive the casting dish **5** of the casting dish **4**. The casting dish **4** also has two notches **14**, that extend U-shaped around the sidewalls **2**, so that the form fit of the casting dish **4** prevents it from horizontally shifting. When the crucible **8** is removed from the notches **7** of the sidewalls **2**, the casting dish **4** can then be easily guided upward and out of the crucible holder.

The entire crucible holder **1** is secured against shifting: a profiled formation of the oven floor creates a form-fit for receiving the crucible holder **1** and fixing the crucible holder against shifting in any horizontal direction. The profiling is constructed as a unit that is assembled from multiple single components that are made of a conventional metal alloy known as "NICROFER". This alloy has good mechanical loadability, even at high temperatures, so that the crucible holder **1** may be repeatedly put to use and then removed, without unnecessarily creating wear on the oven floor. The profile may be easily replaced, should it become worn, because the profile is held by appropriate cut-outs between four vertical ceramic pins **20**, which may, as needed, be pulled out from the top and replaced with new ones.

The portion of the oven floor that is illustrated is constructed as a turntable **18** that has a stepped diameter that gets smaller to the top. The turntable **18** is made of a thermally high-temperature-resilient ceramic base material, the same material that is used to line other areas of the oven. A cover plate **19** made of silicone nitride is arranged on the upper face of the turntable **18**. The cover plate **19** forms a protective layer that protects the ceramic base material from chemical loads, for example, against splashes from the sample material.

This turntable **18** may be rotated and the off-center position of the crucible **18** enhances the most homogeneous mixing of the sample material contained therewithin by changing the direction of rotation. **FIG. 3** shows the turntable **18** in a lowered position,

making it possible to access the crucible holder **1**. The drive control that controls the rotational motion of the turntable **18** is designed such, that the turntable **18** is positioned at a pre-determined rotational angle when the turntable **18** reaches its lowered position.

The platform **12** of the crucible holder **1** forms a protective layer for the bars **15** and **16**, that are also made of "NICROFER." Splashes from the sample material attack the silicon nitride much less than the NICROFER material, which itself is relatively robust. Particles that can possibly detach from the surface of the components of the NICROFER could, however, have a negative influence on the sample analysis, and for that reason it is advantageous to have the ceramic protective layer of silicon nitride. Upper bars **15** extend in a direction that is labeled a "crosswise direction" and the two lower bars **16** extend in a direction labeled a "lengthwise direction." A solid plate made of the NICROFER material may also be used, instead of the upper bars **15**. The higher volume weight of the NICROFER material compared to the weight of the silicon nitride, lowers the center of gravity of the crucible holder **1** and thus increases its stability on the rotating turntable **18**.

An element of a lifting tool can be driven in a horizontal direction between the two lengthwise extending bars **16**, that are made of the robust NICROFER material, for example, the tongue or a fork that comes in beneath the upper bars **15** and lifts the crucible holder **1** along with the crucible **8** and the casting dish **4**. The turntable **18** is secured at a position that is a pre-determined rotational angle and is set at a pre-determined height. The lifting tool element can then be moved fully automatically and free of hindrance between the lower lengthwise extending bars **16** and then be raised.

Raising the crucible holder **1** along with the crucible **8** and the casting dish **4** moves the crucible **8** out of range of a stop **17** that is shown in the embodiment as a vertical pin and that prevents the crucible **8** from tilting, which would result in an emptying of the

crucible. If the full crucible **8** on the rotating turntable **18** starts to tilt, as a result of the centrifugal force, then the stop **17** prevents this in an early uncritical stage.

The lifting tool previously mentioned has an actuator that extends out, similarly to the tongue or fork, for example, extends horizontal and parallel to the tongue or fork, and reaches under the handle **11** of the crucible **8**. The actuator is part of a crank that is swingably mounted, for example swingable about a center of rotation that lies on the same axis as that of the two protrusions **9** of the crucible **8**. By means of a motion in an upward swinging arc, the actuator guides the handle **11** upward and causes the crucible **8** to empty its contents into the casting dish **5** in the casting dish **4**.

