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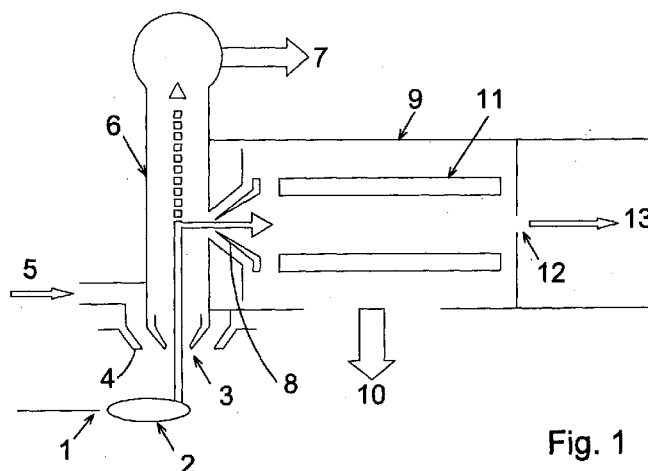


Fig. 1

(57) Abstract: A sampling cone (3) of a mass spectrometer is disclosed wherein the sampling cone (3) is made from a transition metal which has been subjected to ion implantation.

SAMPLING CONE OF MASS SPECTROMETER

This application claims priority to and benefit of U.S. Provisional Patent Application Serial No. US 61/181,377 filed on 27 May 2009 and United Kingdom Patent Application No. 0908251.2 filed on 13 May 2009. The entire contents of these applications are incorporated herein by reference.

BACKGROUND OF THE INVENTION

The present invention relates to a sampling cone, cone-gas cone and/or extraction cone of a mass spectrometer.

Mass spectrometers comprising a Liquid chromatography ion source are well known. Liquid chromatography is a method by which species from a mixture can be separated into their individual components. The basic components of a liquid chromatography system are a pumping system comprising at least two solvent channels and a tube filled with stationary phase and a column onto which components are initially trapped. By adjusting the percentage composition of the solvent channels, species are released from the stationary phase to be detected by various means at the column output.

The inside diameters of LC columns vary widely from, for example, $<50\text{ }\mu\text{m}$ to $>4.6\text{ mm}$. The delivery flow rate required from the pumping system increases with the inside diameter of the column and ranges from several nanolitres per minute to several millilitres per minute. To produce a gradient at a flow rate of several nL/min it is often necessary to split the delivery flow rate from a liquid chromatograph. The LC eluent may then pass to an Atmospheric Pressure Ionisation ("API") ion source where a range of ionisation processes may occur. The ion source may, for example, comprise an Electrospray Ionisation ("ESI") ion source, an Atmospheric Pressure Chemical Ionisation ("APCI") ion source or an Atmospheric Pressure Photoionisation ("APPI") ion source.

Electrospray Ionisation is a widely used technique in mass spectrometry in which species present in a flowing solution are ionised by the application of a high voltage. Electrospray is known as a soft ionisation technique because the resulting ions typically comprise relatively large molecular weight species (e.g. peptides) which can then be detected as intact ions by a mass analyser. Electrospray Ionisation can be achieved at several different flow rates ranging from several nL/min to several mL/min. The ion counts observed in a mass spectrometer during Electrospray Ionisation are not, to a first approximation, flow rate dependent and as such large sensitivity gains for the same signal to noise ratios can be achieved at lower flow rates due to much lower sample consumption.

The coupling of liquid chromatography and Electrospray mass spectrometry (LCMS) and tandem mass spectrometry (LCMS/MS) is a powerful technique that is widely used in many laboratories.

Mass spectrometers commonly comprise a sampling cone together with a cone-gas cone which forms the interface between the mass spectrometer and an ion source such as an Electrospray Ionisation ion source. A cone gas or curtain gas may be provided to the annulus

between the inner sampling cone and the outer cone-gas cone. Ions which pass through the sampling cone are then transmitted through a first vacuum chamber and are transmitted onwardly through an extraction cone into a second vacuum chamber. Conventionally, the sampling cone, cone-gas cone and extraction cone are made from stainless steel. Stainless steel is considered to be relatively inert and non-reactive. However, conventional sampling cones, cone-gas cones and extraction cones need regular cleaning in order to maintain high performance.

Conventional sampling cones, cone-gas cones and extraction cones can suffer from increased surface contamination following regular analysis of complex matrix extracts such as urine, saliva, plasma, whole blood, waters and soils. In addition complex buffered eluent systems such as ammonium acetate, ammonium formate, sodium phosphate, sodium borate and sodium formate can also cause contamination. Other potential additives which can increase surface activity and/or contamination include formic acid, trifluoroacetic acid and ammonia.

It is desired to provide an improved sampling cone, cone-gas cone and extraction cone for a mass spectrometer. In particular, it is desired to provide a more robust sampling cone, cone-gas cone and extraction cone which is less reactive than stainless steel and which requires less intensive cleaning than conventional sampling cones, cone-gas cones and extraction cones.

SUMMARY OF THE INVENTION

According to an aspect of the present invention there is provided a mass spectrometer comprising a sampling cone and/or a cone-gas cone formed from titanium which has been subjected to ion implantation.

The sampling cone and/or the cone-gas cone preferably forms an interface between an atmospheric pressure ion source and a first vacuum chamber of the mass spectrometer.

The sampling cone preferably comprises a first or inner conical or frusto-conical body defining a first orifice or circular aperture through which ions pass in use.

According to an embodiment: (i) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an outer surface of the first or inner conical or frusto-conical body has been subjected to ion implantation; and/or (ii) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an inner surface of the first or inner conical or frusto-conical body has been subjected to ion implantation.

The cone-gas cone preferably comprises a second or outer conical or frusto-conical body defining a second orifice or annular aperture through which a cone gas emerges, in use, and wherein the second orifice or annular aperture substantially circumscribes at least part or substantially the whole of the first orifice or circular aperture.

According to an embodiment: (i) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an outer surface of the second or outer conical or frusto-conical body has been subjected to ion

implantation; and/or (ii) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an inner surface of the second or outer conical or frusto-conical body has been subjected to ion implantation.

