

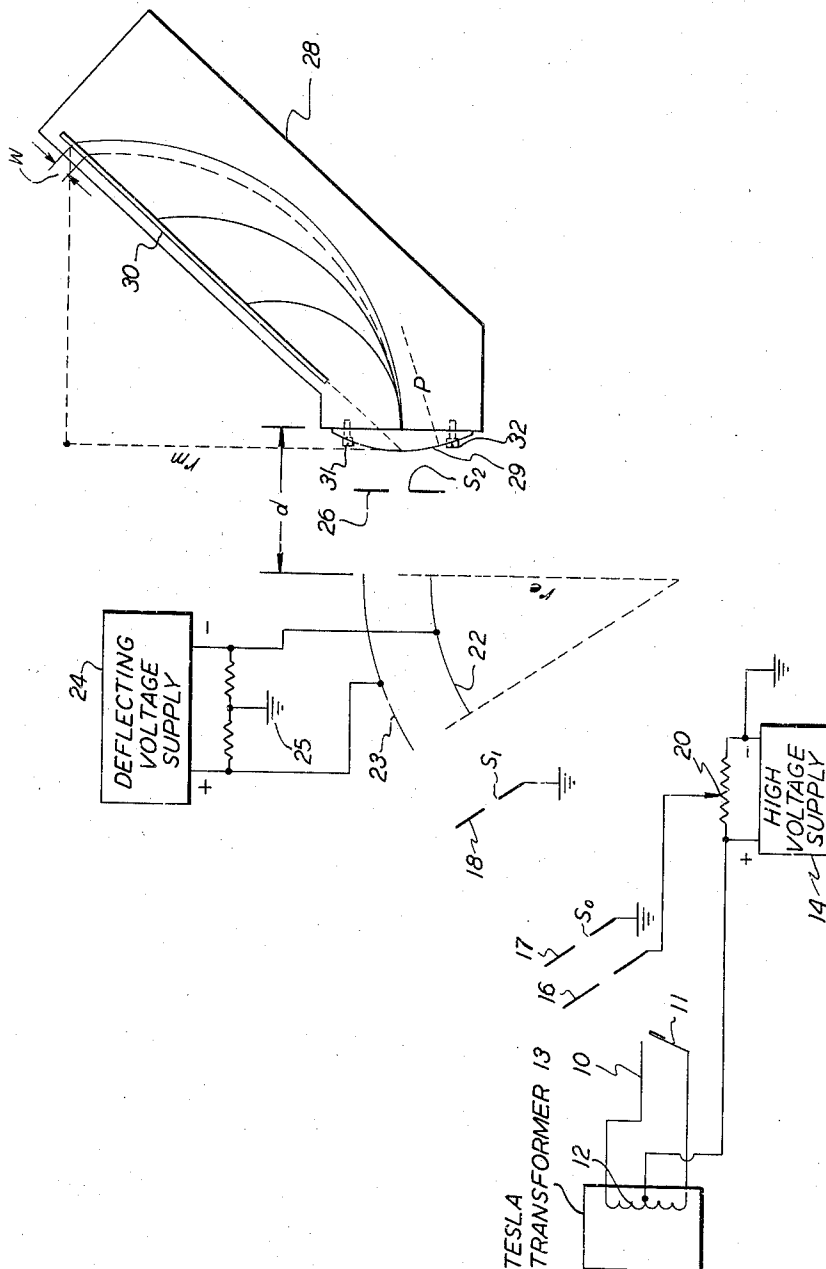
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MASS SPECTROMETER

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2,851,608

MASS SPECTROMETER

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6 Claims. (Cl. 250—41.9)

The invention relates to double-focusing mass spectrometers.

There is a type of mass spectrometer, to date finding only relatively limited use, in which first order velocity and angular aberrations are reduced essentially to zero. Because this type of instrument effectively focusses with respect to both velocity and angular deflection, it has become known as a double-focusing instrument, the term being defined as applied to a mass spectrometer in which C_a (constant of angular aberration) is zero at the focal line, and C_v (the constant of velocity aberration) is zero at the focal line.

This type of instrument is becoming increasingly important in the analysis of materials of very low vapor pressure, such as metals, in which ions are made available over a wide energy range and hence with an appreciable spread in initial velocity. A spark ion source is a highly useful source in the ionization of solid samples, but it does produce ions of widely differing energies. In 1934, Messrs. Mattauch and Herzog published a paper describing the double-focusing instrument and as a result this type of mass spectrometer is frequently referred to as the Mattauch mass spectrometer (see Zeitschrift für Physik, 89, p. 786, 1934).