ARTICLE 34 AMENDED CLAIMS

Claim 1: Apparatus for producing analysis samples for X-ray fluorescence spectroscopy,

with an oven constructed as a tabletop device and having an inner chamber that is heatable to at least 900 degrees C,

a crucible (8) for carrying sample material that is to be melted, the crucible being placed in the oven and having a capacity of several cubic centimeters,

a crucible holder (1) for holding the crucible (8) that is placed in the oven,

and with a casting dish (4) placed beneath the crucible (8), the casting dish dimensioned to receive the sample material that is in the crucible (8),

wherein the crucible (8) is placed in the oven so as to be set in a mixing motion, that the sample material in the crucible (8) is mixable by means of movements of the crucible (8),

and wherein the crucible (8) is tiltably mounted in the oven, such that the sample material in the crucible (8) is fillable into the casting dish (4) from the crucible (8) by means of a tilt movement of the crucible (8),

characterized in that,

the crucible holder (1) is unattachedly placed in the oven.

Claim 2: The apparatus of claim 1,

characterized in that,

several crucibles (8), each in its own crucible holder (1), are placed in the oven.

Claim 3: The apparatus of claim 1 or 2,

characterized in that,

the crucible (8) is tiltably mounted in the crucible holder, the tilt movement relative to the crucible holder (1).

ARTICLE 34 AMENDED CLAIMS

Claim 4: The apparatus of one of the preceding claims,

characterized in that,

the entire oven is movably supported, such, that the crucible (8) placed in the oven is set in a motion that mixes the sample material by means of movement of the oven.

Claim 5: A crucible holder for X-ray fluorescence spectroscopy for producing analysis samples for X-ray fluorescence spectroscopy for apparatus constructed according to claim 1,

characterized in that,

the crucible holder (1) has a tilt support for supporting the crucible (8).

Claim 6: The crucible holder of claim 5,

characterized in that,

the crucible holder (1) has juxtaposed recesses (7) for receiving protrusions (9) on the crucible (8), such, that the recesses (7) form the tilt support for a crucible (8) held in these recesses (7).

Claim 7: The crucible holder of claim 5 or 6,

characterized in that,

the crucible holder (1) has a retainer for the casting dish (4) beneath the crucible (8), such, that the casting dish (4) is placed in a defined position beneath the crucible (8).

Claim 8: The crucible holder of one of the claims 5 to 7,

characterized in that,

the tilt support is placed as close as possible to the edge in the crucible holder (1).

ARTICLE 34 AMENDED CLAIMS

Claim 9: The crucible holder of one of the claims 5 to 8,

characterized in that,

the crucible holder (1) is constructed at least partially of a high temperature-resistant, high-carbon-content nickel-chrome-iron alloy.

Claim 10: The crucible holder of one of the claims 5 – 9,

characterized in that,

the crucible holder (1) is constructed at least partially of a ceramic material.

Claim 11: The crucible holder of claim 10,

characterized in that,

the crucible holder (1) contains silicon nitride.

Claim 12: A crucible as analysis sample crucible for producing analysis samples for X-ray fluorescence spectroscopy for apparatus constructed according to claim 1,

characterized in that,

the crucible (8) has two juxtaposed protrusions (9) that form a tilt axis of the crucible (8).

Claim 13: The crucible of claim 12,

characterized in that,

the crucible (8) has a protrusion (11) serving as a handle for a tilt motion of the crucible (8).

Claim 14: The crucible of claim 13,

characterized in that,

the crucible (8) has a pour spout (10) for emptying the crucible (8) and the handle (11) is placed opposite the pour spout (10).

ARTICLE 34 AMENDED CLAIMS

Claim 15: The crucible of one of the claims 12 to 14,

characterized in that,

the crucible (8) is made of a material that contains platinum.