According to another aspect of the present invention there is provided a mass spectrometer comprising an extraction cone formed from titanium which has been subjected to ion implantation.

The extraction cone preferably forms an interface between a first or further vacuum chamber of the mass spectrometer and a second or further vacuum chamber of the mass spectrometer.

The extraction cone preferably comprises a first or inner conical or frusto-conical body defining a first orifice or circular aperture through which ions pass in use.

According to an embodiment: (i) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an outer surface of the first or inner conical or frusto-conical body has been subjected to ion implantation; and/or (ii) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an inner surface of the first or inner conical or frusto-conical body has been subjected to ion implantation.

The extraction cone preferably further comprises a second or outer conical or frusto-conical body defining a second orifice or annular aperture, wherein the second orifice or annular aperture substantially circumscribes at least part or substantially the whole of the first orifice or circular aperture.

According to an embodiment: (i) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an outer surface of the second or outer conical or frusto-conical body has been subjected to ion implantation; and/or (ii) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an inner surface of the second or outer conical or frusto-conical body has been subjected to ion implantation.

The sampling cone and/or the cone-gas cone and/or the extraction cone preferably comprise titanium which has been subjected to ion implantation with ions selected from the group consisting of: (i) nitrogen; (ii) carbon; (iii) boron; (iv) oxygen; (v) argon; (vi) calcium; (vii) phosphorous; (viii) carbon-oxygen; (ix) neon; (x) sodium; (xi) chromium; (xii) vanadium; and (xiii) fluorine.

The sampling cone and/or the cone-gas cone and/or the extraction cone is preferably subjected to an ion implantation dose selected from the group consisting of: (i) $< 10^{13}$ ions/cm²; (ii) 10^{13} - 10^{14} ions/cm²; (iii) 10^{14} - 10^{15} ions/cm²; (iv) 10^{15} - 10^{16} ions/cm²; (v) 10^{16} - 10^{17} ions/cm²; (vi) 10^{17} - 10^{18} ions/cm²; and (vii) $> 10^{18}$ ions/cm².

The surface of the sampling cone and/or the cone-gas cone and/or the extraction cone which has been subjected to ion implantation preferably has either:

(a) a resistivity selected from the group consisting of: (i) $< 10^{-3}$ Ω -m; (ii) $< 10^{-4}$ Ω -m; (iii) $< 10^{-5}$ Ω -m; (iv) $< 10^{-6}$ Ω -m; (v) $< 10^{-7}$ Ω -m; (vi) 10^{-3} - 10^{-4} Ω -m; (vii) 10^{-4} - 10^{-5} Ω -m; (viii) 10^{-5} - 10^{-6} Ω -m; and (ix) 10^{-6} - 10^{-7} Ω -m; and/or

(b) a Vickers hardness number or Vickers Pyramid Number (HV) selected from the group consisting of: (i) > 1000; (ii) 1000-1100; (iii) 1100-1200; (iv) 1200-1300; (v) 1300-1400; (vi) 1400-1500; (vii) 1500-1600; (viii) 1600-1700; (ix) 1700-1800; (x) 1800-1900; (xi) 1900-2000; (xii) 2000-2100; (xiii) 2100-2200; (xiv) 2200-2300; (xv) 2300-2400; (xvi) 2400-2500; (xvii) 2500-2600; (xviii) 2600-2700; (xix) 2700-2800; (xx) 2800-2900; (xxi) 2900-3000; (xxii) 3000-3100; (xxiii) 3100-3200; (xxiv) 3200-3300; (xv) 3300-3400; (xvi) 3400-3500; and (xvii) > 3500, wherein the Vickers hardness number or Vickers Pyramid Number is determined at a load of 30, 40, 50, 60 or 70 kg; and/or

(c) a Vickers microhardness selected from the group consisting of: (i) > 1000 kg/mm; (ii) 1000-1100 kg/mm; (iii) 1100-1200 kg/mm; (iv) 1200-1300 kg/mm; (v) 1300-1400 kg/mm; (vi) 1400-1500 kg/mm; (vii) 1500-1600 kg/mm; (viii) 1600-1700 kg/mm; (ix) 1700-1800 kg/mm; (x) 1800-1900 kg/mm; (xi) 1900-2000 kg/mm; (xii) 2000-2100 kg/mm; (xiii) 2100-2200 kg/mm; (xiv) 2200-2300 kg/mm; (xv) 2300-2400 kg/mm; (xvi) 2400-2500 kg/mm; (xvii) 2500-2600 kg/mm; (xviii) 2600-2700 kg/mm; (xix) 2700-2800 kg/mm; (xx) 2800-2900 kg/mm; (xxi) 2900-3000 kg/mm; (xxii) 3000-3100 kg/mm; (xxiii) 3100-3200 kg/mm; (xxiv) 3200-3300 kg/mm; (xv) 3300-3400 kg/mm; (xvi) 3400-3500 kg/mm; and (xvii) > 3500 kg/mm, and/or

(d) a thickness selected from the group consisting of: (i) < 1 μm ; (ii) 1-2 μm ; (iii) 2-3 μm ; (iv) 3-4 μm ; (v) 4-5 μm ; (vi) 5-6 μm ; (vii) 6-7 μm ; (viii) 7-8 μm ; (ix) 8-9 μm ; (x) 9-10 μm ; (xi) > 10 μm ; and/or

