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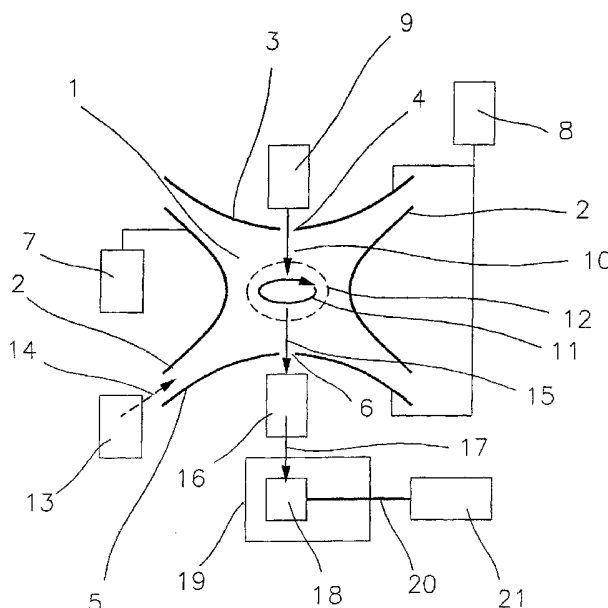
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(54) Title: QUADRUPOLE ION TRAP MASS SPECTROMETER WITH CRYOGENIC PARTICLE DETECTOR



(57) Abstract: This invention relates to a quadrupole ion trap mass spectrometer (1-9) with improved sensitivity for massive molecules (10, 15) by using cryogenic particle detectors (18) as molecule detectors. Cryogenic particle detectors have a mass independent detection efficiency and do not show a decrease of detection efficiency for increasing molecule mass as compared to ionizing detectors which are used in common quadrupole ion trap mass spectrometers.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

# INTERNATIONAL SEARCH REPORT

International Application No  
T/IB2004/001005

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 H01J49/02 H01J49/42				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols) IPC 7 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, INSPEC, COMPENDEX, BIOSIS, WPI Data, PAJ				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Y	US 5 696 376 A (DOROSHENKO VLADIMIR M ET AL) 9 December 1997 (1997-12-09) column 9, line 56 - column 11, line 42; figure 4	1-61		
Y	----- US 4 540 884 A (STAFFORD GEORGE C ET AL) 10 September 1985 (1985-09-10) cited in the application abstract column 3, line 8 - column 7, line 24; figures 1,2 ----- -/--	1		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.				
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° Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <ul style="list-style-type: none"> <li>*A* document defining the general state of the art which is not considered to be of particular relevance</li> <li>*E* earlier document but published on or after the international filing date</li> <li>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</li> <li>*O* document referring to an oral disclosure, use, exhibition or other means</li> <li>*P* document published prior to the international filing date but later than the priority date claimed</li> </ul> </td> <td style="width: 50%; border: none; vertical-align: top;"> <ul style="list-style-type: none"> <li>*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</li> <li>*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</li> <li>*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.</li> <li>*Z* document member of the same patent family</li> </ul> </td> </tr> </table>			<ul style="list-style-type: none"> <li>*A* document defining the general state of the art which is not considered to be of particular relevance</li> <li>*E* earlier document but published on or after the international filing date</li> <li>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</li> <li>*O* document referring to an oral disclosure, use, exhibition or other means</li> <li>*P* document published prior to the international filing date but later than the priority date claimed</li> </ul>	<ul style="list-style-type: none"> <li>*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</li> <li>*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</li> <li>*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.</li> <li>*Z* document member of the same patent family</li> </ul>
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <p style="text-align: center;">Lang, T</p>		