Claim 16: An oven constructed as a tabletop oven, for producing analysis samples for X-ray fluorescence spectroscopy for apparatus constructed according to claim 1,

characterized in that,

the oven has a floor on which the crucible holder (1) is placed, and that the area of the floor that supports the crucible holder (1) is constructed as a rotationally oscillating turntable (18).

Claim 17: The oven of claim 16,

characterized in that,

the turntable is movable between a lowered loading position and a raised operating position that provides a limit to the inner chamber of the oven,

wherein the turntable is lowerable from its operating position to an extent that enables the crucible (8) to be removed from the crucible holder (1) in the loading position.

Claim 18: The oven of claim 17,

characterized in that,

the turntable is lowerable to an extent that enables the crucible holder (1) to be removed from the turntable.

Claim 19: The oven of one of the claims 16 to 18,

characterized in that,

ARTICLE 34 AMENDED CLAIMS

the turntable (18) has a profile that is adapted to the crucible holder (1), such, that the crucible holder (1) standing on the turntable (18) is secured with a positive lock fit against shifting.

Claim 20: The oven of one of the claims 16 to 19,

characterized in that,

the turntable (18) has a stop (17) that limits the swing movement of the crucible (8) within the crucible holder (1).

Claim 21: A casting dish (4) for catching molten sample material of apparatus according to Claim 1 for producing analysis samples for X-ray fluorescence spectroscopy,

characterized in that,

the casting dish (4) has a recess and/or protrusion along its circumferential edge,

such, that in fitting against the shape of the crucible holder (1) that holds the crucible (8), a positive locking fit is created between the casting dish (4) and the crucible holder (1) that secures the casting dish (4) from shifting in horizontal directions.

Claim 22: The casting dish of Claim 21,

characterized in that,

the casting dish (4) has two notches along its circumferential edge.

Claim 23: A method for producing analysis samples for X-ray fluorescence spectroscopy,

wherein sample material to be melted is placed in a crucible (8) that has a volume capacity of several cubic centimeters.

wherein the crucible (8) is held in a crucible holder (1) inside an oven,

ARTICLE 34 AMENDED CLAIMS

and wherein the sample material inside the oven is heated to at least 900 degrees C, such, that the sample material melts,

and wherein the crucible (8) is placed in the oven so as to move for mixing and that the sample material in the crucible (8) is mixed by means of the movements of the crucible,

and wherein the molten sample material is poured into a casting dish (4) located beneath the crucible (8) by tilting the crucible,

wherein the crucible (8) is filled with the sample material to be melted before the start of the melting step, outside the oven,

wherein also the crucible holder (1), which is constructed as a component separate from the oven, is outside the oven prior to beginning the melting step,

the crucible holder (1) is loaded with the crucible holder (8) prior to begin of the melting step, outside the oven,

and is placed in the oven along with the crucible (8),

where the crucible holder (1) remains, set in unattached, for the duration of the melting step.

Claim 24: The method of claim 23,

characterized in that,

the crucible holder (1) along with the crucible (8) is removed from the oven after the end of the melting step,

is loaded with a new crucible (8),

and is placed again in the oven, along with the new crucible (8), for a new melting step.

Claim 25: The method of Claim 23 or 24,

characterized in that,

ARTICLE 34 AMENDED CLAIMS

a first crucible holder (1) is loaded with a first crucible (8) before the begin of a first melting step,

together with the first crucible (8) is placed in the oven,

and is removed from the oven after completion of the melting step, along with the first crucible (8),

and that, before removing the first crucible holder (1) from the oven, a second crucible holder (1) is prepared by being loaded with a second crucible (8), which also contains sample material to be melted,

and that, after removing the first crucible holder (1) from the oven, the second crucible holder (1) which is already prepared and already loaded with the second crucible (8), is placed in the oven.

