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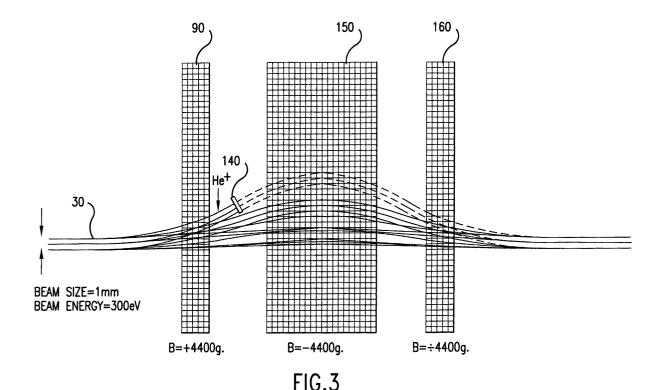
- (71) Applicant: The Perkin-Elmer Corporation Norwalk, Connecticut 06859-0199 (US)
- (72) Inventors:
 - Bahatt, Dar Stamford, CT 06906 (US)

- Welkie, David G. Trumbull, CT 06611 (US)
- (74) Representative: Schumann, Klaus, Dr. et al Grünecker, Kinkeldey, Stockmair & Schwanhäusser Anwaltssozietät Maximilianstrasse 58 80538 München (DE)

(54) Carrier gas separator for mass spectroscopy

(57) A system for separating certain ions from an ion beam in a mass spectrometer. A magnetic or electrostatic field is applied at an angle to the ion beam, causing the ions to disperse according to their mass to charge ratio. The ions are dispersed enough to allow certain

ions to be blocked and removed from the beam using a physical stop. A subsequent plurality of fields is then applied to reform the beam and adjust its direction and dispersion. The system can be used to remove carrier gas ions from an ion beam in a gas chromatography-mass spectroscopy instrument.



Description

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FIELD OF THE INVENTION

[0001] This invention generally relates to a mass spectrometer with an ion source, where the ion source is producing an ion beam containing both carrier ions and analyte ions. This invention specifically comprises a separation system for removing the carrier ions from the ion beam.

BACKGROUND OF THE INVENTION

[0002] In a gas chromatography-mass spectroscopy (GC-MS) instrument, gas chromatography is usually performed first and the resulting gas stream is then introduced into the mass spectrometer. As a result, both the carrier gas used during gas chromatography and the analytes become ionized and are directed as an ion beam into the mass spectrometer detector. While the ionization cross section for the carrier gas is typically more than ten times less than those of the analyte ions of interest, the carrier gas concentration is orders of magnitude greater than the analytes. As a result, the carrier gas ion concentration in the ion beam is many times more intense than the analyte ions.

[0003] One adverse consequence of this is that the electrostatic space charge effects due to the intense carrier gas ion concentration cause the ion beam to diverge. The divergence can be determined by the equation:

$$\frac{Z}{r_o} = \frac{0.75 V^{3/4}}{I^{1/2}}$$
 Equation 1

Where

Z is the distance in which the beam diameter will double r_{o} is the initial radius of the beam I is the beam current V is the beam potential

[0004] The divergent beam may cause signal loss during detection if some of the beam falls outside the detector entrance. Another adverse consequence of the high carrier ion concentration is detector distortion or saturation. If the concentration causes the detector to exceed its linear range, its output will be distorted and the system may report erroneous results. In the event that the detector becomes saturated, those erroneous results will continue until the detector overcomes any inherent hysteresis.

[0005] One solution has been to gate the detector off during the arrival of the carrier gas ions, but this has the disadvantage of burdening the system with additional circuitry. Another solution has been to include an electrostatic deflection gate in the flight region that is activated during the passage of carrier ions, thereby preventing them from reaching the detector. This solution requires additional circuitry, additional mechanisms, precise timing and critical placement in the flight region.