(e) a density selected from the group consisting of: (i) < 3.0 g cm⁻³; (ii) 3.0-3.5 g cm⁻³; (iii) 3.5-4.0 g cm⁻³; (iv) 4.0-4.5 g cm⁻³; (v) 4.5-5.0 g cm⁻³; (vi) 5.0-5.5 g cm⁻³; (vii) 5.5-6.0 g cm⁻³; (viii) 6.0-6.5 g cm⁻³; (ix) 6.5-7.0 g cm⁻³; (x) 7.0-7.5 g cm⁻³; (xi) 7.5-8.0 g cm⁻³; (xii) 8.0-8.5 g cm⁻³; (xiii) 8.5-9.0 g cm⁻³; (xiv) 9.0-9.5 g cm⁻³; (xv) 9.5-10.0 g cm⁻³; (xvi) 10.0-10.5 g cm⁻³; (xvii) 10.5-11.0 g cm⁻³; (xviii) 11.0-11.5 g cm⁻³; (xix) 11.5-12.0 g cm⁻³; (xx) 12.0-12.5 g cm⁻³; (xxi) 12.5-13.0 g cm⁻³; (xxii) 13.0-13.5 g cm⁻³; (xxiii) 13.5-14.0 g cm⁻³; (xxiv) 14.0-14.5 g cm⁻³; (xxv) 14.5-15.0 g cm⁻³; (xxvi) 15.0-15.5 g cm⁻³; (xxvii) 15.5-16.0 g cm⁻³; (xxviii) 16.0-16.5 g cm⁻³; (xxix) 16.5-17.0 g cm⁻³; (xxx) 17.0-17.5 g cm⁻³; (xxxi) 17.5-18.0 g cm⁻³; (xxxii) 18.0-18.5 g cm⁻³; (xxxiii) 18.5-19.0 g cm⁻³; (xxxiv) 19.0-19.5 g cm⁻³; (xxxv) 19.5-20.0 g cm⁻³; and (xxxvi) > 20.0 g cm⁻³; and/or

(f) a coefficient of friction selected from the group consisting of: (i) < 0.01; (ii) 0.01-0.02; (iii) 0.02-0.03; (iv) 0.03-0.04; (v) 0.04-0.05; (vi) 0.05-0.06; (vii) 0.06-0.07; (viii) 0.07-0.08; (ix) 0.08-0.09; (x) 0.09-0.10; and (xi) > 0.1.

According to an aspect of the present invention there is provided a method of mass spectrometry comprising:

passing ions through a sampling cone and/or a cone-gas cone of a mass spectrometer, wherein the sampling cone and/or the cone-gas cone is formed from titanium which has been subjected to ion implantation.

According to an aspect of the present invention there is provided a method of mass spectrometry comprising:

passing ions through an extraction cone of a mass spectrometer, wherein the extraction cone is formed from titanium which has been subjected to ion implantation.

According to an aspect of the present invention there is provided a method of making a sampling cone and/or a cone-gas cone for a mass spectrometer comprising:
forming a sampling cone and/or a cone-gas cone of a mass spectrometer from titanium; and

subjecting the sampling cone and/or the cone-gas cone to ion implantation.

According to an aspect of the present invention there is provided a method of making an extraction cone for a mass spectrometer comprising:

forming an extraction cone of a mass spectrometer from titanium; and

subjecting the extraction cone to ion implantation.

The method preferably further comprises subjecting the sampling cone and/or the cone-gas cone and/or the extraction cone to an ion implantation dose selected from the group consisting of: (i) $< 10^{13}$ ions/cm²; (ii) 10^{13} - 10^{14} ions/cm²; (iii) 10^{14} - 10^{15} ions/cm²; (iv) 10^{15} - 10^{16} ions/cm²; (v) 10^{16} - 10^{17} ions/cm²; (vi) 10^{17} - 10^{18} ions/cm²; and (vii) $> 10^{18}$ ions/cm².

The method preferably further comprises accelerating ions to be implanted into the sampling cone and/or the cone-gas cone and/or the extraction cone to a kinetic energy selected from the group consisting of: (i) < 10 keV; (ii) 10-50 keV; (iii) 50-100 keV; (iv) 100-150 keV; (v) 150-200 keV; (vi) 200-250 keV; (vii) 250-300 keV; (viii) 300-350 keV; (ix) 350-400 keV; (x) 400-450 keV; (xi) 450-500 keV; and (xii) > 500 keV.

According to another aspect of the present invention there is provided a mass spectrometer comprising a sampling cone and/or a cone-gas cone formed from a transition metal which has been subjected to ion implantation.

According to another aspect of the present invention there is provided a mass spectrometer comprising an extraction cone formed from a transition metal which has been subjected to ion implantation.

The transition metal is preferably selected from the group consisting of: (i) scandium; (ii) titanium; (iii) vanadium; (iv) chromium; (v) manganese; (vi) iron; (vii) cobalt; (viii) nickel; (ix) copper; (x) zinc; (xi) yttrium; (xii) zirconium; (xiii) niobium; (xiv) molybdenum; (xv) technetium; (xvi) ruthenium; (xvii) rhodium; (xviii) palladium; (xix) silver; (xx) cadmium; (xxi) lanthanum; (xxii) hafnium; (xxiii) tantalum; (xxiv) tungsten; (xxv) rhenium; (xxvi) osmium; (xxvii) iridium; (xxviii) platinum; and (xxix) gold.

According to another aspect of the present invention there is provided a method of mass spectrometry comprising:

passing ions through a sampling cone and/or a cone-gas cone of a mass spectrometer, wherein the sampling cone and/or the cone-gas cone is formed from a transition metal which has been subjected to ion implantation.

According to another aspect of the present invention there is provided a method of mass spectrometry comprising:

passing ions through an extraction cone of a mass spectrometer, wherein the extraction cone is formed from a transition metal which has been subjected to ion implantation.

According to another aspect of the present invention there is provided a method of making a sampling cone and/or a cone-gas cone for a mass spectrometer comprising:

forming a sampling cone and/or a cone-gas cone of a mass spectrometer from a transition metal; and

subjecting the sampling cone and/or the cone-gas cone to ion implantation.

According to another aspect of the present invention there is provided a method of making an extraction cone for a mass spectrometer comprising:

forming an extraction cone of a mass spectrometer from a transition metal; and
subjecting the extraction cone to ion implantation.

