US 7,119,330 and US 7,872,227 and Thermo Fisher Scientific Technical Note Nr. 40705.

It would therefore be desirable to provide a way of either reducing such deposition, or reducing the effect of 5 such deposition, on the instrument so that the resulting loss of throughput may be reduced. The invention aims to address the above and other objectives by providing an improved or alternative skimmer cone apparatus and method. Summary of the invention

- 10 According to one aspect of the invention, there is provided a method of operating a mass spectrometer vacuum interface comprising a skimmer apparatus having an internal <u>surface and</u> a skimmer aperture and downstream ion extraction optics, the method comprising: skimming an expanding plasma
- 15 through the skimmer aperture, and separating within the skimmer apparatus a portion of the skimmed plasma adjacent the skimmer apparatus from the remainder of the skimmed plasma by providing means to prevent (i.e., inhibit or impede) the separated portion from reaching the ion
- 20 extraction optics while allowing the remainder to expand towards the ion extraction optics, wherein the means comprises one or more channels provided by a channel<u>-forming</u> member disposed within <u>a recess in the internal surface of</u> the skimmer apparatus <u>and in conductive contact with the</u> 25 <u>skimmer apparatus whereby the channel-forming member is</u>

electrically neutral relative to the skimmer apparatus and the portion of the skimmed plasma adjacent the skimmer apparatus is separated by diverting the portion into the one or more channels. The skimmer apparatus is preferably a 30 skimmer cone having a cone aperture.

As mentioned above, some of the material comprised within the plasma being skimmed by the skimmer apparatus may be deposited on the skimmer apparatus; in particular, on the internal surface of the skimmer apparatus, i.e. surfaces including the downstream surface of the skimmer apparatus. In particular, it has been found that considerable relatively high, pressure. The pressure of the expanding plasma arriving at the skimmer apparatus is therefore reduced; typically to a few mbar.

According to a further aspect of the invention, there is

- 5 provided a skimmer apparatus for a mass spectrometer vacuum interface comprising: a skimmer apparatus having an internal surface , downstream ion extraction optics, and a skimmer aperture for skimming plasma therethrough to provide skimmed plasma to the ion extraction optics downstream of the
- 10 skimmer aperture; and a plasma-separation means comprising one or more channels defined by a channel-forming member disposed within a recess in the internal surface of the skimmer apparatus and in conductive contact with the skimmer apparatus whereby the channel-forming member is electrically
- 15 neutral relative to the skimmer apparatus, the skimmer apparatus, wherein the plasma is separated within the skimmer apparatus by diverting a portion of the skimmed plasma adjacent the internal surface of the skimmer apparatus into the one or more channels whilst the remainder 20 of the skimmed plasma is allowed to expand downstream

towards the ion extraction optics.

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The plasma-separation means is disposed or formed on, or associated with, the internal surface of the skimmer apparatus by being deposited thereon; adhered, attached or affixed thereto; or otherwise physically coupled, engaged or connected thereto. In this way, the passing boundary layer of skimmed plasma, comprising unwanted previously deposited matter, is subjected to an adsorbent region within the skimmer apparatus which acts to remove matter from the

30 boundary layer. This separation takes place within the skimmer apparatus itself, so that the potentially contaminating material can be removed upstream of the ion extraction optics, thereby reducing the opportunity for such deposited matter to mix with and contaminate the skimmed sample plasma before extraction.

The skimmer apparatus is preferably a skimmer cone 5 having a cone aperture. The term "cone" is used herein to refer to any body which comprises at least a generally conical portion at its upstream end, whether or not the remainder of the body is conical. The term "skimmer cone" is therefore to be understood as a body which performs a

5 skimming function in a mass spectrometer vacuum interface and has a conical form at least at a region of its upstream, or atmosphere/plasma-facing, side.

According to a further aspect of the invention, there is provided a method of operating a mass spectrometer

- 10 plasma-vacuum interface comprising a skimmer apparatus having a skimmer aperture and an internal surface, the method comprising: providing a channel-forming member defining one or more channels adjacent the internal surface of the skimmer apparatus to establish an outwardly directed
- 15 flow along the one or more channels, the channel formingmember being disposed within a recess in the internal surface and in conductive contact with the skimmer apparatus whereby the channel-forming member is electrically neutral relative to the skimmer apparatus.