SUMMARY OF THE INVENTION

[0006] The present invention is based on the realization that it would be more advantageous to remove the carrier gas ions from the beam as soon as possible after the ion source, in order to prevent space charge effects and to minimize detector saturation problems. It is the object of this invention to provide for the removal of carrier ions from the ion beam after the ion source but before entering the mass spectrometer detector. In accordance with the invention this is achieved by applying a magnetic or electrostatic field to the ion beam soon after it emerges from the ion source which causes the constituents of the ion beam to disperse according to their mass to charge ratios. Because the amount of dispersion is related to the individual ion's mass charge ratio and the strength of the applied magnetic or electrostatic field, the location of ions in the plane perpendicular to the ion stream can be accurately predicted. A mechanical stop can then be placed to block ions from the stream as desired.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007]

Figure 1 shows a schematic of a mass spectrometer

Figure 2 shows a detailed view of the effects of the first magnetic field

Figure 3 shows one embodiment of the invention using three magnetic fields.

Figure 4 shows a second embodiment of the invention using two magnetic fields.

Figure 5 shows a third embodiment of the invention using three electrostatic fields.

Figure 6 shows a fourth embodiment of the invention using two electrostatic fields.

DETAILED DESCRIPTION OF THE INVENTION

[0008] Figure 1 shows a schematic of a mass spectrometer utilizing the invention. Carrier gas containing analytes is introduced into the mass spectrometer through a sample inlet 10. From there it travels into the ion source 20 where the gas stream is ionized. The resulting ion stream 30 may be subjected to optionally either electrostatic or magnetic fields in a first region 40. The ion stream then passes through a separator 50 in accordance with the present invention and specific ions are blocked from the stream. The ion stream may again be optionally subjected to additional electrostatic or magnetic fields in a second region 60 and is then directed into a mass analyzer 70. A typical mass analyzer might consist of a quadrapole, ion trap, or time of flight system including a detector. A vacuum system 80 keeps the main components of the mass spectrometer at negative pressure.

[0009] Figure 2 shows a diagram of the first field according to the invention, in this embodiment a magnetic field. In Figure 2 the ion stream **30** is previously accelerated and collimated so that the ions are brought to a homogeneous potential of 300 eV and the stream is approximately 1mm wide. In a GC-MS instrument the carrier gas might be helium, hydrogen or nitrogen or any other typical GC carrier gas. The beam is then subjected to a first magnetic field **90** approximately 6 mm long along its axis of travel, having a strength and polarity of +4400 gauss, applied perpendicular to the beam. Within the magnetic field the ions disperse, following circular paths defined by the following equation:

$$r = \left(\frac{144}{B}\right)\left(\sqrt{mV}\right)$$
 Equation 2

Where

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r = the radius of the path

B = the magnetic field strength in gauss

m = the mass of a particular ion in atomic mass units

V = the potential of the particular ion

[0010] After passing through the magnetic field, the ions continue to disperse, traveling tangentially to their previous circular paths. A particular ion's total perpendicular deflection x_t , from the ion beam at a particular distance from the beginning of the magnetic field is determined by the equation:

$$x_{l} = \frac{lL}{\sqrt{r^{2} - l^{2}}} + r \left(1 - \sqrt{1 - \left(\frac{l}{r}\right)^{2}} \right)$$
 Equation 3

[0011] Where

xt is the total distance the ion is deflected from the beam

I is the length of the magnetic field,

L is the length the ion has traveled along the ion beam's axis of travel after the magnetic field, and r is the radius of the path from Equation 2

[0012] While traveling through the magnetic field, helium ions in the stream with a mass of 4 follow a path having a

29 mm radius, hydrogen ions with a mass of 2 follow a 20 mm radius and nitrogen ions with a mass of 28 follow a 76 mm radius. Using a magnetic field width of 6 mm, at approximately 25 mm past the magnetic field, helium diverges approximately 6.5 mm to follow path **100** from the beam, hydrogen approximately 9.3 mm to follow path **120** and nitrogen approximately 2.4 mm to follow path **130**. A physical stop **140** is constructed and placed to block particular ions and remove them from the stream. Preferably the stop is positioned anywhere along the beam as long as the beam has diverged enough so the stop blocks those particular ions and effectively removes them from the stream.

[0013] Figure 3 shows an embodiment where a second magnetic field **150** of equal magnitude, reverse polarity and double the length of magnetic field **90** in the direction of ion travel is then applied to the stream causing it to reconverge. The stream is then subjected to a third magnetic field **160** having the same magnitude and polarity as the first, in order to re-collimate and direct the beam.