FIG.1

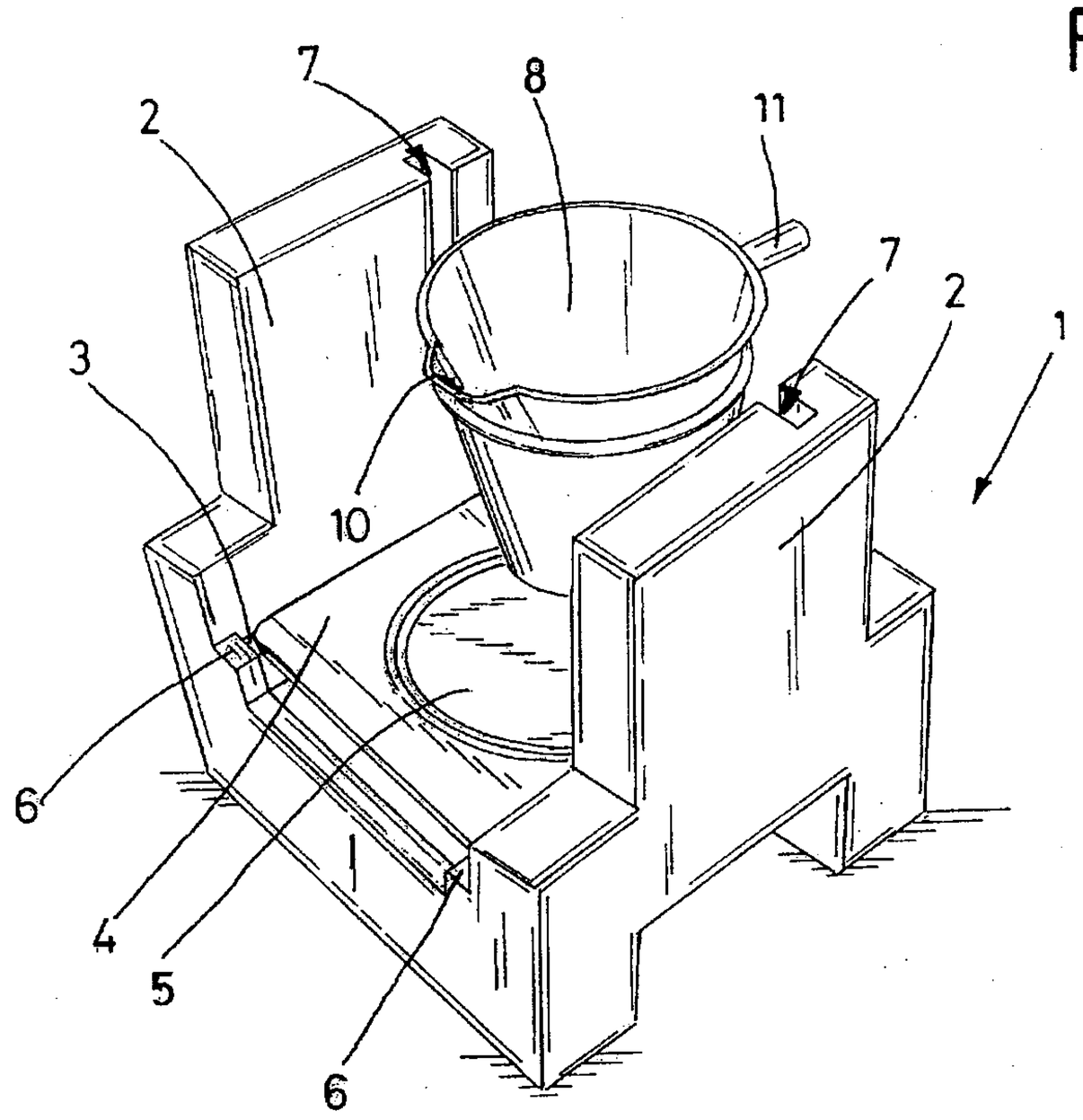