In spite of the development of the basic precepts of this form of mass spectrometer by Mattauch in the early 1930s, mass spectrometry has been used primarily for the analysis of gases and readily vaporizable liquids, with which constituents ionization can be accomplished by means of an electron beam and with a very narrow energy spread. Ionization in such an electron beam susceptible to a high degree of collimation results in velocity dispersion that has usually been negligible in the past, and double-focusing instruments have accordingly found little use. More recently it has become apparent that the analysis of compounds of very low volatility is a logical extension of the capabilities of mass spectrometry.

In the Mattauch mass spectrometer of conventional type the electric and magnetic sectors deflect the ions through angles of 31.8° and 90° respectively, and the system shows double-focusing (angular and velocity focusing) to first order for all masses simultaneously.

For any mass spectrometer the dependence of image-width w on the angular aberration α and the fractional velocity aberration β can be expressed as a power series in α and β as follows:

$$w = r_m [C_a \alpha + C_v \beta + C_a^2 \alpha^2 + C_{av} \alpha \beta + C_v^2 \beta^2 \dots] \quad (1)$$

where:

r_m is the magnetic sector radius;

C_a is a constant of angular aberration as a function of the instrument parameters, and is zero by definition at the focal point;

C_v is a constant of fractional velocity aberration as a function of the instrument parameters, and is zero by definition in double-focusing mass spectrometers.

In the standard Mattauch instrument, C_a and C_v are

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zero at the focal plane by definition, and C_a^2 , C_{av} , and C_v^2 are given by the following expressions:

$$C_a^2 = -1.416 + \frac{1}{2} \left(\frac{r_e}{r_m} \right)^2 \quad (2a)$$

$$C_{av} = 3.25 + \frac{r_e}{r_m} \left(1 + \frac{d}{r_m} + 0.293 \frac{r_e}{r_m} \right) \quad (2b)$$

$$C_v^2 = 0.39 + 0.293 \frac{r_e}{r_m} + \frac{d}{r_m} + \frac{1}{2} \left(0.293 \frac{r_e}{r_m} + \frac{d}{r_m} \right)^2 \quad (2c)$$

where:

r_e = radius of curvature of electric sector;

r_m = radius of curvature of a specified ion in the magnetic sector; and

d = separation of electric and magnetic sectors.

It can be shown by plotting the functions C_a^2 , C_{av} and C_v^2 that it is desirable in a standard Mattauch system to keep the separation of the electric and magnetic sectors (d) as small as mechanical considerations will permit in order to keep C_{av} and C_v^2 from becoming excessively large. If this is done it becomes difficult to effect clean and independent control of α and β . This fact together with the fact that C_{av} and C_v^2 are not very small may make it very difficult to achieve high resolving power and reasonable intensity simultaneously when the velocity spread (β) in the ion beam is high as from a spark ion source or an ion bombardment ion source.

In accordance with the present invention I have found that by curving the entrant pole face of the magnetic sector, convexly with respect to the entering ion beam and on a radius of curvature ρ , leaving the electric and magnetic deflections at their normal values of 31.8° and 90° respectively, the second order effects of angular and velocity aberration can be reduced to a minimum. As a result there is realized greatly improved resolving power compared to a standard double-focusing instrument.

Accordingly, the invention comprises a mass spectrometer having an ion source, an electrostatic velocity compensator, means including spaced magnetic pole pieces forming a magnetic field, the entrance faces of the magnetic pole pieces being convex, means for causing ions formed at the source to pass sequentially through the electrostatic velocity compensator and the magnetic field, and means for sensing ions passing through the magnetic field.

The analysis of the consequences of this alteration in instrument structure is deferred pending the following detailed description of a double-focusing mass spectrometer in accordance with the invention as taken from the accompanying schematic drawing.

Referring to the drawing, the instrument shown schematically includes an ion source, in this instance illustrated as spark electrodes 10 and 11, connected at opposite ends to the secondary winding 12 of a Tesla transformer 13. The midpoint of the transformer winding is connected to the positive side of a high voltage supply 14.

First, second and third apertured electrodes 16, 17 and 18 are arranged serially, electrode 16 being connected through a suitable voltage divider 20 to the high voltage supply and serving as an accelerating electrode to propel ions from the spark source as a beam through the electrodes 17 and 18. Electrode 17 has an aperture S_0 defining the geometrical width of the beam, and electrode 18 has an aperture S_1 acting as a limit on angular divergence in the beam passing therethrough.