The transition metal is preferably selected from the group consisting of: (i) scandium; (ii) titanium; (iii) vanadium; (iv) chromium; (v) manganese; (vi) iron; (vii) cobalt; (viii) nickel; (ix) copper; (x) zinc; (xi) yttrium; (xii) zirconium; (xiii) niobium; (xiv) molybdenum; (xv) technetium; (xvi) ruthenium; (xvii) rhodium; (xviii) palladium; (xix) silver; (xx) cadmium; (xxi) lanthanum; (xxii) hafnium; (xxiii) tantalum; (xxiv) tungsten; (xxv) rhenium; (xxvi) osmium; (xxvii) iridium; (xxviii) platinum; and (xxix) gold.

According to a preferred embodiment of the present invention a sampling cone and/or cone-gas cone and/or extraction cone of a mass spectrometer is preferably used to passivate the surfaces associated with an Atmospheric Pressure Ionisation ("API") ion source region.

The preferred embodiment preferably improves the robustness of the sampling cone and/or cone-gas cone and/or extraction cone by reducing surface reactions with ions and/or molecules as ions flow from an atmospheric pressure region to the vacuum chambers of a mass spectrometer. The improved sampling cone and/or cone-gas cone and/or extraction cone preferably has a greater durability, greater resistance to scratching, provides a robust inert surface that reduces the decomposition of contaminants, solvents, and unwanted compounds and is readily cleaned (chemically) without damage or degradation to the inert surface character.

The preferred sampling cone and/or cone-gas cone and/or extraction cone preferably exhibits improved performance characteristics when compared with conventional stainless steel sampling cones, cone-gas cones and extraction cones.

The preferred embodiment preferably advantageously reduces adsorption of material on contact with the surface since if material is deposited onto the surface of the sampling cone, cone-gas cone or extraction cone then it may result in a reduction in signal transmission and may cause an increase in the noise.

Comparative data is presented which shows the differences in intensity and peak area which are observed when using a newly cleaned stainless steel sampling cone/skimmer cone, an aged (or used) stainless steel sampling cone/skimmer cone and an aged (or used) sampling cone/skimmer cone which has been adapted to have a surface coating.

The adapted sampling cone/skimmer cone maintains its signal transmission while slightly increasing its noise levels (after an extended time period of intermittent use) relative to the cleaned stainless steel sampling cone/skimmer cone. The aged or used stainless steel sampling cone/skimmer cone drops by a greater amount (after an extended time period of intermittent use) and the noise level also increases more significantly.

A sampling cone, skimmer cone and cone-gas cone according to the preferred embodiment only require an organic/acid wash whereas a conventional stainless steel sampling cone, cone-gas cone and extraction cone may require abrasive cleaning.

BRIEF DESCRIPTION OF THE DRAWINGS

Various embodiments of the present invention together with other arrangements given for illustrative purposes only will now be described, by way of example only, and with reference to the accompanying drawings in which:

Fig. 1 shows the initial vacuum stages of a mass spectrometer comprising a sampling cone and a cone-gas cone at the entrance to a first vacuum chamber;

Fig. 2 shows the signal intensity factor difference obtained by comparing the intensity of ion signals relating to six compounds obtained using cleaned stainless steel sampling and extraction cones and sampling and extraction cones coated with titanium carbide against an aged stainless steel cone set which was assigned a unity factor;

Fig. 3 shows the signal intensity factor difference for the data shown in Fig. 2;

Fig. 4 shows the peak area factor difference for each of the six compounds with the aged stainless steel cone set being assigned a unity factor; and

Fig. 5 shows a table of the signal to noise factor difference for the six compounds with the aged stainless steel cone set being assigned a unity factor.

DETAILED DESCRIPTION OF THE INVENTION

A preferred embodiment of the present invention will now be described in more detail with reference to Fig. 1. Fig. 1 shows the initial vacuum stages of a mass spectrometer and an Electrospray capillary 1 which forms part of an Electrospray ion source which emits, in use, an ion plume 2. Ions and neutral gas molecules are drawn through a sampling cone 3 into the first vacuum chamber 6 of a mass spectrometer. A cone-gas cone 4 surrounds the sampling cone 3 and a cone gas or curtain gas 5 is preferably supplied to the cone-gas cone 4. Neutral gas molecules continue through the first vacuum chamber 6 which is preferably evacuated by a rough pump 7 such as a rotary pump or scroll pump. The rough pump, rotary pump or scroll pump serves to provide the backing pressure to a second vacuum chamber 9 which is preferably pumped by a fine pump such as a turbomolecular pump or diffusion pump. The term "backing pressure" refers to the pressure in the first vacuum chamber 6. Ions are preferably diverted in an orthogonal direction by an electric field or extraction lens into the second vacuum chamber 9. Ions preferably pass through an extraction cone 8 as they pass from the first vacuum chamber 6 into the second vacuum chamber 9.

An ion guide 11 is preferably provided in the second vacuum chamber 9 which preferably guides ions through the second vacuum chamber 9 and which preferably onwardly transmits ions to subsequent lower pressure vacuum chambers. The second vacuum chamber 9 is preferably pumped by a turbomolecular pump or a diffusion pump.

10. Ions exiting the second vacuum chamber 9 preferably pass through a differential pumping aperture 12 into subsequent stages of the mass spectrometer.

According to an embodiment the backing pressure or the pressure in the first vacuum chamber 6 may be maintained, in use, in the range 5 to 9 mbar. The cone-gas cone 4 and the sampling cone 3 of the mass spectrometer may be maintained at a potential of 175 V.

The cone-gas cone 4 and the sampling cone 3 preferably comprise two co-axial cones which are preferably in direct contact with each other and which are preferably maintained at the same potential.

In order to test the performance of a modified sampling and extraction cones, a six component mixture of different compounds namely sulphadimethoxine, verapamil, caffeine, acetaminophen, chloramphenicol and 17α hydroxyprogesterone was analysed. A liquid chromatography column (for chromatographic separation) with a tandem quadrupole mass spectrometer was used to produce the resulting data.

The six compound mixture was analysed by positive and negative ion Electrospray ionisation (ESI+/ ESI-) using a liquid chromatography column (for chromatographic separation) with a tandem quadrupole mass spectrometer.