[0014] Figure 4 shows an embodiment using two magnetic fields of opposite polarity. The ion stream 30 is accelerated and collimated so that the ions are brought to a homogeneous potential of 300 eV and the stream is approximately 1mm wide. The first magnetic field 90 is applied, causing the ions to disperse according to Equation 2. The physical stop 140 is positioned to block the ions of interest and subsequently a second magnetic field 150 is applied, causing the beam to reconverge. Because there is no third magnetic field, the beam will converge in an area 170 and then begin to disperse, however, the detector can be located effectively in the region 180 around the convergence point where the beam is condensed enough to meet detection requirements.

[0015] The actual strengths and lengths of the magnetic fields in the embodiments of figures 2, 3 and 4 may vary according to the dispersion and reconvergence required in order to achieve acceptable detection and the available area in which to achieve separation. The angle at which the magnetic fields are applied with respect to the direction of the ion stream and the beam energy also may vary depending on the desired location of the stop.

[0016] Electrostatic fields may be used with similar results. Before application of an electrostatic separation arrangement, the ion stream is accelerated so that the ions have a homogeneous velocity as opposed to potential. Within an electrostatic field applied perpendicular to the ion stream's direction of travel, a particular ion follows a parabolic path defined by the equation:

$$x = \frac{1}{2} a_x t^2$$
 Equation 4

30 **[0017]** Where

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x is the distance the ion is deflected from the beam,

 a_x is the acceleration of the ion in the direction of the field, and

t is the time the ion is present in the field

The acceleration is further defined as qE_x/m , where q is the ion's charge, E_x is the strength of the electrostatic field and m is the mass of the ion. The time the ion is present in the field is further defined as I/v, where I is the length of the field and v is the initial velocity of the ion along the beam's direction of travel. Substituting these values into Equation 4 yields:

$$x = 1/2 (qE_x/m)(I/v)^2$$
 Equation 5

[0018] After passing through the electrostatic field, the ion continues to deflect from the beam, traveling tangentially to its previous parabolic path. The deflection outside the field, x_0 is defined by:

$$x_0 = L(\tan A)$$
 Equation 6

where L is the length the ion has traveled along the ion beam's axis of travel after the magnetic field, and **[0019]** A is the angle of deflection from the beam outside the field

The tangent of the angle of deflection outside the field is determined by v_x/v where v_x is the velocity attained by the ion in the direction of the electrostatic field and v is the initial velocity in the direction of travel. The velocity attained by the ion in the direction of the electrostatic field is further defined as $v_x = v_{ix} + a_x t$ where v_{ix} is the initial velocity in the direction of the field, a_x is the acceleration of the ion in the direction of the field and t is the time the ion is present in the field. Assuming the initial velocity in the direction of the field is zero (0) and using the denotation of acceleration from Equation 5 above the tangent of A becomes $(qE_x)/(mv_y^2)$. The total deflection from the beginning of the electro-

static field is defined by:

 $x_{t} = x + x_{0}$ Equation 7

or

$$x_t = 1/2 (qE_v/m)(I/v)^2 + L(qE_vI)/(mv^2)$$
 Equation 8

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[0020] Figure 5 shows an embodiment where three electrostatic fields are applied to the stream. In Figure 5 the ion stream **30** is previously accelerated and collimated so that the ions are brought to a homogeneous velocity and the stream is approximately 1mm wide. The beam is then subjected to a first electrostatic field **190** along its axis of travel, applied perpendicular to the beam.

- Calculations similar to those performed for the magnetic field example above are performed using equation 8 to determine the deflection for specific ions and the ideal location for the stop. The physical stop **140** is constructed and placed to block particular ions and remove them from the stream. As stated previously, the stop is positioned anywhere along the beam as long as the beam has diverged enough so the stop blocks those particular ions and effectively removes them from the stream.
- A second electrostatic field **200** of equal magnitude, reverse polarity and double the length of electrostatic field **190** in the direction of ion travel is then applied to the stream causing it to reconverge. The stream is then subjected to a third electrostatic field **210** having the same magnitude and polarity as the first, in order to re-collimate and direct the beam. Figure 6 shows an embodiment using only two electrostatic fields of opposite polarity.
- The ion stream **30** is accelerated and collimated so that the ions are brought to a homogeneous velocity and the stream is approximately 1mm wide. The first electrostatic field **190** is applied, causing the ions to disperse according to Equation 8. The physical stop **140** is positioned to block the ions of interest and subsequently a second electrostatic field **150** is applied, causing the beam to reconverge. Because there is no third electrostatic field, the beam will converge in an area **170** and then begin to disperse, however, the detector can be located effectively in the region **180** around the convergence point where the beam is condensed enough to meet detection requirements.
- As with the magnetic fields embodiment, the actual strengths and lengths of the electrostatic fields in the embodiments of figures 5 and 6 may vary according to the dispersion and reconvergence required in order to achieve acceptable detection and the available area in which to achieve separation. The angle at which the electrostatic fields are applied with respect to the direction of the ion stream and the beam energy also may vary depending on the desired location of the stop.

