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(54) **LASER ABLATION CELL**

(57) An ablation cell for laser ablation of a sample material comprises a sample chamber (21) for housing a sample. A carrier gas (G1) is fed to the sample chamber. A laser beam (41) impinges on a sample (23) in the sample chamber. The carrier gas together with ablated aerosol is removed from the sample chamber (21) through an outlet channel (12). In order to reduce dispersion of the ablated aerosol, a make-up gas (G2) is fed to the

outlet channel through at least one make-up gas channel. The make-up gas channel merges with the outlet channel at a channel junction (17). The make-up gas channel either concentrically surrounds the outlet channel at the channel junction (17), or at least two make-up gas channels (14, 15) are provided, the make-up gas channels merging symmetrically into the outlet channel.

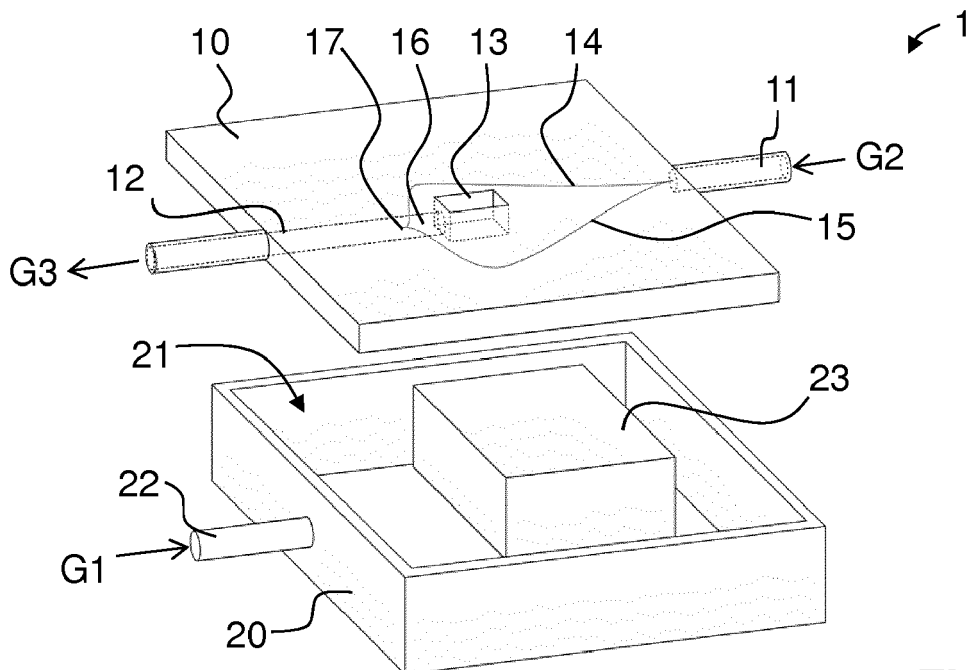


FIG. 1

Description

TECHNICAL FIELD

[0001] The present invention relates to a laser ablation cell, to an ablation apparatus and an ion source employing such a laser ablation cell, and to a method of using such a laser ablation cell.

PRIOR ART

[0002] Inductively coupled plasma mass spectrometry (ICPMS) provides accurate quantitative information on major, minor, trace, and ultra-trace elements of industrial, geological, environmental, and biological samples. In ICPMS, an aerosol sample is carried by a carrier gas stream to a so-called ICP torch. In this torch, the gas is subjected to intense highfrequency electromagnetic fields, which lead to the formation of a plasma by induction. The ions from the plasma are then extracted into a mass spectrometer, where they are separated on the basis of their mass-to-charge ratios. The ion current detected by a suitable detector is then used as a measure for the amount of the isotope present in the sample introduced into the ICP.

[0003] ICPMS can be coupled with laser ablation (LA) to ablate material from a solid sample so as to create the aerosol required for ICP. Ablation may be carried out directly in the ICP torch, or the sample may be placed in an external laser ablation cell upstream of the ICP torch, and the aerosol created by laser ablation is transported to the ICP torch by the carrier gas stream.

[0004] A large variety of designs for a laser ablation cell has been proposed in the prior art. Examples include the following publications: J. Pisonero et al., "High efficiency aerosol dispersion cell for laser ablation-ICPMS", J. Anal. At. Spectrom., 2006, 21, 922-931; D. Asogan et al., "An open, non-contact cell for laser ablation-inductively coupled plasma-mass spectrometry", J. Anal. At. Spectrom., 2009, 24, 917-923; and L. Halicz and D. Günther, "Quantitative analysis of silicates using LA-ICP-MS with liquid calibration", J. Anal. At. Spectrom., 2004, 19, 1539-1545.

[0005] WO 2014/127034 discloses a laser ablation system comprising a sample chamber in which a target is placed. A separate sample capture cell is located in the sample chamber proximate to the target. The sample capture cell has a capture cavity configured to receive target material.

[0006] WO 2014/146724 A1 discloses a laser ablation cell comprising a flow channel having an essentially constant cross-sectional area so as to ensure a strictly laminar flow in the flow channel. A sample chamber is provided adjacent to a lateral opening of the flow channel. A laser beam enters the sample chamber through a lateral window and impinges on a surface of a sample to ablate material from the sample.

[0007] Laser-ablation ICPMS (LA-ICPMS) can be

used as a chemical imaging tool by scanning the laser spot over the sample surface. The effective spatial resolution is determined by the laser spot size convoluted with the system's aerosol dispersion. The effective spatial resolution is thus often dominated by a compromise between the aerosol washout time after each laser shot and the scanning speed. The longer the washout time (i.e., the time duration of the ion signals created from a single laser pulse), the more overlap will occur between signals originating from neighboring sample spots if the scanning speed is kept fixed. Therefore, aerosol washout time can be one of the key limiting factors for improving spatial resolution without increasing total scan time.