20 Preferably, the outwardly directed flow is a laminar flow.

As used herein, outwardly directed flow means a flow directed generally downstream and/or radially outward from an axis of the skimmer cone apparatus. Hence in embodiments 25 in which the skimmer apparatus comprises a cone aperture, an outwardly directed flow is established both downstream and radially outward from an axis of the skimmer cone apparatus as the flow is directed along the internal surface of the skimmer apparatus. In other embodiments in which the

30 skimmer apparatus comprises an aperture in a planar surface, the planar surface being generally perpendicular to an axis of the skimmer cone apparatus, an outwardly directed flow is

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established radially outward from an axis of the skimmer cone apparatus as the flow is directed along the internal surface of the skimmer apparatus.

8a

Other preferred features and advantages of the

invention are set out in the description and in the dependent claims which are appended hereto.

Brief description of the drawings

The invention may be put into practice in a number of 5 ways and some embodiments will now be described, by way of non-limiting example only, with reference to the following figures, in which:

Figure 1 shows schematically a mass spectrometer device in accordance with one embodiment of the invention;

Figure 2 shows part of a plasma ion source comprising a skimmer cone apparatus in accordance with another embodiment of the invention;

Figure 3 shows a schematic representation of the flow through a prior art skimmer cone;

Figure 4 shows a schematic representation of the flow through a skimmer cone which does not embody the present inventionaccording to one embodiment of the invention;

Figure 5 shows a schematic representation of the flow through a skimmer cone <u>which does not embody the present</u> <u>inventionaccording to another embodiment of the invention</u>; and

Figure 6 shows part of a plasma ion source comprising a skimmer cone apparatus which is not in accordance with the invention.

25 Description of preferred embodiments

Referring to Figure 1, there is schematically shown a

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is, with this arrangement, there is no need to confine the plasma expansion, so no need for a fully or partially enclosed collision chamber. One further use for such gas inlets is to provide a 'backwards' flow of gas through the skimmer for cleaning purposes, especially when not

processing a sample plasma.

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Preferably, tThe ring-like member 140 is electrically neutral (relative to the skimmer cone 133, with which it is typically—in conductive contact), so that it has no effect on, and is not affected by, the extraction field generated by the ion extraction optics 150. This is advantageous in helping to minimise the effect of the ion extraction optics on the ring-like member 140, with respect to its function of forming the channel(s) through which deposition ions may be removed.

As discussed above, any deposited matter which is liberated is at least initially concentrated in a boundary layer with the internal surface of the skimmer cone. In operation, providing the ring-like member to create a

- 20 channel in the skimmer cone establishes a laminar flow over the internal surface of the skimmer cone. The laminar flow is a radially outward flow, from the entrance aperture of the skimmer cone towards the channel. This laminar flow provides a mechanism for carrying away liberated material in 25 the boundary layer which has been previously deposited on
 - the internal surface.

However, a further advantage provided by this mechanism is a reduction in the deposition of material on the internal surface in the first place. The inventors understand that the deposition of material on the internal surface of a conventional skimmer cone is at least partly due to a zone of turbulent flow and/or a zone of relative "stillness" or

- 20 -

"silence" within the skimmer cone, the turbulent flow typically including a back-flow of material at or near the internal surface, away from the axis. A schematic representation of this is shown in figure 3. This figure

- 5 shows a skimmer cone 33 and ion extraction optics 51, with a generally axial/paraxial flow of sample plasma 35 therebetween. Along the downstream internal surface of the skimmer cone 33, some of the flow which does not pass through the ion extraction optics 51 may be turbulent flow
- 10 37 or relatively dead flow 39. Deposition of matter onto the internal surface is understood to arise at least in part because the matter in these flows 37, 39 remains near the internal surface of the skimmer cone for a relatively extended period of time.
- 15 Figure 4 shows a schematic representation of the flows with a skimmer cone according to an embodiment <u>which does</u> <u>not embody the present invention</u> for the invention. In this embodiment, a skimmer cone 133, ion extraction optics 150, and a channel-forming member 144 are provided. It will be
- 20 noted that skimmer cone 133 and the channel-forming member 144 are of different forms from the embodiment of figure 2. Here, the internal surface of the skimmer cone 133 remains conical throughout and the channel-forming member 144 is ring-like with conical inner and outer profiles at its
- 25 upstream end. As will be appreciated, the function of the channel-forming member is to divide the region within the skimmer apparatus into a central region through which it is desired to pass sample plasma and an outwardly extending channel region adjacent the internal surface of the skimmer
- 30 apparatus through which it is desired to pass liberated deposition matter.