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Claims

1. A method of separating ions from an ion beam comprising:

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- applying a first field at an angle to said ion beam, causing said ions to disperse according to their mass to charge ratios;
- blocking dispersed ions having a particular range of mass to charge ratios;
- applying a second field to said ion beam to reverse the effects of said first field on said ion beam; and applying a third field to said ion beam to direct and collimate said ion beam.

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2. The method of claim 1 where said ion beam comprises carrier ions and analyte ions and said blocked ions are carrier ions.

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- 3. The method of claim 1 wherein said first field, said second field and said third field are a type of the group consisting of electrostatic and magnetic.
- 4. The method of claim 1 where said blocked ions are removed from said ion beam.

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- 5. The method of claim 1 as utilized in a mass spectrometer having an ion source.
- **6.** An apparatus for separating ions from an ion beam comprising:

- a first field means positioned so as to apply a first field at an angle to said ion beam causing said ions to disperse according to their mass charge ratios;
- a mechanical stop located along said ion beam for blocking dispersed ions having a particular range of mass to charge ratios;
- a second field means positioned so as to apply a second field to said ion beam to reverse the effects of said first field upon said ion beam; and
- a third field means positioned so as to apply a third field to said ion beam to direct and collimate said ion beam.
- 7. The apparatus of claim 6 where said ion beam comprises carrier ions and analyte ions and said blocked ions are carrier ions.
 - **8.** The apparatus of claim 6 wherein said first field means, said second field means and said third field means apply a type of field of the group consisting of electrostatic and magnetic.
- 15 **9.** The apparatus of claim 6 where said blocked ions are removed from said ion beam.
 - **10.** The apparatus of claim 6 as utilized in a mass spectrometer having an ion source.
- **11.** A mass spectrometer having a sample inlet, an ion source, an ion mass analyzer and a vacuum system in combination with the apparatus of claim 6.
 - **12.** A method of separating ions from an ion beam comprising:

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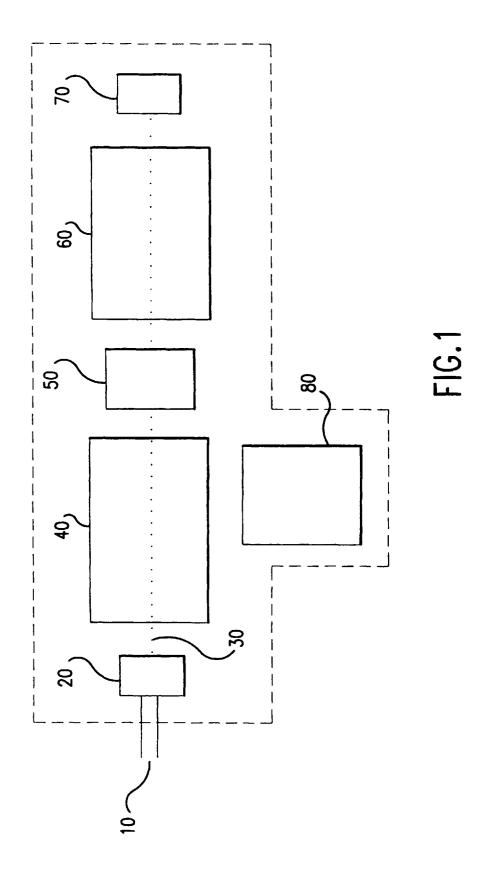
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- applying a first field at an angle to said ion beam, causing said ions to disperse according to their mass to charge ratios;
- blocking dispersed ions having a particular range of mass to charge ratios;
- applying a second field to said ion beam to reverse the effects of said first field on said ion beam, and to direct and collimate said ion beam.
- 30 13. The method of claim 12 where said ion beam comprises carrier ions and analyte ions and said blocked ions are carrier ions.
 - **14.** The method of claim 12 wherein said first field and said second field are a type of the group consisting of electrostatic and magnetic.
 - **15.** The method of claim 12 where said blocked ions are removed from said ion beam.
 - **16.** The method of claim 12 as utilized in a mass spectrometer having an ion source.
- 40 **17.** An apparatus for separating ions from an ion beam comprising:
 - a first field means positioned so as to apply a first field at an angle to said ion beam causing said ions to disperse according to their mass charge ratios;
 - a mechanical stop located along said ion beam for blocking dispersed ions having a particular range of mass to charge ratios;
 - a second field means positioned so as to apply a second field to said ion beam to reverse the effects of said first field upon said ion beam and to direct and collimate said ion beam.
 - **18.** The apparatus of claim 17 where said ion beam comprises carrier ions and analyte ions and said blocked ions are carrier ions.
 - **19.** The apparatus of claim 17 wherein said first field means and said second field means apply a type of field of the group consisting of electrostatic and magnetic.
- 20. The apparatus of claim 17 where said blocked ions are removed from said ion beam.
 - 21. The apparatus of claim 17 as utilized in a mass spectrometer having an ion source.