INTERNATIONAL SEARCH REPORT

International Application No  
PCT/IB2004/001005

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHIEN B M ET AL: "THE DESIGN AND PERFORMANCE OF AN ION TRAP STORAGE-REFLECTRON TIME-OF-FLIGHT MASS SPECTROMETER" INTERNATIONAL JOURNAL OF MASS SPECTROMETRY AND ION PROCESSES, ELSEVIER SCIENTIFIC PUBLISHING CO. AMSTERDAM, NL, vol. 131, no. 1/3, 24 February 1994 (1994-02-24), pages 149-179, XP000446268 ISSN: 0168-1176 abstract; figures 1,3-6</p>	1,55
Y	<p>FRANK M ET AL: "Energy-sensitive cryogenic detectors for high-mass biomolecule mass spectrometry." MASS SPECTROMETRY REVIEWS. 1999 MAY-AUG, vol. 18, no. 3-4, May 1999 (1999-05), pages 155-186, XP009035307 ISSN: 0277-7037 the whole document page 161, left-hand column, last line - page 164, left-hand column, line 1; figures 1-6; table 1 page 167, right-hand column, last line - page 180, right-hand column, line 2</p>	1-61
Y	<p>US 5 640 010 A (TWERENBOLD DAMIAN) 17 June 1997 (1997-06-17) cited in the application</p> <p>the whole document column 5, line 21 - column 6, line 22; claims 3-17,26-29,36-39; figures 1,2,1a</p>	1-3,7-9, 34,35, 38,40, 42-44, 47, 50-52, 54-56, 59-61
Y	<p>US 5 994 694 A (LABOV SIMON E ET AL) 30 November 1999 (1999-11-30) cited in the application abstract column 2, line 42 - column 5, line 9 column 7, line 4 - column 9, line 25; figures 1-5</p>	1,2, 4-47,54, 55,59

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## INTERNATIONAL SEARCH REPORT

International Application No

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G.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>HILTON G C ET AL: "Impact energy measurement in time-of-flight mass spectrometry with cryogenic microcalorimeters"            NATURE (UK), NATURE, 12 FEB. 1998, MACMILLAN MAGAZINES, UK, vol. 391, no. 6668, 1998, pages 672-675, XP002293589            ISSN: 0028-0836            cited in the application abstract            page 672, left-hand column, last line -            page 673, left-hand column, line 1            -----</p>	<p>1,2,4,6,            16-33,            51,52,            54,58,59</p>
Y	<p>GONIN YVAN ET AL: "Vers un envol de la masse maximale mesurable des macromolécules? La spectrométrie de masse avec détecteurs cryogéniques 'Towards the maximally measurable mass of macromolecules: Mass spectrometry with cryogenic detectors!'"            BULLETIN DE LA SOCIETE NEUCHATELOISE DES SCIENCES NATURELLES,            vol. 125, no. 1,            31 October 2002 (2002-10-31), pages 5-22, XP009035299            ISSN: 0366-3469            the whole document            page 9, left-hand column, last paragraph -            page 17, right-hand column, last paragraph; figures 4,9,12,13            -----</p>	<p>1,2,            5-15,18,            22,47,            50-52,            54,59-61</p>

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/IB2004/001005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5696376	A	09-12-1997	AU 3129497 A 09-12-1997
			EP 0900452 A1 10-03-1999
			JP 2000511340 T 29-08-2000
			WO 9744814 A1 27-11-1997
US 4540884	A	10-09-1985	AT 43753 T 15-06-1989
			AU 568615 B2 07-01-1988
			AU 2187283 A 05-07-1984
			CA 1207918 A1 15-07-1986
			DE 3380001 D1 06-07-1989
			EP 0113207 A2 11-07-1984
			JP 1321036 C 11-06-1986
			JP 59134546 A 02-08-1984
			JP 60032310 B 27-07-1985
			ZA 8309039 A 25-07-1984
US 5640010	A	17-06-1997	CH 690405 A5 31-08-2000
			AT 185450 T 15-10-1999
			AU 3120995 A 04-03-1996
			CA 2196291 A1 15-02-1996
			DE 69512669 D1 11-11-1999
			DE 69512669 T2 23-11-2000
			DE 774160 T1 16-09-1999
			EP 0774160 A1 21-05-1997
			ES 2141368 T3 16-03-2000
			WO 9604676 A1 15-02-1996
			JP 10505417 T 26-05-1998
			US 5994694