Data was acquired using: (i) a conventional stainless steel (SS) sampling and extraction cone; (ii) a sampling and extraction cone coated with titanium carbide (TiC); and (iii) a cleaned stainless steel (SS) sampling and extraction cone.

The stainless steel and titanium carbide sampling and extraction cones were used for an extended time period to investigate their robustness characteristics.

Figs. 2 and 3 show a comparison of the average intensities observed for each of the six compounds when using a used or aged stainless steel sampling and extraction cone set up, a used or aged sampling and extraction cone coated with titanium carbide (TiC), and a recently cleaned stainless steel sampling and extraction cone.

Fig. 4 shows a comparison of the average areas observed for each of the six compounds when using a used or aged stainless steel sampling and extraction cone set up, a used or aged sampling and extraction cone set up coated with titanium carbide (TiC) and a recently cleaned stainless steel sampling and extraction cone.

From the above data it is apparent that as the stainless steel system ages, the response (sensitivity) and in addition the peak area of the analytes drops between 30-90% (depending upon the compound) with time. By contrast, the coated system maintains its sensitivity and hence the modified sample and extraction cone exhibits improved robustness.

The signal to noise response was also investigated and the data is shown in Fig. 5.

Fig. 5 shows the Signal to Noise factor of an aged or used stainless steel sample and extraction cone, an aged or used TiC sampling and extraction cone and a cleaned stainless steel sampling and extraction cone.

The results show that the S:N response for the aged stainless steel system is lower than that obtained from both the aged TiC sampling and extraction cone and the cleaned stainless steel sampling and extraction cone set up. This is due to the increased signal

intensity obtained from the TiC and cleaned stainless steel sampling and extraction cones and also the lower noise produced from these systems compared to using an aged stainless steel sampling and extraction cone.

In summary, an improvement in robustness was observed using a modified extraction and sampling cone coated with titanium carbide. The coated surface maintains a higher signal intensity and lower noise response compared to the aged stainless steel environment for all compounds investigated. Cleaning the stainless steel surface regenerated the sample response and lowered the noise response resulting in equivalent results to the aged TiC.

The result of cleaning the TiC surface conferred no further improvement over that of the cleaned stainless steel system.

Although the experimental results described above were obtained using components coated with titanium carbide, initial investigations suggest that similar results occur when the components are formed from titanium and other transition metals which have been subjected to ion implantation according to the preferred embodiment of the present invention.

Although the present invention has been described with reference to the preferred embodiments, it will be understood by those skilled in the art that various changes in form and detail may be made without departing from the scope of the invention as set forth in the accompanying claims.

Claims

1. A mass spectrometer comprising a sampling cone and/or a cone-gas cone formed from titanium which has been subjected to ion implantation.
2. A mass spectrometer as claimed in claim 1, wherein said sampling cone and/or said cone-gas cone forms an interface between an atmospheric pressure ion source and a first vacuum chamber of said mass spectrometer.
3. A mass spectrometer as claimed in claim 1 or 2, wherein said sampling cone comprises a first or inner conical or frusto-conical body defining a first orifice or circular aperture through which ions pass in use.
4. A mass spectrometer as claimed in claim 3, wherein:
 - (i) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an outer surface of said first or inner conical or frusto-conical body has been subjected to ion implantation; and/or
 - (ii) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an inner surface of said first or inner conical or frusto-conical body has been subjected to ion implantation.
5. A mass spectrometer as claimed in claim 3 or 4, wherein said cone-gas cone comprises a second or outer conical or frusto-conical body defining a second orifice or annular aperture through which a cone gas emerges, in use, and wherein said second orifice or annular aperture substantially circumscribes at least part or substantially the whole of said first orifice or circular aperture.
6. A mass spectrometer as claimed in claim 5, wherein:
 - (i) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an outer surface of said second or outer conical or frusto-conical body has been subjected to ion implantation; and/or
 - (ii) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an inner surface of said second or outer conical or frusto-conical body has been subjected to ion implantation.
7. A mass spectrometer comprising an extraction cone formed from titanium which has been subjected to ion implantation.

8. A mass spectrometer as claimed in claim 7, wherein said extraction cone forms an interface between a first or further vacuum chamber of said mass spectrometer and a second or further vacuum chamber of said mass spectrometer.
9. A mass spectrometer as claimed in claim 7 or 8, wherein said extraction cone comprises a first or inner conical or frusto-conical body defining a first orifice or circular aperture through which ions pass in use.
10. A mass spectrometer as claimed in claim 9, wherein:
(i) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an outer surface of said first or inner conical or frusto-conical body has been subjected to ion implantation; and/or
(ii) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an inner surface of said first or inner conical or frusto-conical body has been subjected to ion implantation.
11. A mass spectrometer as claimed in claim 9 or 10, wherein said extraction cone further comprises a second or outer conical or frusto-conical body defining a second orifice or annular aperture, wherein said second orifice or annular aperture substantially circumscribes at least part or substantially the whole of said first orifice or circular aperture.
12. A mass spectrometer as claimed in claim 11, wherein:
(i) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an outer surface of said second or outer conical or frusto-conical body has been subjected to ion implantation; and/or
(ii) at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 100% of an inner surface of said second or outer conical or frusto-conical body has been subjected to ion implantation.
13. A mass spectrometer as claimed in any preceding claim, wherein said sampling cone and/or said cone-gas cone and/or said extraction cone comprise titanium which has been subjected to ion implantation with ions selected from the group consisting of: (i) nitrogen; (ii) carbon; (iii) boron; (iv) oxygen; (v) argon; (vi) calcium; (vii) phosphorous; (viii) carbon-oxygen; (ix) neon; (x) sodium; (xi) chromium; (xii) vanadium; and (xii) fluorine.
14. A mass spectrometer as claimed in any preceding claim, wherein said sampling cone and/or said cone-gas cone and/or said extraction cone is subjected to an ion implantation dose selected from the group consisting of: (i) $< 10^{13}$ ions/cm²; (ii) 10^{13} - 10^{14} ions/cm²; (iii) 10^{14} - 10^{15} ions/cm²; (iv) 10^{15} - 10^{16} ions/cm²; (v) 10^{16} - 10^{17} ions/cm²; (vi) 10^{17} - 10^{18} ions/cm²; and (vii) $> 10^{18}$ ions/cm².