22. A mass spectrometer having a sample inlet, an ion source, an ion mass analyzer and a vacuum system in com-

	bination with the apparatus of claim 17.
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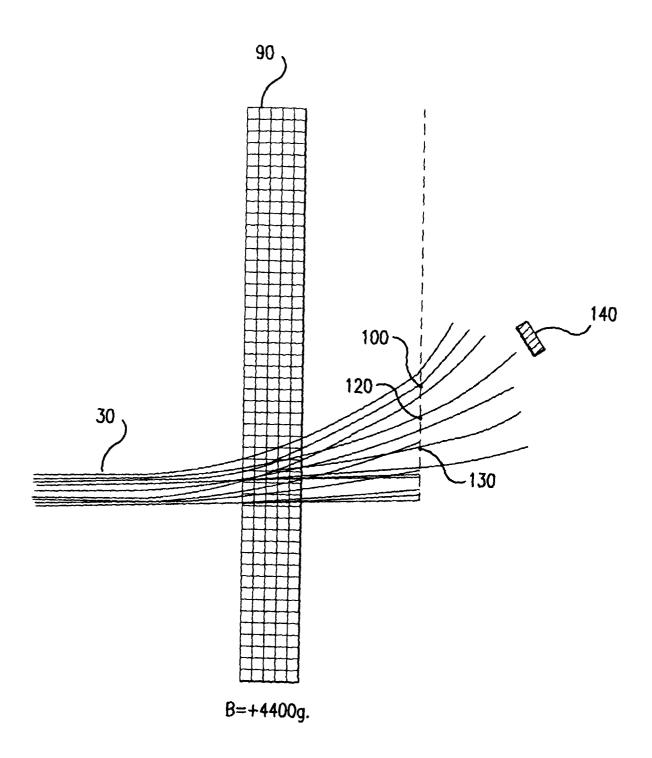
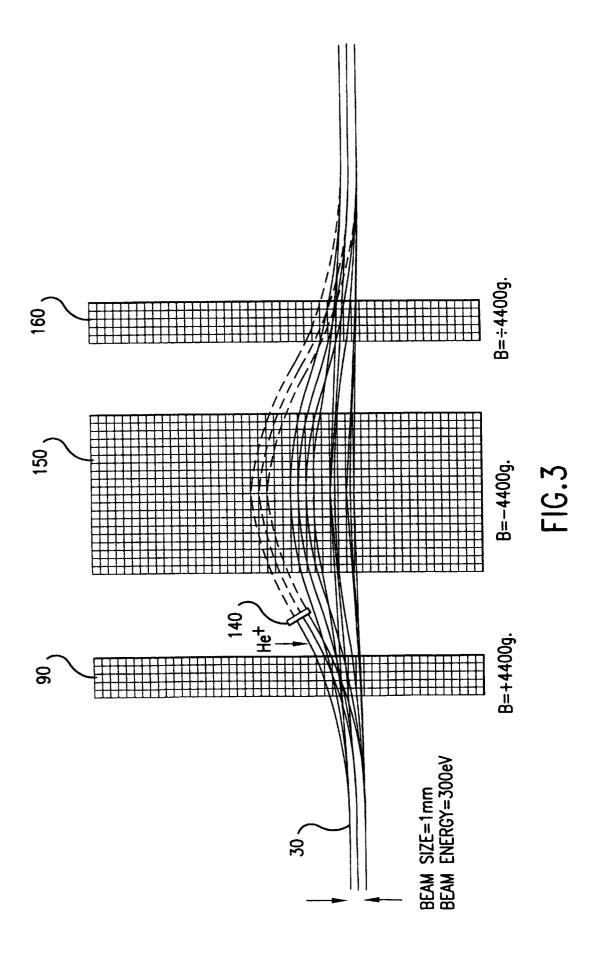
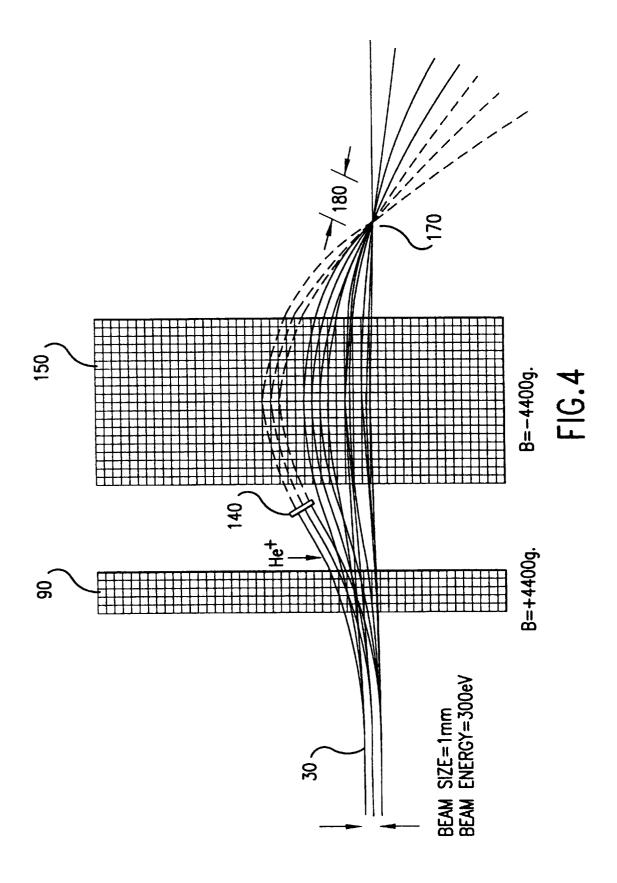
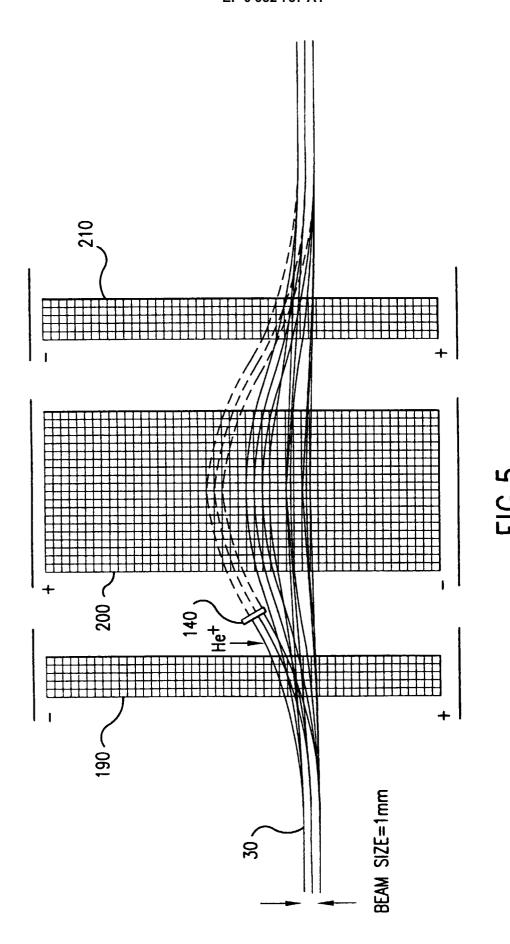