An electrostatic deflector constituting curved plates 22, 23 is arranged serially with respect to the electrodes, the beam issuing from the electrode array and entering the deflector, as shown. The two plates, 22, 23 of the deflector

are connected to opposite sides of a deflecting voltage supply 24 and, as illustrated, both plates are at a pre-assigned potential with respect to ground 25. A fourth apertured electrode 26 may be disposed adjacent the exit end of the electrostatic deflector. Electrode 26 has an aperture S_2 acting as a so-called velocity stop, i. e. stopping ions which, because of extremes in velocity dispersion, are not focused on the aperture S_2 .

A transverse magnetic field is formed in the conventional manner by a pair of magnetic poles, one of which, pole piece 28, is shown in the drawing. In accordance with normal practice, the second identical pole piece (not shown) is disposed parallel to and spaced from the pole piece 28 to form a magnetic field therebetween transversely of the direction of ion travel into the magnetic field from the deflector. Ion sensing means, such as the photographic plate 30, is immersed in the magnetic field for detecting mass dispersion therein.

Unlike previous Mattauch type mass spectrometers, the pole piece 28 and its companion pole piece (not shown) which together define the magnetic field, are provided with curved entrant pole faces, pole piece 28 having curved face member 29 which is convex with respect to the entering ion beam and resulting in the improved operation as pointed out below. Preferably the convex face is provided as a detachable shim, as shown, held to the parent face surface by any desired means, such as bolts 31, 32. In this manner, the radius of curvature (ρ) can be changed at will by the simple expedient of changing shims.

Certain parameters are identified in the drawing to facilitate the following discussion of the operation of the instrument. Thus the notation r_e gives the mean radius of curvature of the electrostatic deflector, the notation d shows the distance between the exit from the deflector to the entrant face of the magnetic field, the notation r_m (max) shows the maximum radius of ion travel in the magnetic field, and the notation ρ gives the radius of curvature of the entrant face of the pole pieces.

With a curved entrant pole face the second order factors from Equation 1 can be shown by mathematical derivation not included herein to be as follows:

$$C_{\alpha^2} = -1.416 + \frac{\gamma}{2} \left(\frac{r_e}{r_m} \right)^2 \quad (3a)$$

$$C_{\alpha\beta} = 3.25 + \frac{r_e}{r_m} + \frac{r_e}{r_m} \left[0.293 \frac{r_e}{r_m} + \frac{d}{r_m} \right] \gamma \quad (3b)$$

$$C_{\beta^2} = 0.39 + 0.293 \frac{r_e}{r_m} + \frac{d}{r_m} + \frac{\gamma}{2} \left[0.293 \frac{r_e}{r_m} + \frac{d}{r_m} \right]^2 \quad (3c)$$

in which

r_m = the radius of curvature in the magnetic sector;
 r_e = the mean radius of curvature in the electric sector;
 d = sector separation; and

$$\gamma = 1 - \frac{r_m}{\rho}$$

In a conventional double-focusing instrument the pole face of the magnet is not curved in effect, ρ is therefore infinite, γ equals one and the second order aberration coefficients as given in Equations 2 are of appreciable significance. Where ρ is less than infinity in accordance with the present invention, γ is less than one and, by proper choice of instrument parameters, i. e. of r_e , r_m , d and ρ , the second order of Equations 3 can be reduced to an insignificant minimum. It can be shown, although no attempt will be made to do so here, that the third order aberrations are negligible.

It is not possible to find positive values for

$$\frac{d}{r_m}$$

and

$$\frac{r_e}{r_m}$$

such that all three of these coefficients vanish from the above equations. For this reason it is not possible to achieve values in which C_{α^2} , $C_{\alpha\beta}$ and C_{β^2} all become zero at the same time. However, it is possible to find a considerable range of values for these parameters such that C_{α^2} and C_{β^2} coefficients vanish simultaneously and $C_{\alpha\beta}$ is of quite reasonable magnitude. Equally important is the fact that this condition can be met for values of d which are not as small as those heretofore thought to be necessary but roughly equal to r_m so that the operation of the energy selector slit (26 in the drawing) is greatly improved over its function in the more usual form of the Mattauch instrument. Not only is the operation of the energy slit improved, but its operation is no longer as critical since $C_{\alpha\beta}$ and C_{β^2} have been reduced to zero.

As an aid to the selection of values of

$$\frac{r_e}{r_m}$$

and γ , it can be shown by mathematical derivation that for an arbitrary value of

$$\frac{d}{r_m}$$

and with the objective of reducing C_{α^2} and C_{β^2} to zero, the ratio may be selected in accordance with the following expression:

$$\frac{r_e}{r_m} = -1.7 \frac{d}{r_m} + 0.3 + \frac{1}{2} \sqrt{\left(3.4 \frac{d}{r_m} - 0.6 \right)^2 + 44 \frac{d}{r_m}} \quad (4)$$

and γ may be determined from:

$$\gamma = - \frac{3.2 + r_e/r_m}{0.3(r_e/r_m)^2 + (d/r_m)(r_e/r_m)}$$

where as before

$$\gamma = 1 - \frac{r_m}{\rho}$$

These expressions provide a means of selecting suitable values of the instrument parameters but do not constitute limits on the parameters.