15. A mass spectrometer as claimed in any preceding claim, wherein the surface of said sampling cone and/or said cone-gas cone and/or said extraction cone which has been subjected to ion implantation has either:

(a) a resistivity selected from the group consisting of: (i) $< 10^{-3} \Omega\text{-m}$; (ii) $< 10^{-4} \Omega\text{-m}$; (iii) $< 10^{-5} \Omega\text{-m}$; (iv) $< 10^{-6} \Omega\text{-m}$; (v) $< 10^{-7} \Omega\text{-m}$; (vi) $10^{-3}\text{-}10^{-4} \Omega\text{-m}$; (vii) $10^{-4}\text{-}10^{-5} \Omega\text{-m}$; (viii) $10^{-5}\text{-}10^{-6} \Omega\text{-m}$; and (ix) $10^{-6}\text{-}10^{-7} \Omega\text{-m}$; and/or

(b) a Vickers hardness number or Vickers Pyramid Number (HV) selected from the group consisting of: (i) > 1000 ; (ii) 1000-1100; (iii) 1100-1200; (iv) 1200-1300; (v) 1300-1400; (vi) 1400-1500; (vii) 1500-1600; (viii) 1600-1700; (ix) 1700-1800; (x) 1800-1900; (xi) 1900-2000; (xii) 2000-2100; (xiii) 2100-2200; (xiv) 2200-2300; (xv) 2300-2400; (xvi) 2400-2500; (xvii) 2500-2600; (xviii) 2600-2700; (xix) 2700-2800; (xx) 2800-2900; (xxi) 2900-3000; (xxii) 3000-3100; (xxiii) 3100-3200; (xxiv) 3200-3300; (xv) 3300-3400; (xvi) 3400-3500; and (xvii) > 3500 , wherein said Vickers hardness number or Vickers Pyramid Number is determined at a load of 30, 40, 50, 60 or 70 kg; and/or

(c) a Vickers microhardness selected from the group consisting of: (i) > 1000 kg/mm; (ii) 1000-1100 kg/mm; (iii) 1100-1200 kg/mm; (iv) 1200-1300 kg/mm; (v) 1300-1400 kg/mm; (vi) 1400-1500 kg/mm; (vii) 1500-1600 kg/mm; (viii) 1600-1700 kg/mm; (ix) 1700-1800 kg/mm; (x) 1800-1900 kg/mm; (xi) 1900-2000 kg/mm; (xii) 2000-2100 kg/mm; (xiii) 2100-2200 kg/mm; (xiv) 2200-2300 kg/mm; (xv) 2300-2400 kg/mm; (xvi) 2400-2500 kg/mm; (xvii) 2500-2600 kg/mm; (xviii) 2600-2700 kg/mm; (xix) 2700-2800 kg/mm; (xx) 2800-2900 kg/mm; (xxi) 2900-3000 kg/mm; (xxii) 3000-3100 kg/mm; (xxiii) 3100-3200 kg/mm; (xxiv) 3200-3300 kg/mm; (xv) 3300-3400 kg/mm; (xvi) 3400-3500 kg/mm; and (xvii) > 3500 kg/mm; and/or

(d) a thickness selected from the group consisting of: (i) $< 1 \mu\text{m}$; (ii) 1-2 μm ; (iii) 2-3 μm ; (iv) 3-4 μm ; (v) 4-5 μm ; (vi) 5-6 μm ; (vii) 6-7 μm ; (viii) 7-8 μm ; (ix) 8-9 μm ; (x) 9-10 μm ; (xi) $> 10 \mu\text{m}$; and/or

(e) a density selected from the group consisting of: (i) $< 3.0 \text{ g cm}^{-3}$; (ii) 3.0-3.5 g cm^{-3} ; (iii) 3.5-4.0 g cm^{-3} ; (iv) 4.0-4.5 g cm^{-3} ; (v) 4.5-5.0 g cm^{-3} ; (vi) 5.0-5.5 g cm^{-3} ; (vii) 5.5-6.0 g cm^{-3} ; (viii) 6.0-6.5 g cm^{-3} ; (ix) 6.5-7.0 g cm^{-3} ; (x) 7.0-7.5 g cm^{-3} ; (xi) 7.5-8.0 g cm^{-3} ; (xii) 8.0-8.5 g cm^{-3} ; (xiii) 8.5-9.0 g cm^{-3} ; (xiv) 9.0-9.5 g cm^{-3} ; (xv) 9.5-10.0 g cm^{-3} ; (xvi) 10.0-10.5 g cm^{-3} ; (xvii) 10.5-11.0 g cm^{-3} ; (xviii) 11.0-11.5 g cm^{-3} ; (xix) 11.5-12.0 g cm^{-3} ; (xx) 12.0-12.5 g cm^{-3} ; (xxi) 12.5-13.0 g cm^{-3} ; (xxii) 13.0-13.5 g cm^{-3} ; (xxiii) 13.5-14.0 g cm^{-3} ; (xxiv) 14.0-14.5 g cm^{-3} ; (xxv) 14.5-15.0 g cm^{-3} ; (xxvi) 15.0-15.5 g cm^{-3} ; (xxvii) 15.5-16.0 g cm^{-3} ; (xxviii) 16.0-16.5 g cm^{-3} ; (xxix) 16.5-17.0 g cm^{-3} ; (xxx) 17.0-17.5 g cm^{-3} ; (xxxi) 17.5-18.0 g cm^{-3} ; (xxxii) 18.0-18.5 g cm^{-3} ; (xxxiii) 18.5-19.0 g cm^{-3} ; (xxxiv) 19.0-19.5 g cm^{-3} ; (xxxv) 19.5-20.0 g cm^{-3} ; and (xxxvi) $> 20.0 \text{ g cm}^{-3}$; and/or

(f) a coefficient of friction selected from the group consisting of: (i) < 0.01 ; (ii) 0.01-0.02; (iii) 0.02-0.03; (iv) 0.03-0.04; (v) 0.04-0.05; (vi) 0.05-0.06; (vii) 0.06-0.07; (viii) 0.07-0.08; (ix) 0.08-0.09; (x) 0.09-0.10; and (xi) > 0.1 .