[0008] Laser ablation cells that enable short washout times are not only of interest in the context of ICP ion sources, but also for other types of ion sources, such as atmospheric pressure ionization (API) sources.

SUMMARY OF THE INVENTION

[0009] In a first aspect, the present invention provides a laser ablation cell that can be operated in a simple and robust fashion while enabling short washout times of laser generated aerosols. Such a laser ablation cell is specified in claim 1. Further embodiments of the invention are laid down in the dependent claims.

[0010] Accordingly, an ablation cell for laser ablation of a sample material is provided, the ablation cell comprising:

- a sample chamber for housing a sample;
- a carrier gas inlet for feeding a carrier gas to the sample chamber;
- a window opening for coupling a laser beam into the sample chamber; and
- an outlet channel for removing the carrier gas together with ablated aerosol from the sample chamber.

[0011] In order to enable rapid removal of the carrier gas together with the ablated aerosol from the ablation cell at reduced dispersion, the ablation cell further comprises at least one make-up gas channel for feeding a make-up gas to the outlet channel, the make-up gas channel merging with the outlet channel at a channel junction. The make-up gas channel either concentrically surrounds the outlet channel at the channel junction, or at least two make-up gas channels are provided, the make-up gas channels merging symmetrically into the outlet channel at the channel junction.

[0012] By feeding the make-up gas concentrically or symmetrically to the gas stream in the outlet channel, the make-up gas acts to sheath the carrier gas together with the ablated aerosol so as to keep the aerosol away from the walls of the outlet channel and to concentrate the aerosol near the channel axis where the flow velocity is highest. In addition, the make-up gas accelerates the overall gas flow through the outlet channel.

[0013] In order to ensure a directed flow of the make-

up gas into the outlet channel at the channel junction and to minimize turbulence, each make-up gas channel preferably opens out into the outlet channel at an angle of less than 70° relative to the flow direction in the outlet channel. In a particularly preferred embodiment, the make-up gas channels open out tangentially into the outlet channel, i.e., the angle between each make-up gas channel and the outlet channel approaches 0°.

[0014] The channel junction is preferably as close as possible to the ablation site, and therefore the length of the proximal section of the outlet channel, which is defined as being the section that is upstream of the channel junction, should be kept as short as possible. Advantageously, the length of the proximal section is between 1 millimeter and 30 millimeters, preferably between 1 millimeter and 10 millimeters.

[0015] Preferably the outlet channel originates in the window opening, i.e. its proximal end opens out into the window opening. In this case, the length of the proximal section corresponds to the distance between the window opening and the channel junction.

[0016] The proximal section can taper towards the channel junction in a funnel-like manner in order to accelerate and confine the flow of the carrier gas with the aerosol.

[0017] In order to accommodate the volumetric flow of the make-up gas, to reduce turbulences and to improve the sheathing effect of the make-up gas, the outlet channel can have a cross sectional area that is larger downstream from the channel junction than upstream of the channel junction.

[0018] The make-up gas channel(s) can receive the make-up gas from a single make-up gas inlet. To this end, the laser ablation cell can further comprise a single make-up gas inlet, the make-up gas channel(s) being connected to the make-up gas inlet.

[0019] At least a proximal section of the outlet channel that is adjacent to the window opening is preferably perpendicular to the laser beam used for ablating the sample material. In other words, the window opening is preferably configured to allow the laser beam to pass through the window opening in a direction that is perpendicular to the outlet channel.

[0020] The ablation cell can comprise a UV-transparent window that closes the window opening, so as to prevent escape of the carrier gas from the sample chamber through the window opening.

[0021] In order to enable easy sample exchange, the laser ablation cell preferably has a two-part design, comprising a first cell part (in the following referred to as a "cell bottom") that forms a sample chamber that is open towards its top, and a second cell part (in the following referred to as a "cell top") that removably covers the sample chamber. The cell bottom is preferably removable from the cell top for exchanging the sample. The window opening is then preferably provided in the cell top. Also the outlet channel is preferably formed in the cell top. Advantageously, the channel junction is also located

within the cell top, i.e. the make-up gas channel(s) merge(s) into the outlet channel within the cell top. To this end, also the make-up gas channel(s) can be located within the cell top.

[0022] The terms "top" and "bottom" are to be understood as not defining an absolute orientation of these parts; these terms are only used to better distinguish between the different cell parts, and the laser ablation cell may as well be used in an inverted orientation where the cell top is pointing towards the floor and the cell bottom is pointing towards the ceiling.

[0023] If the outlet channel is arranged in the cell top, the outlet channel and the sample chamber are separated by a separating wall. In order to allow the sample to be positioned sufficiently close to the outlet channel, it is preferred to minimize the thickness of the separating wall. The separating wall preferably has a minimum thickness of less than 500 micrometers, more preferably less than 200 micrometers. It should be noted that the thickness of the separating wall may vary along the length and circumference of the outlet channel; the separating wall will normally have its smallest thickness immediately adjacent to the proximal end of the outlet channel.

[0024] The ablation cell can be readily manufactured by 3D printing techniques. Alternatively, the cell top and the cell bottom can be formed by machining from a block of material.

[0025] The present invention further provides an ablation apparatus comprising an ablation cell as described above, a laser for shining a laser beam onto the sample through the window opening, and a positioning device for changing a relative position between the sample and the laser beam. The positioning device may comprise, e.g., any of the following: an x-y or x-y-z stage for moving the entire laser ablation cell relative to the laser; an x-y or x-y-z stage for moving the sample within the laser ablation cell while keeping the relative position between the ablation cell and the laser fixed; a beam deflector for deflecting the laser beam while keeping the relative position between the ablation cell and the laser fixed; etc. The positioning device may be employed to scan the laser beam over the sample surface. The resulting aerosol may subsequently be analyzed with respect to its elemental, isotopic or molecular composition, e.g., by ICPMS or any other analytical technique. In this manner, the sample surface may be imaged according to its elemental or isotopic composition. However, the present invention is not limited to the use of the ablation cell in conjunction with ICPMS imaging and may also be employed in other methods in which short aerosol pulses are required.