FIG.2

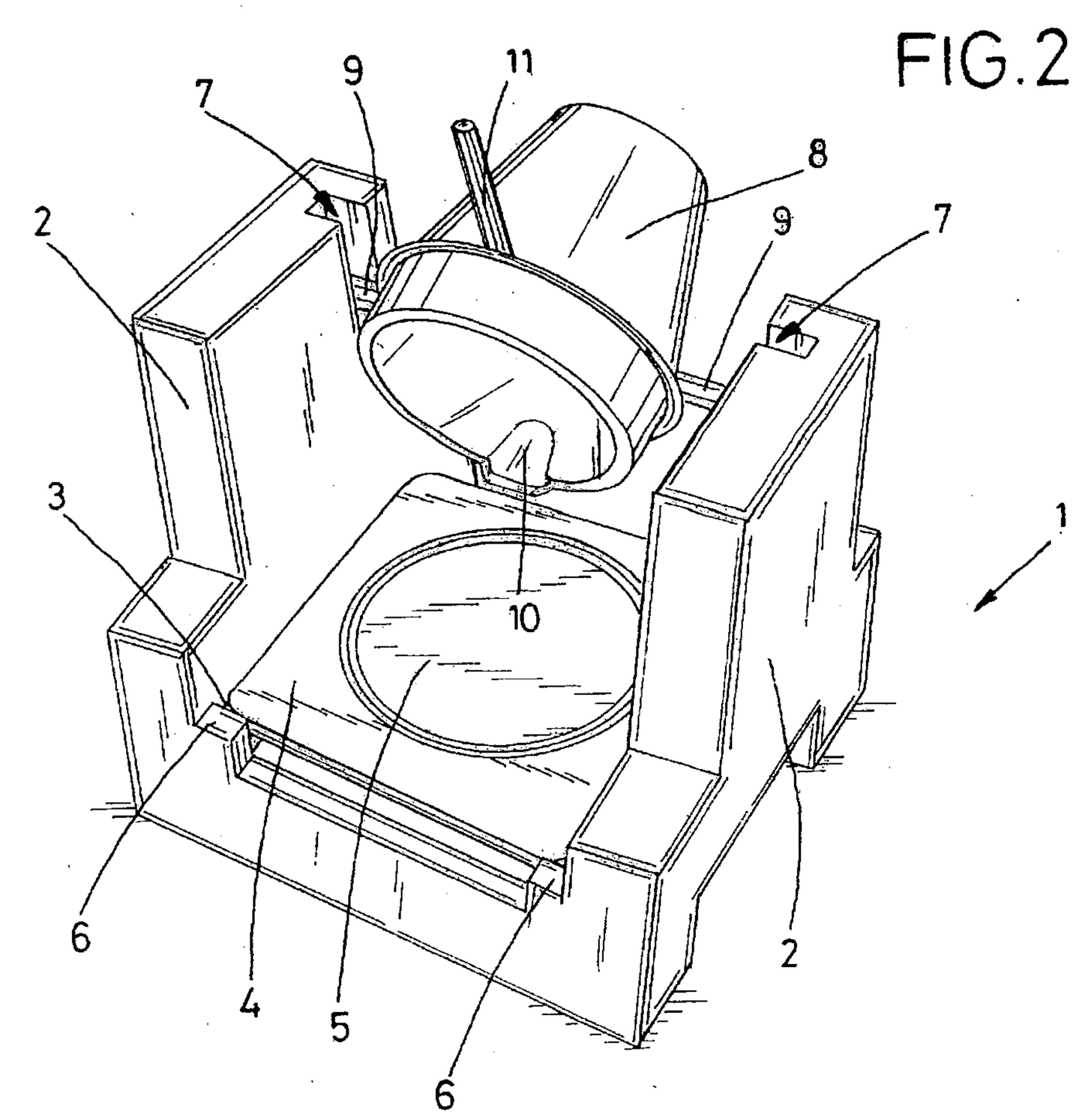

FIG.3