16. A method of mass spectrometry comprising:

passing ions through a sampling cone and/or a cone-gas cone of a mass spectrometer, wherein said sampling cone and/or said cone-gas cone is formed from titanium which has been subjected to ion implantation.

17. A method of mass spectrometry comprising:

passing ions through an extraction cone of a mass spectrometer, wherein said extraction cone is formed from titanium which has been subjected to ion implantation.

18. A method of making a sampling cone and/or a cone-gas cone for a mass spectrometer comprising:

forming a sampling cone and/or a cone-gas cone of a mass spectrometer from titanium; and

subjecting said sampling cone and/or said cone-gas cone to ion implantation.

19. A method of making an extraction cone for a mass spectrometer comprising:

forming an extraction cone of a mass spectrometer from titanium; and

subjecting said extraction cone to ion implantation.

20. A method as claimed in claim 18 or 19, further comprising subjecting said sampling cone and/or said cone-gas cone and/or said extraction cone to an ion implantation dose selected from the group consisting of: (i) $< 10^{13}$ ions/cm²; (ii) 10^{13} - 10^{14} ions/cm²; (iii) 10^{14} - 10^{15} ions/cm²; (iv) 10^{15} - 10^{16} ions/cm²; (v) 10^{16} - 10^{17} ions/cm²; (vi) 10^{17} - 10^{18} ions/cm²; and (vii) $> 10^{18}$ ions/cm².

21. A method as claimed in claim 18, 19 or 20, further comprising accelerating ions to be implanted into said sampling cone and/or said cone-gas cone and/or said extraction cone to a kinetic energy selected from the group consisting of: (i) < 10 keV; (ii) 10-50 keV; (iii) 50-100 keV; (iv) 100-150 keV; (v) 150-200 keV; (vi) 200-250 keV; (vii) 250-300 keV; (viii) 300-350 keV; (ix) 350-400 keV; (x) 400-450 keV; (xi) 450-500 keV; and (xii) > 500 keV.

22. A mass spectrometer comprising a sampling cone and/or a cone-gas cone formed from a transition metal which has been subjected to ion implantation.

23. A mass spectrometer comprising an extraction cone formed from a transition metal which has been subjected to ion implantation.

24. A mass spectrometer as claimed in claim 22 or 23, wherein said transition metal is selected from the group consisting of: (i) scandium; (ii) titanium; (iii) vanadium; (iv) chromium; (v) manganese; (vi) iron; (vii) cobalt; (viii) nickel; (ix) copper; (x) zinc; (xi) yttrium; (xii) zirconium; (xiii) niobium; (xiv) molybdenum; (xv) technetium; (xvi) ruthenium; (xvii) rhodium; (xviii) palladium; (xix) silver; (xx) cadmium; (xxi) lanthanum; (xxii) hafnium;

(xxiii) tantalum; (xxiv) tungsten; (xxv) rhenium; (xxvi) osmium; (xxvii) iridium; (xxviii) platinum; and (xxix) gold.

25. A method of mass spectrometry comprising:

passing ions through a sampling cone and/or a cone-gas cone of a mass spectrometer, wherein said sampling cone and/or said cone-gas cone is formed from a transition metal which has been subjected to ion implantation.

26. A method of mass spectrometry comprising:

passing ions through an extraction cone of a mass spectrometer, wherein said extraction cone is formed from a transition metal which has been subjected to ion implantation.

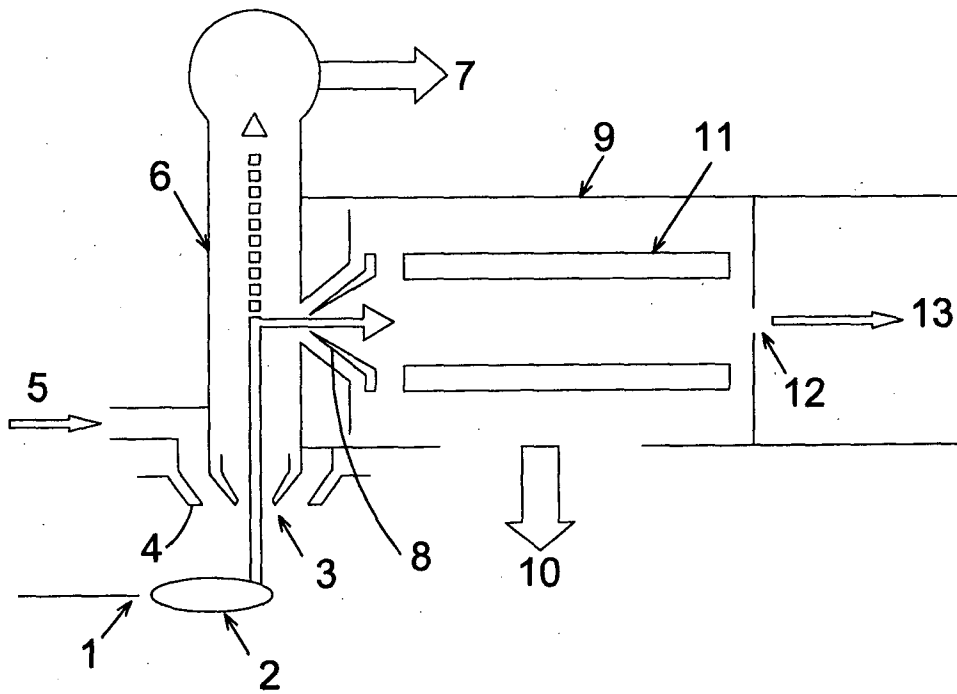
27. A method of making a sampling cone and/or a cone-gas cone for a mass spectrometer comprising:

forming a sampling cone and/or a cone-gas cone of a mass spectrometer from a transition metal; and
subjecting said sampling cone and/or said cone-gas cone to ion implantation.