The formation of a channel gives rise to a radially

outward laminar flow 145. This flow 145 carries away

liberated material, as explained above. However, with the laminar flow 145, the zones of turbulent flow and/or relatively dead flow have been removed, or at least displaced further downstream on the internal surface of the

- 5 skimmer cone (depending on how far the channel-forming member extends downstream and on its geometry). The laminar flow results in the opportunity for material to be deposited on the internal surface of the skimmer cone being removed or significantly reduced, especially close to or just
- 10 downstream of the cone entrance aperture. This in turn reduces the chances of deposited material being liberated from this region and mixing with the sample plasma.

This laminar flow may extend downstream over the first 0.1 mm, 0.2 mm, 0.5 mm, 1 mm, 2 mm or 5 mm from the skimmer 15 cone entrance aperture. This distance may be adjusted by changing the location of the channel-forming member within the skimmer cone and/or by adjusting the degree of pumping of the vacuum pump in the region. It will be appreciated that the skimmer cone geometry, the channel-forming member 20 geometry and the pumping/flow rates may be optimised by the skilled person.

Figure 5 shows a further embodiment <u>which does not</u> <u>embody the present invention</u> the invention, in which the channel-forming member is provided by two cones 146a, 146b, separated in the axial direction within the skimmer cone

- 133. A first channel 147a is thereby formed between the internal surface of the skimmer cone and the first channelforming member 146a and a second channel 147b is formed between the first channel-forming member 146a and the second
- 30 channel-forming member 146b. The second channel provides a second laminar flow for additional removal of undesired material.

Referring to figure 6, there is shown an alternative

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CLAIMS:

 A method of operating a mass spectrometer vacuum
 interface comprising a skimmer apparatus having <u>an internal</u> <u>surface and</u> a skimmer aperture and downstream ion extraction optics, the method comprising:

skimming an expanding plasma through the skimmer aperture, and

- 10 separating within the skimmer apparatus a portion of the skimmed plasma adjacent the skimmer apparatus from the remainder of the skimmed plasma by providing means to prevent the separated portion from reaching the ion extraction optics while allowing the remainder to expand
- 15 towards the ion extraction optics, wherein the means comprises one or more channels provided by a channel<u>-forming</u> member disposed within <u>a recess in the internal surface of</u> the skimmer apparatus <u>and in conductive contact with the</u> <u>skimmer apparatus whereby the channel-forming member is</u>
- 20 electrically neutral relative to the skimmer apparatus and the portion of the skimmed plasma adjacent the skimmer apparatus is separated by diverting the portion into the one or more channels.
- 25 2. The method of claim 1, wherein the separating step takes place upstream of a region in which shock waves are generated in the remainder of the plasma.

3. The method of claim 1 or 2, wherein the portion of the 30 skimmed plasma adjacent the skimmer apparatus comprises a boundary layer of the plasma with <u>the</u> an internal surface of the skimmer apparatus. 4. The method of any of the preceding claims, wherein the portion of the skimmed plasma adjacent the skimmer apparatus is separated by diverting the portion away from an ion

5 extraction field produced by the ion extraction optics.

5. The method of any of the preceding claims, wherein <u>the</u> an internal surface of the skimmer apparatus has a first profile and an outer surface of the channel<u>-forming</u> member has a second profile, the second profile being complementary to the first profile to define the one or more channels

therebetween.

6. The method of any of the preceding claims, wherein the 15 | channel<u>-forming</u> member comprises one or more openings therethrough and/or one or more troughs therein and the portion of the skimmed plasma is diverted into the one or more openings and/or troughs.

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7. The method of any of the preceding claims, wherein the one or more channels is vacuum pumped.

8. The method of any of the preceding claims, wherein the 25 | channel<u>-forming</u> member further comprises one or more gas inlets and a supply of gas is provided to the skimmed plasma.

9. The method of claim 8, wherein the gas is a reaction 30 gas.

10. The method of claim 8 or 9, wherein the gas is supplied

to direct the remainder of the plasma towards an axis of the skimmer apparatus.

 The method of any of the preceding claims, wherein the
 diverted portion of the skimmed plasma regulates heat flow in the skimmer apparatus.

12. The method of any of the preceding claims, wherein the channel member is electrically neutral relative to the skimmer apparatus.

15 <u>12.13.</u> The method of any of the preceding claims, wherein the an-internal surface of the skimmer apparatus adjacent to the skimmer aperture comprises a plasma deposition region where matter from previous or present plasma flows may be deposited and the separating step takes place downstream of the plasma deposition region.

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<u>13.</u>14. A method of performing plasma mass spectrometry comprising the method steps of any of the preceding claims.