[0026] The present invention further provides an ion source comprising an ablation cell as described above and an ionizing device for ionizing the aerosol that exits the outlet channel. In particular, the ion source can be an ICP ion source, wherein the ionizing device comprises an ICP torch connected to the outlet channel, or another type of atmospheric pressure ion source, wherein the ionization device can e.g. comprise a corona discharge

electrode or similar.

[0027] The invention also encompasses a mass spectrometry system comprising such an ion source and a mass analyzer coupled to the ion source. The mass analyzer may, e.g., be a quadrupole mass analyzer, a time-of-flight (TOF) mass analyzer, or a sector field mass analyzer, in particular, a Mattauch-Herzog mass analyzer. However, the invention is not restricted to any particular type of mass analyzer.

[0028] The invention further provides a method of operating an ablation cell as described above. The method comprises, not necessarily in the given order:

placing a sample in the sample chamber;
feeding a carrier gas to the carrier gas inlet;
feeding a make-up gas to the make-up gas channel(s); and
ablating material from the sample by shining a pulsed laser beam through the window opening onto a surface of the sample.

[0029] Each laser pulse will cause a quasi-instantaneous laser-generated aerosol mass distribution ("plume"). Here, "quasi-instantaneous" means a time scale that is much shorter than the time scale of mass transport by the carrier gas stream. The laser-generated aerosol mass distribution is caused by the action of the laser pulse alone, neglecting the normal gas flow of the carrier gas. This mass distribution is usually established within less than 1 millisecond after the first interaction of the laser pulse with the sample. The quasi-instantaneous laser-generated aerosol mass distribution preferably has its center of mass on or near the longitudinal axis of the outlet channel. In particular, the outlet channel can have a proximal end portion, which defines an outlet channel axis and has a channel height along a direction that is perpendicular to the outlet channel axis and parallel to the laser beam. The sample is preferably positioned at such a distance from the outlet channel axis that the laser-generated mass distribution has its center at a distance from the outlet channel axis that is less than the channel height. In this manner, the majority of the aerosol plume is directly injected into a region immediately in front of the outlet channel and may be transported away by the stream of the carrier gas with minimum dispersion. Here, the center of the mass distribution is defined in the usual manner, in the same way as the center-of-mass of a rigid body, integrating over the entire aerosol plume.

[0030] In the context of the present invention, any method that removes material from a solid or liquid surface by means of a pulsed laser beam of sufficient energy or power density is considered to be a laser ablation method. In particular, the ablation process can take place at a gas pressure between 0.1 bar and 2 bar, preferably at ambient pressure.

[0031] The optimum distance between the sample surface and the longitudinal axis of the flow channel will depend on the type of laser, the energy of the laser beam,

the type of carrier gas, and the flow rates of the carrier gas. For instance, for a standard ArF excimer laser with pulses in the nanosecond range and helium as carrier gas at a flow rate of 0.6 l/min, a distance of about 2 mm has turned out to be optimal. In more general terms, the sample should preferably be positioned in such a manner that the surface of the sample has a distance from the longitudinal axis of the outlet channel in the range of 0.5 millimeters to 5 millimeters for laser pulses in the range of 50 femtoseconds to 50 nanoseconds and wavelengths between 157 nanometers and 800 nanometers.

[0032] In order to achieve a good sheathing effect, the carrier gas preferably has a lower viscosity than the make-up gas. Thereby, the make-up gas may act to reduce expansion of the aerosol mass distribution. In particular, the carrier gas can be helium (He). Helium may be replaced by or mixed with other gases, e.g., hydrogen, nitrogen, or water vapor. The make-up gas can be argon or a gas mixture that comprises at least 80% argon. Argon is particularly well-suited as a make-up gas, as it is known to stop the aerosol expansion, and it is also required for an improved instrumental sensitivity in most of the Ar gas based ICP. At 25° C, Ar has a viscosity of 22.6 μ Pas, whereas He has a viscosity of 19.8 μ Pas.

[0033] The optimum flow rates of the carrier gas and the make-up gas will depend on a variety of factors, first of all on geometry, in particular, on the cross-sectional area of the outlet channel and of the make-up gas channel(s). It is preferred that the cross sections and flow rates lead to a similar mean gas velocity of carrier and make-up gas to avoid turbulence.

[0034] The method of the present invention is particularly suited for chemical imaging. To this end, the above method may comprise scanning the laser beam over the surface of the sample and analyzing the resulting aerosol to obtain a chemical image of the sample surface. Analysis may be carried out by mass spectrometry, in particular, by ICPMS, but may also be carried out by any other suitable method.

[0035] The method is well suited for the investigation of biological samples, in particular, of tissue samples of human or animal tissue. However, the method is not limited to biological samples and may as well be applied to other kinds of samples.

BRIEF DESCRIPTION OF THE DRAWINGS

[0036] Preferred embodiments of the invention are described in the following with reference to the drawings, which are for the purpose of illustrating the present preferred embodiments of the invention and not for the purpose of limiting the same. In the drawings,

Fig. 1 shows a schematic sketch (not to scale) of a first embodiment of a laser ablation cell in perspective view;

Fig. 2 shows a schematic sketch (not to scale) of a second embodiment of a laser ablation cell in

- a horizontal section through the cell top;
- Fig. 3 shows a schematic sketch (not to scale) of the laser ablation cell of Fig. 2 in a central vertical section;
- Fig. 4 shows detail A of Fig. 2 at enlarged scale;
- Fig. 5 shows the region of detail A for a third embodiment of a laser ablation cell;
- Fig. 6 shows a schematic sketch (not to scale) of the third embodiment in a central vertical section, including a schematic illustration (not to scale) of the laser-generated plume;
- Fig. 7 shows the region of detail A for a fourth embodiment of a laser ablation cell;
- Fig. 8 shows a schematic sketch (not to scale) of the fourth embodiment in a central vertical section; and
- Fig. 9 illustrates, in a highly schematic manner, a complete LA-ICPMS system employing the laser ablation cell of Figs. 2 and 3.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0037] Figures 1 illustrates, in a schematic manner, a laser ablation cell 1 according to a first exemplary embodiment of the present invention. The ablation cell 1 comprises two parts: a cell top 10 and a cell bottom 20.