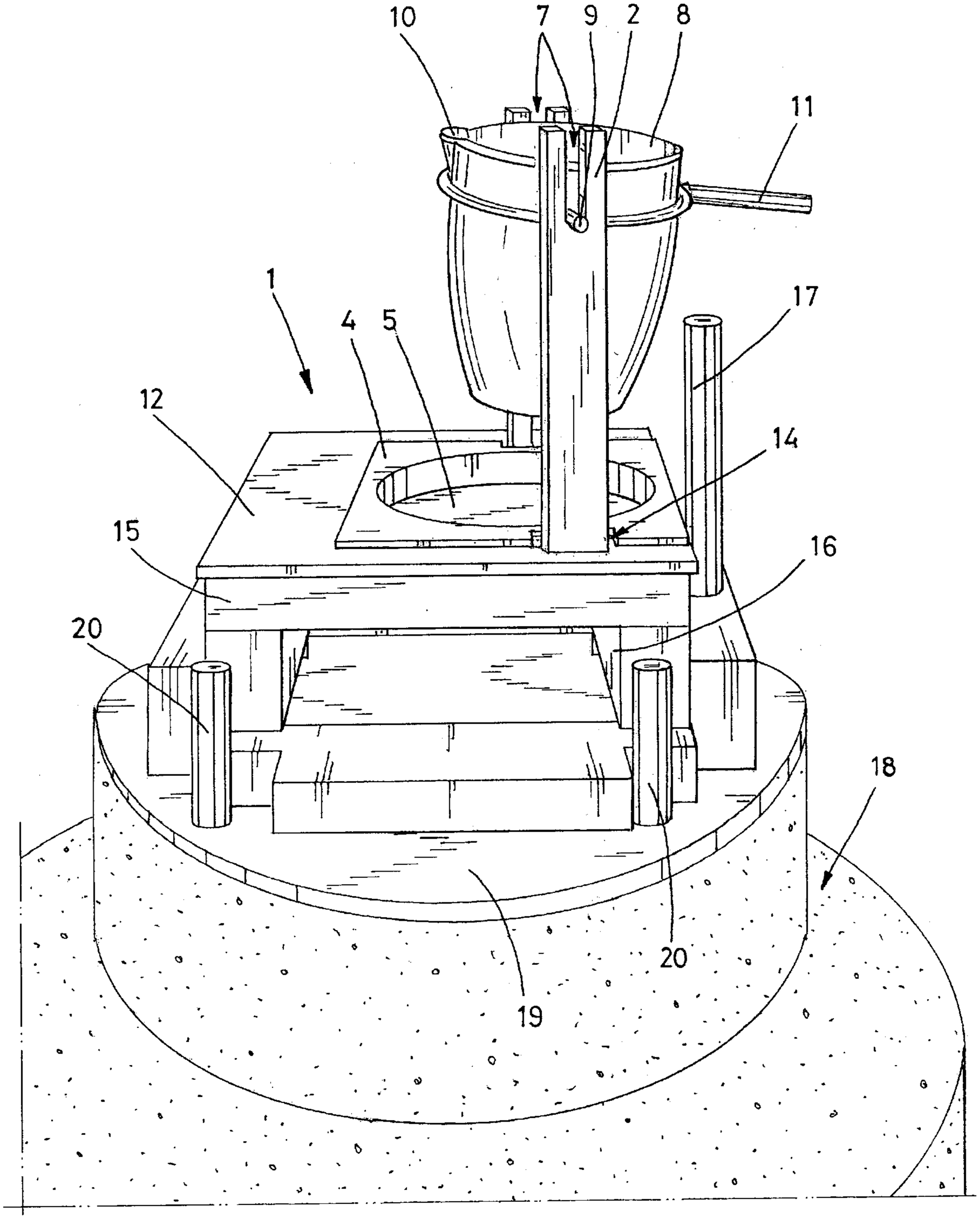

FIG. 3