28. A method of making an extraction cone for a mass spectrometer comprising:

forming an extraction cone of a mass spectrometer from a transition metal; and
subjecting said extraction cone to ion implantation.

29. A method as claimed in any of claims 25-28, wherein said transition metal is selected from the group consisting of: (i) scandium; (ii) titanium; (iii) vanadium; (iv) chromium; (v) manganese; (vi) iron; (vii) cobalt; (viii) nickel; (ix) copper; (x) zinc; (xi) yttrium; (xii) zirconium; (xiii) niobium; (xiv) molybdenum; (xv) technetium; (xvi) ruthenium; (xvii) rhodium; (xviii) palladium; (xix) silver; (xx) cadmium; (xxi) lanthanum; (xxii) hafnium; (xxiii) tantalum; (xxiv) tungsten; (xxv) rhenium; (xxvi) osmium; (xxvii) iridium; (xxviii) platinum; and (xxix) gold.



Prior Art

Fig. 1

Intensity	Factor		
Compound	Aged stainless steel	aged TiC	clean stainless steel
Acetaminophen	1	1.29	1.30
Caffeine	1	1.52	1.49
Sulphodimethoxine	1	1.58	1.54
Verapamil	1	1.74	1.54
17a Hydroxyprogesterone	1	1.92	1.98
Chloramphenicol	1	1.85	1.65

Fig. 2

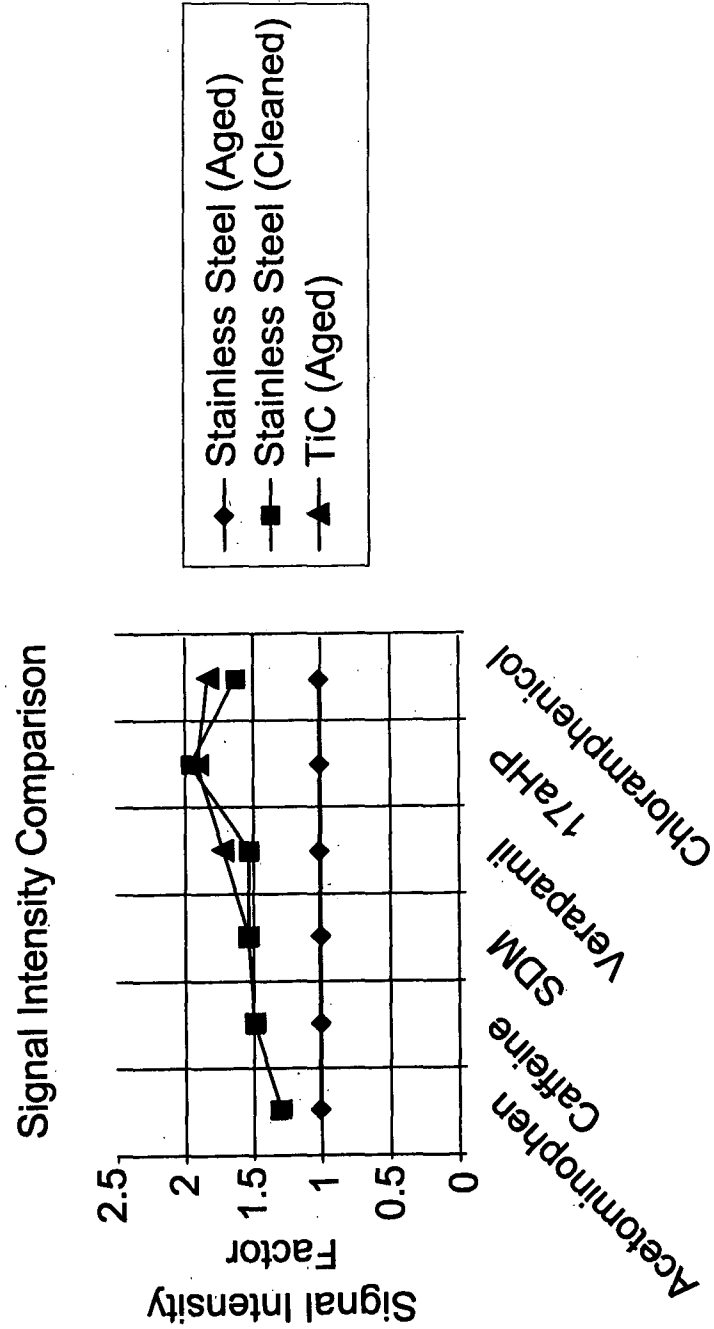


Fig. 3

Area	Factor		
Compound	Aged stainless steel	Aged TiC	clean stainless steel
Acetaminophen	1	1.31	1.32
Caffeine	1	1.53	1.49
Sulphodimethoxine	1	1.53	1.52
Verapamil	1	1.78	1.60
17a Hydroxyprogesterone	1	1.97	1.93
Chloramphenicol	1	1.92	1.67

Fig. 4

Area	Factor					
Compound	SS (Aged)		SS (cleaned)		TiC (Aged)	
	S:N	Noise	S:N	Noise	S:N	Noise
AM	1	1	1.47	0.92	1.36	0.94
Caffeine	1	1	1.92	0.77	1.86	0.82
SDM	1	1	2.93	0.48	1.85	0.84
Verapamil	1	1	2.48	0.57	2.57	0.74
17a HP	1	1	3.06	0.62	2.23	0.79
CMP	1	1	2.74	1.78	1.78	0.96

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000957

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01J49/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/194530 A1 (THAKUR ROHAN [US]) 8 September 2005 (2005-09-08) paragraph [0003] - paragraph [0014] figures 3-5	1-29
Y	SUGIZAKI, Y., YASUNAGA, T., TOMARI, H.: "Improvement of corrosion resistance of titanium by co-implantation" SURFACE AND COATINGS TECHNOLOGY, vol. 83, 1996, pages 167-174, XP002592624 the whole document	1-29

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

20 July 2010

Date of mailing of the international search report

30/07/2010

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2010/000957

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005194530	A1	08-09-2005	NONE