[0038] The cell bottom 20 defines a sample chamber 21. A carrier gas inlet 22 for a carrier gas G1 leads to the sample chamber 21. A sample 23 is placed in the sample chamber 21.

[0039] The cell top 10 covers the sample chamber 21 from above in a gastight manner. The cell top 10 has a vertical window opening 13, which is covered from above by a UV transparent window (not shown), so that a vertical laser beam can enter the sample chamber 21 through the window opening 13 and impinge upon the top surface of sample 23. A horizontal outlet channel 12 originates in the window opening 13 and extends horizontally within cell top 10 to tubing outside cell top 10. The cell top 10 further comprises a make-up gas inlet 11, which splits up inside cell top 10 into two make-up gas channels 14, 15. The make-up gas channels 14, 15 are only shown in a highly schematic manner as simple lines in Fig. 1. They have identical dimensions, the cross-sectional area of each of the make-up gas channels being in a similar range as the cross-sectional area of outlet channel 12. The make-up gas channels 14, 15 are arranged in a mirror-symmetric manner within cell top 10. They symmetrically merge with outlet channel 12 at a channel junction 17. More than two make-up gas channels can be provided.

[0040] For operating the ablation cell, a carrier gas G1, preferably helium, is fed to carrier gas inlet 22, and a make-up gas G2, preferably argon, is fed to make-up gas inlet 11. A pulsed UV laser beam enters the window that covers window opening 13 and hits the top surface of sample 23. Each laser pulse generates an aerosol plume, which is carried into outlet channel 12 by carrier gas G1.

The stream of carrier gas with the ablated aerosol reaches channel junction 17, where the make-up gas is symmetrically added to the carrier gas stream. The combined gas stream G3 leaves the cell top at the distal end of outlet channel 12.

[0041] The fact that the make-up gas is fed symmetrically to the carrier gas stream exiting sample chamber 21 helps to confine the aerosol near the center of outlet channel 12. In addition, the make-up gas stream acts to accelerate the gas flow in outlet channel 12. The overall action of the symmetrically fed make-up gas stream is thereby to more rapidly flush the aerosol from the ablation cell while minimizing aerosol dispersion along the length of outlet channel 12.

[0042] Outlet channel 12 has a proximal section 16 extending between window opening 13 and channel junction 17. This proximal section 16 is preferably as short as possible. Advantageously, proximal section 16 is shorter than 20 mm, more preferably shorter than 10 mm.

[0043] Figures 2 and 3 illustrate a second embodiment of a laser ablation cell according to the present invention. The second embodiment differs from the first embodiment mainly in that carrier gas G1 is fed into sample chamber 21 in a different direction than in the first embodiment. In fact, the direction in which carrier gas G1 is fed into sample chamber 21 is not important and can be any direction, while preferably being horizontal. Another difference exists in the shape of window opening 13. The window opening 13 of the second embodiment has an oval shape that is advantageous in that it helps to funnel the carrier gas stream with the ablated aerosol into outlet channel 12 while avoiding the creation of turbulences.

[0044] Figure 4 illustrates the region of channel junction 17 in greater detail. Each make-up gas channel 14, 15 opens out into outlet channel 12 at an angle α , which here is approximately $\alpha = 60^\circ$. This angle can of course be different from 60. Advantageously the flow vector in the make-up has channels 14, 15 includes a non-negligible forward component along the flow direction in outlet channel 12 in order to minimize turbulences, and the angle is therefore preferably not larger than about 70° .

[0045] Figures 5 and 6 illustrate a third embodiment of a laser ablation cell according to the present invention. In this embodiment, each make-up gas channel 14, 15 opens out tangentially into outlet channel 12. This arrangement has the advantage that turbulence is at channel junction 17 is further minimized.

[0046] In particular, each make-up gas channel 14, 15 has a roughly semicircular cross-sectional shape at channel junction 17, and the make-up gas channels 14, 15 thus merge into a single make-up gas channel of roughly circular cross section that completely surrounds proximal section 16 immediately upstream of channel junction 17. Thereby an annular make-up gas flow is created, which essentially completely sheathes the carrier gas flow entering channel junction 17 from proximal section 16. In the same spirit, it is of course also possible to provide more than two make-up gas channels that merge

into a single channel that concentrically surrounds proximal portion 16.

[0047] In the embodiment of Figs. 5 and 6, proximal section 16 initially tapers from its origin at window opening 13 towards the channel junction. This funnel-like taper accelerates the carrier gas stream with the aerosol. It is further to be noted that proximal section 16 has both reduced width W1 (see Fig. 5) and reduced height H1 (see Fig. 6), and therefore reduced cross-sectional area, as compared to the distal section of outlet channel 12 downstream from channel junction 17, which has width W2 and height H2. This allows the distal section to better accommodate the additional volumetric flow entering from the make-up gas channels, reduces turbulences and improves the sheathing effect of the make-up gas. Such a configuration of the outlet channel, tapering upstream of the channel junction in a funnel-like manner and/or having increased cross-sectional area downstream from the channel junction, can also be advantageous if the channels merge in a different manner than in the presently illustrated embodiments.