25 <u>14.15.</u> A skimmer apparatus for a mass spectrometer vacuum interface, the skimmer apparatus comprising:

an internal surface, downstream ion extraction optics, and a skimmer aperture for skimming plasma therethrough to provide skimmed plasma to the ion extraction optics

30 downstream of the skimmer aperture; and

a plasma-separation means comprising one or more channels defined by a channel<u>-forming</u> member disposed within

a recess in the internal surface of the skimmer apparatus and in conductive contact with the skimmer apparatus whereby the channel-forming member is electrically neutral relative to the skimmer apparatus, wherein the plasma is separated

5 within the skimmer apparatus by diverting a portion of the skimmed plasma adjacent the internal surface of the skimmer apparatus into the one or more channels whilst the remainder of the skimmed plasma is allowed to expand downstream <u>towards the ion extraction optics</u>.

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<u>15.</u>16. The apparatus of claim <u>1514</u>, wherein the internal surface of the skimmer apparatus has a first profile and an outer surface of the channel<u>-forming</u> member has a second profile, the second profile being complementary to the first profile to define the one or more channels therebetween.

<u>16.17.</u> The apparatus of claim <u>15</u><u>14</u> or <u>1615</u>, wherein the one or more channels is defined by one or more openings through the channel<u>-forming</u> member and/or defined between one or more troughs formed in the channel<u>-forming</u> member and the internal surface of the skimmer apparatus.

18.17. The apparatus of any of claims 15 14 to 1617,
wherein the channel-forming member further comprises one or more gas inlets for supply of gas to the skimmed plasma.

19.18. The apparatus of claim 1817, further comprising a supply of a reaction gas.

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20.19. The apparatus of claim $\frac{18}{17}$ or $\frac{1918}{1918}$, wherein the one or more gas inlets are arranged to direct the supply of

gas towards an axis of the skimmer apparatus.

21.20. The apparatus of any of claims 15–14 to 2019, wherein the internal surface of the skimmer apparatus comprises a conical section having an open tip defining the skimmer aperture.

22.21. The apparatus of claim 2120, wherein a skimmer apparatus axis is defined through the skimmer aperture and the conical section defines an angle α of between 15° and 30°, preferably 23.5°, with the skimmer apparatus axis.

23.22. The apparatus of any of claims 15 14 to 2221, wherein a skimmer apparatus axis is defined through the
15 skimmer aperture and an inner surface of the channel-forming member defines an angle β of between -15° and 30°, preferably 3°, with the skimmer apparatus axis.

24.23. The apparatus of any of claims 15-14 to 2322, wherein the one or more channels has a width of between 0.3 mm and 1 mm, preferably 0.5 mm.

25.24. The apparatus of any of claims 15–14 to 2423, wherein an inner diameter of the skimmer aperture is from 25 0.25 mm to 1.0 mm, preferably 0.5 mm.

26.25. The apparatus of any of claims 15-14 to 2524, wherein a distance from the skimmer aperture to the one or more channels is between 1 mm and 6 mm, preferably 3.5 mm.

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27.26. The apparatus of any of claims $\frac{15}{14}$ to $\frac{2625}{26}$, wherein a distance from the skimmer aperture to a downstream

end of the channel<u>-forming</u> member is between 2 mm and 12 mm, preferably 7.5 mm.

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28.27. The apparatus of any of claims $\frac{15}{14}$ to $\frac{2726}{27}$, wherein <u>the an</u>-internal surface of the skimmer apparatus adjacent to the skimmer aperture comprises a plasma deposition region where matter from previous or present

10 plasma flows may be deposited and the plasma-separation means is disposed downstream of the plasma deposition region.

2928. A plasma mass spectrometer comprising the skimmer
15 apparatus of any of claims 15–14 to 2827.

3029. A method of operating a mass spectrometer plasmavacuum interface comprising a skimmer apparatus having a skimmer aperture and an internal surface, the method

comprising:

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providing a channel-forming member defining one or more channels adjacent the internal surface of the skimmer apparatus to establish an outwardly directed flow along the

25 one or more channels, the channel forming-member being disposed within a recess in the internal surface and in conductive contact with the skimmer apparatus whereby the channel-forming member is electrically neutral relative to the skimmer apparatus.

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31.30. The method of claim 3029, wherein the outwardly directed flow is a laminar flow from the skimmer aperture.

32.31. The method of claim 3130, wherein the outwardly directed flow is a laminar flow over a range of 0.1 mm to 5 mm from the skimmer aperture.

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33.32. The method of any of claims 30-29 to 3231, when further dependent upon any of claims 1 to 1413.

35<u>34</u>. A skimmer apparatus or a plasma mass spectrometer substantially as herein described with reference to any of figures 1, and 2, 4 and 5.