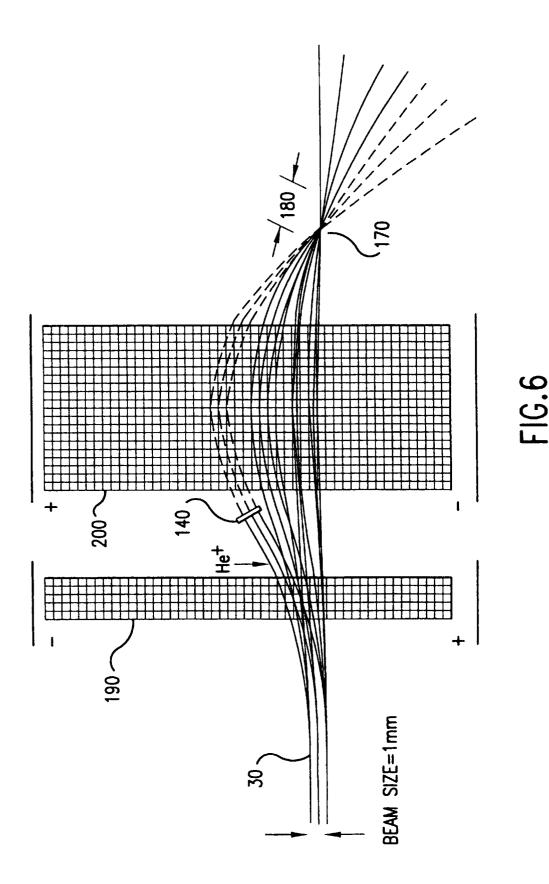
FIG.2







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EUROPEAN SEARCH REPORT

Application Number EP 98 11 6015

Category	Citation of document with it of relevant pass	ndication, where appropriate, sages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.6)
χ	US 5 534 699 A (FER	1,3-6, 8-11	H01J49/04 H01J49/30	
Y	* abstract; figure * column 5, line 49		1-11	
X	US 3 641 339 A (MCC 8 February 1972	ORMICK ANDREW)	12-22	
Υ		- column 2, line 75;	1-11	
X	US 4 649 316 A (CLE 10 March 1987 * the whole documen		1,3-6, 8-10	•
X	US 4 047 030 A (LOB 6 September 1977 * the whole documen		1,6	
Α	US 4 066 895 A (IWA 3 January 1978		1-22	
	* the whole document *			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	US 5 767 512 A (KOPPENAAL DAVID W ET AL) 16 June 1998 * abstract *		2,7,13, 18	H01J
A	REINSFELDER R. E. A "Theory and charact separator analyzer INT. J. MASS SPECTR vol. 37, no. 2, Feb 241-250, XP00209320 netherlands * the whole document	2,7,13, 18		
	The present search report has	been drawn up for all claims Date of completion of the search		Examiner
MUNICH		12 February 1999	Zuc	catti, S
X : part Y part doci	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with another to the same category inclogical background	T : theory or principle E : earlier patent doc after the filing dat ther D : document cited in L document cited to	underlying the ument, but puble the application of other reasons	invention ished on, or

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 98 11 6015

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 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-02-1999

Patent document cited in search repo		Publication date	Patent family member(s)	Publication date
US 5534699	Α	09-07-1996	NONE	
US 3641339	A	08-02-1972	FR 2014521 A GB 1255962 A	17-04-19 08-12-19
US 4649316	A	10-03-1987	EP 0107320 A JP 59121748 A	02-05-19 13-07-19
US 4047030	A	06-09-1977	CH 583460 A DE 2538123 A FR 2286501 A GB 1473054 A NL 7416698 A,	31-12-19 08-04-19 23-04-19 11-05-19 3 01-04-19
US 4066895	А	03-01-1978	JP 1208384 C JP 52034785 A JP 58036464 B FR 2324119 A GB 1564526 A	29-05-19 16-03-19 09-08-19 08-04-19 10-04-19
US 5767512	Α	16-06-1998	AU 1822897 A EP 0871977 A WO 9725737 A	01-08-19 21-10-19 17-07-19

FORM P0459

 $\frac{Q}{m}$ For more details about this annex : see Official Journal of the European Patent Office, No. 12/82