[0048] Figure 6 further illustrates an aerosol plume 25 that is created by each laser pulse. This plume is the direct result of the action of the laser pulse, the initial mass distribution in the plume immediately after the end of the laser pulse being influenced only very little by the stream of carrier gas G1. The design of the laser ablation cell 1 allows placing the center of the laser-generated aerosol mass distribution right in front of the entrance to outlet channel 12 (which in the present embodiments is inside window opening 13), without the need of first transporting the aerosol to the outlet channel by the carrier gas stream. In particular, by a careful choice of sample position and laser pulse energy, the center C of the aerosol mass distribution directly after each laser pulse can be caused to be on the longitudinal axis L defined by the center of outlet channel 12, or at least to be at a distance from this axis L which is less than channel height H3 at the start of outlet channel 12. In this manner, rapid wash-out of the aerosol from the sample chamber 21 can be ensured.

[0049] In absolute numbers, the cross-sectional area of outlet channel 12 upstream and downstream from the channel junction may take a wide range of values, depending on laser spot size and laser energy. The mean diameter of the outlet channel (calculated as

$d = 2\sqrt{A/\pi}$, where A is the cross-sectional area)

downstream from the channel junction may range, e.g., from 50 micrometers to 5 millimeters, preferably from 200 micrometers to 5 millimeters.

[0050] Figures 7 and 8 illustrate a fourth embodiment of the present invention, wherein only a single make-up gas channel 18 is provided. A distal end portion of make-up gas channel 18 concentrically surrounds proximal section 16 of outlet channel 12 immediately upstream of channel junction 17. This arrangement acts in a very sim-

ilar manner as the embodiment of Figures 5 and 6, where two make-up gas channels 14, 15 are provided, which merge into a single channel that concentrically surrounds proximal portion 16 only immediately upstream of channel junction 17.

[0051] Figure 9 schematically illustrates a complete LA-ICPMS system. The laser beam 41 is generated by a laser 40. The laser ablation cell 1 is mounted on an X-Y-Z stage 50 so as to be able to change the position of the sample 23 relative to the laser beam 41. Outlet channel 12 of the laser ablation cell 1 is connected to an ionizing device in the form of an ICP torch 60 to form an ion source. The ICP torch generates a plasma source by operation of an RF coil 61. The ICP torch is connected to a mass analyzer 70 via an ICP source 71. The mass analyzer may be a quadrupole mass analyzer, a time-of-flight (TOF) mass analyzer, a sector mass analyzer etc.

[0052] Of course, many modifications of the laser ablation cell and of the ion source employing the laser ablation cell are possible without leaving the scope of the present invention. In particular, the present invention is not limited to a particular choice of materials for the laser ablation cell, to a particular geometry or size of the sample chamber, to a particular geometry, length, and diameter of the outlet channel and of the make-up gas channels in the ablation cell, to a particular geometry and size of the window opening in the ablation cell, to a particular window size or material, to a particular type of laser for ablation, to particular gas types introduced into the ablation cell, etc.

[0053] In summary, the laser ablation cell of the present invention is able to ensure rapid removal of laser generated aerosols. Thereby discrete pulses of the aerosol can be introduced into an ion source, e.g. of an ICPMS, for time resolved analysis. Low aerosol dispersion is achieved by mixing the gas stream carrying the aerosol directly after the ablation region with a make-up gas flow in a concentric or symmetric way that minimizes turbulences and provides a rapid transfer. The system provides significantly easier operation and optimization than previously used devices.

[0054] The above-described ablation cell alleviates the problem of mixing of subsequent aerosol plumes generated by sequential laser pulses during ablation of solid samples for chemical analysis. In order to determine the chemical composition of individual points at the sample surface or in depth, the material can be ablated by a laser pulse and carried into a detection system like an inductively coupled plasma mass spectrometer (ICPMS). An ablation cell providing low aerosol dispersion allows for higher laser pulse frequencies without significant mixing of the aerosols generated by individual pulses. Thereby a greater number of points at the sample surface can be analyzed individually and exclusively per given period of time. Thus high-resolution images of the chemical composition of the sample can be generated at lower total measurement times or larger sample areas analyzed within the same time. Furthermore, low aerosol disper-

sion improves the signal-to-noise ratio which translates to superior detection capabilities.

[0055] The ablation cell of the present invention can have the following advantageous properties:

a) low volume of the ablation region and b) the addition of an accelerating gas stream directly downstream from the ablation region. This combination achieves a rapid transfer of the laser generated aerosol, typically transported by a flow of helium, to the channel junction, where the make-up gas flow, usually argon, is added. The make-up gas flow is added in a concentric or symmetric fashion from at least two opposite sides and preferably tangentially to the primary aerosol carrier gas.

[0056] An important advantage over the prior art is simple adjustment and robust operation because the make-up gas stream does not interact with the ablation region, and the aerosol dispersion is thus not strongly affected by the flow rate of the make-up gas stream. At the same time the addition of the make-up gas occurs as soon as possible after the aerosol was formed and thus accelerates transport through the tubing and thereby reduces dispersion. The fact that the carrier gas and make-up gas are combined only after the ablation cell makes adjustment of both gas flow rates for optimum dispersion and operation of the subsequent mass analyzer less interdependent.

[0057] The admixing of the make-up gas can in general be carried out in different ways. Ideally, vortex formation is avoided as far as possible. The simplest configuration would use two make-up gas streams entering the aerosol flow path from opposite sides. The geometry can vary, but feeding the make-up gas at an angle with the gas flow having a vector towards the outlet of the cell is more efficient in reducing the occurrence of vortexes. Alternatively the make-up gas can be added coaxially around the primary aerosol flow. This approach is expected to further reduce aerosol dispersion by focusing the aerosol carrier to the center of the transport tube where the flow velocity is highest.

Claims

1. An ablation cell for laser ablation of a sample material, the ablation cell comprising:

a sample chamber (21) for housing a sample (23);
a window opening (13) for coupling a laser beam (41) into the sample chamber (21);
a carrier gas inlet (22) for feeding a carrier gas (G1) to the sample chamber (21); and
an outlet channel (12) for removing the carrier gas together with ablated aerosol from the sample chamber (21);

characterized in that the ablation cell further comprises:

at least one make-up gas channel (18) for feeding a make-up gas (G2) to the outlet channel (12), the make-up gas channel (18) merging with the outlet channel (12) at a channel junction (17),
wherein the make-up gas channel (18) concentrically surrounds the outlet channel (12) at the channel junction (17), or wherein at least two make-up gas channels (14, 15) are provided, the make-up gas channels (14, 15) merging symmetrically into the outlet channel (12) at the channel junction (17).

2. The ablation cell of claim 1, wherein the ablation cell comprises at least two make-up gas channels (14, 15), and wherein each of the make-up gas channels (14, 15) merges into the outlet channel (12) at an angle (α) of less than 70°.

3. The ablation cell of claim 2, wherein the make-up gas channels (14, 15) merge tangentially into the outlet channel (12).

4. The ablation cell of any one of the preceding claims, wherein the outlet channel (12) has a proximal section (16) upstream of the channel junction (17), the proximal section having a length of 1-30 millimeters.

5. The ablation cell of any one of the preceding claims, wherein the outlet channel (12) has a proximal section (16) upstream of the channel junction (17), the proximal section tapering towards the channel junction (17) in a funnel-like manner.

6. The ablation cell of any one of the preceding claims, wherein the outlet channel (12) has a cross sectional area that is larger downstream from the channel junction (17) than upstream of the channel junction (17).

7. The ablation cell of any one of the preceding claims, wherein the outlet channel (12) originates in the window opening (13).

8. The ablation cell of any one of the preceding claims, comprising:

a cell bottom (20) that forms the sample chamber (21); and
a cell top (10) that removably covers the sample chamber (12), the window opening (13) being provided in the cell top (10), and the outlet channel (12) being formed in the cell top (10).

9. The ablation cell of claim 8, wherein the channel junction

tion (17) is located within the cell top (20).

10. The ablation cell of claim 8 or 9, wherein the at least one make-up gas channel (14, 15; 18) is located within the cell top (10). 5

11. An ablation apparatus comprising:

the ablation cell (1) of any one of the preceding claims; 10
 a laser (40) for shining a laser beam (41) onto the sample (23) through the window opening (13); and
 a positioning device (5) for changing a relative position between the sample (23) and the laser beam (41). 15

12. An ion source comprising:

the ablation cell (1) according to any one of claims 1-10; and 20
 an ionizing device (60) connected to the outlet channel (12).

13. A method of operating an ablation cell (1) according to any one of claims 1-10, the method comprising, not necessarily in the given order: 25

placing a sample (23) in the sample chamber (21); 30
 feeding a carrier gas (G1) to the carrier gas inlet (22);
 feeding a make-up gas (G2) to the at least one make-up gas channel (14, 15; 18); and
 ablating material from the sample (23) by shining a pulsed laser beam (41) through the window opening (13) onto a surface of the sample (23). 35

14. The method of claim 13, 40

wherein the outlet channel (12) has a proximal end portion (16) defining an outlet channel axis (L) and having a channel height (H3) along a direction that is perpendicular to the outlet channel axis (L) and parallel to the laser beam (41), wherein the laser beam (41) causes a quasi-instantaneous laser-generated aerosol mass distribution (25), and 45
 wherein the sample (23) is positioned at such a distance from the outlet channel axis (L) that the laser-generated mass distribution (25) has its center (C) at a distance from the outlet channel axis (L) that is less than the channel height (H3). 50

15. The method of claim 13 or 14, wherein the carrier gas (G1) has a lower viscosity than the make-up gas (G2). 55

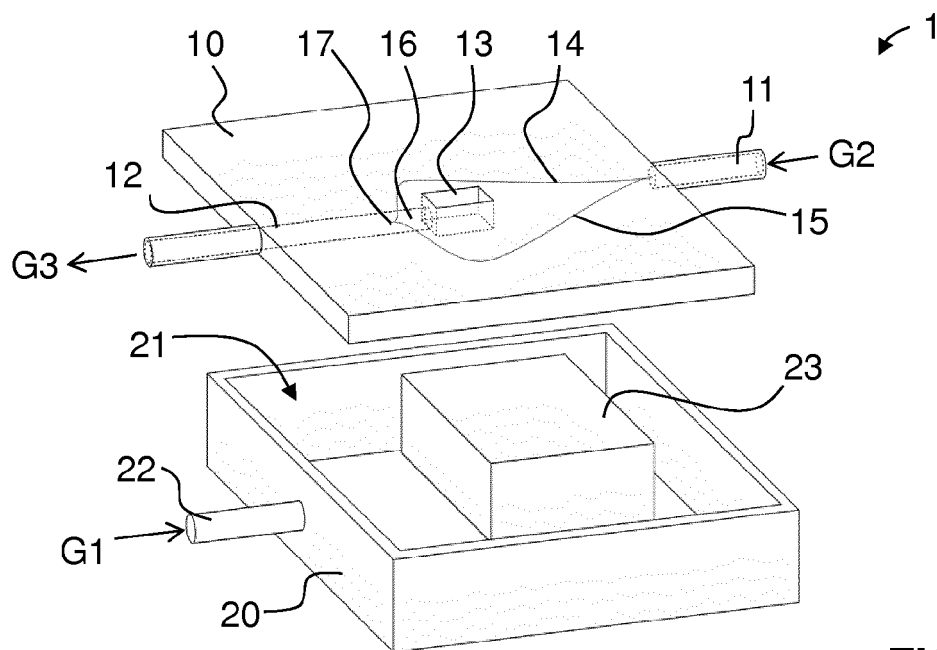


FIG. 1

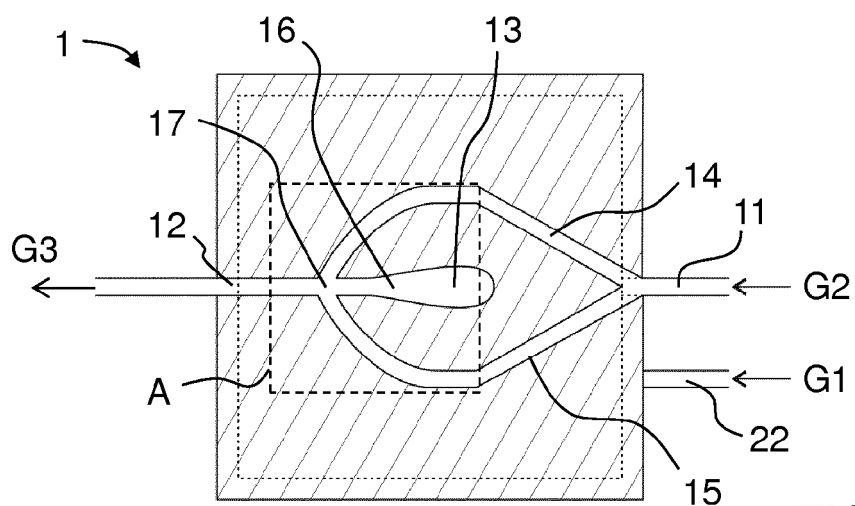


FIG. 2

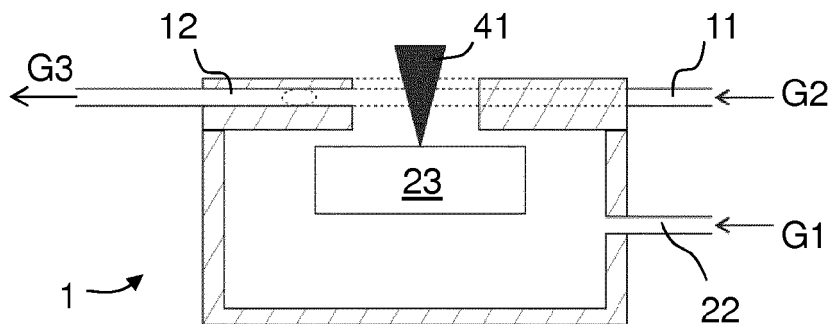


FIG. 3

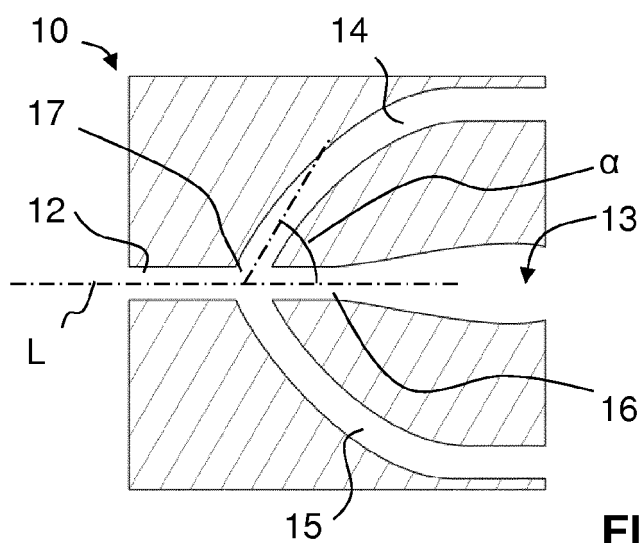


FIG. 4

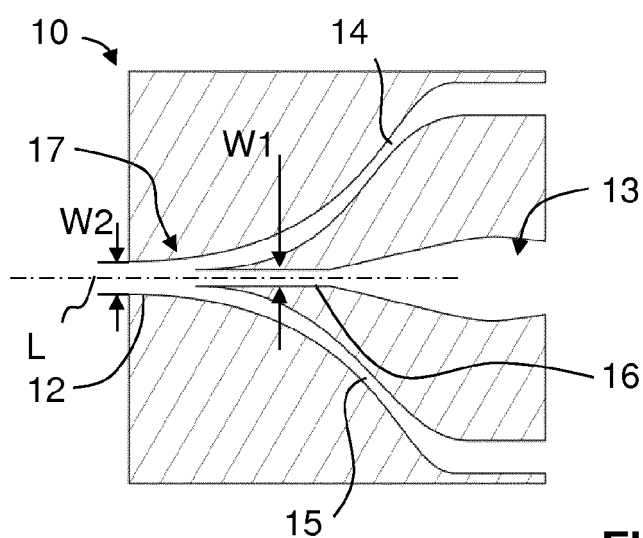


FIG. 5

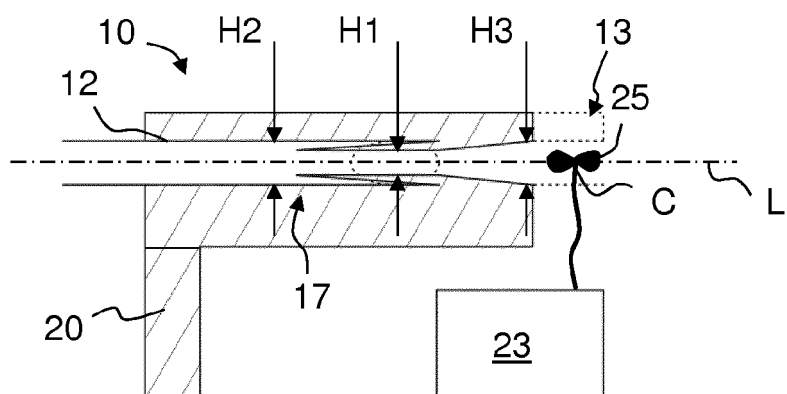


FIG. 6

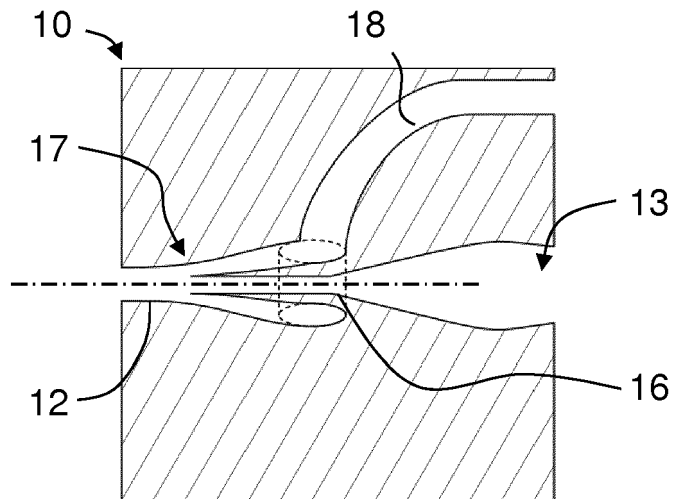


FIG. 7

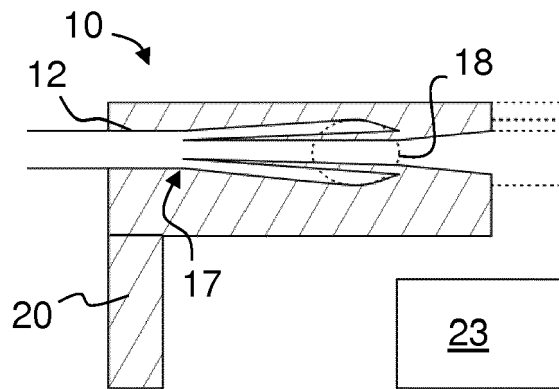


FIG. 8

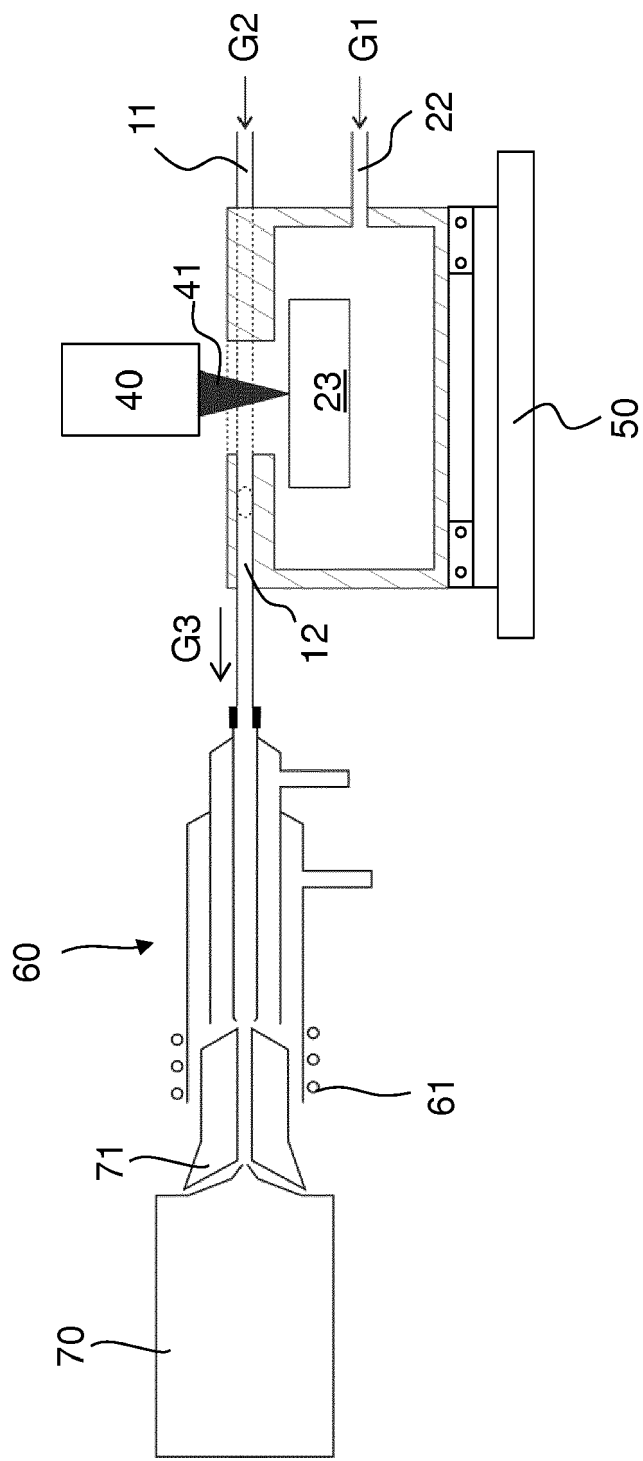


FIG. 9



EUROPEAN SEARCH REPORT

Application Number
EP 16 16 7657

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Y	* page 1, lines 1-19; figure 2 * * page 2, line 23 - page 4, line 9 *	2,3	
X	HALIEZ L ET AL: "Quantitative analysis of silicates using LA-ICP-MS with liquid calibration", JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY, ROYAL SOCIETY OF CHEMISTRY, vol. 19, no. 12, 1 January 2004 (2004-01-01), pages 1539-1545, XP008142376, ISSN: 0267-9477, DOI: 10.1039/B410132D [retrieved on 2004-11-04] * Section "Instrumentation" on page 1540; figure 1 *	1,13,15	TECHNICAL FIELDS SEARCHED (IPC) H01J
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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 30 September 2016	Examiner Rutsch, Gerald
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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 16 16 7657

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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30-09-2016

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