The following Tables 1 and 2 show the values of the second order aberration coefficients, respectively, for a conventional double-focusing mass spectrometer with straight magnetic pole faces and for a mass spectrometer in accordance with the invention with curved magnetic pole faces.

TABLE 1

Second order aberration coefficients for a Mattauch mass spectrometer having straight pole faces in which $r_e = 20.2$, $d = 2.4$ "

r_m	C_{α^2}	$C_{\alpha\beta}$	C_{β^2}
12"	0	6.10	1.3
9"	1.10	7.67	1.74
6"	4.25	11.23	2.74
3"	21.3	28.7	7.01

TABLE 2

Second order aberration coefficients for a Mattauch mass spectrometer in which the leading face of the magnet pole has a radius of curvature $\rho = 4.265$ ", $r_e = 24.876$ ", $d = 9.6$ "

r_m	C_{α^2}	$C_{\alpha\beta}$	C_{β^2}
12	-5.38	0	0
9	-5.73	.024	0.32
6	-4.94	2.69	1.62
3	+9.15	25.9	10.92

The choice of parameters on which Table 2 is based is not intended to evidence an optimum set of values but one which might be reasonable for mechanical convenience. It is noted, however, that both energy dependent aberrations vanish at the design point $r_m=12''$ and that the arrangement reported in Table 2 gives a lower aberration sum ($C_{\alpha^2}+C_{\alpha\beta}+C_{\beta^2}$) through the entire mass range than does the conventional instrument evidenced in Table 1.

Referring to the drawing, typical values for structural and operational features of the instrument may be as follows:

- (1) Output of Tesla secondary approximately 50 kv. R. F.;
- (2) High voltage supply approximately 20 kv. D. C.;
- (3) Deflecting voltage supply approximately 1 kv.;
- (4) r_e approximately 24.876'';
- (5) d approximately 9.6'';
- (6) ρ approximately 4.265'';
- (7) $r_m=12''$ (for mass 250);
- (8) Magnetic field 9,700 gauss.

The foregoing values are in no way limiting but only suggest typical values of one operable instrument in accordance with the invention.

From Equations 3a, 3b and 3c, it is apparent that values of

$$\frac{r_e}{r_m}$$

and

$$\frac{d}{r_m}$$

may be selected in the design of an instrument such that for a particular value of γ , as for example determined from Equation 5, $C_{\alpha\beta}=C_{\beta^2}=0$. Where $C_{\alpha\beta}$ and $C_{\beta^2}=0$ under such circumstances C_{α^2} does not equal zero. With the same values of

$$\frac{r_e}{r_m}$$

and

$$\frac{d}{r_m}$$

a different value of γ can be found such that $C_{\alpha^2}=0$ and in which case $C_{\alpha\beta}$ and C_{β^2} do not equal zero. With the objective of diminishing C_{α^2} to 0,

$$\frac{r_e}{r_m}$$

may again be determined from Equation 4 and γ as follows:

$$\gamma=2.8\left(\frac{r_m}{r_e}\right)^2$$

Table 2 shows a selection of parameters such that $C_{\alpha\beta}$ and C_{β^2} are 0 and under which conditions C_{α^2} is not zero.

With this option to select γ (by variation of ρ) so as to eliminate either $C_{\alpha\beta}$ and C_{β^2} or C_{α^2} it is possible without changing the fixed geometry of the instrument (r_e , r_m and d) to specifically adapt it to use with different types of ion sources. Where a source is used which produces an extreme energy spread such as the illustrated spark source, the principal objective is to reduce $C_{\alpha\beta}$ and C_{β^2} to a minimum without undue disturbance of C_{α^2} . However, if a surface ionization source is used, the energy spread is so low that the $\alpha\beta$ and β^2 aberrations do not warrant concern at the expense of the α^2 aberration. In such event, thereof, a value of γ is selected to reduce C_{α^2} to zero with little or no concern for $C_{\alpha\beta}$ and C_{β^2} . By using the same geometry specified in Table 2 save for a change in ρ from 4.265'' to 35.5'', C_{α^2} is reduced to zero and the $C_{\alpha\beta}$ and C_{β^2} coefficients become 7.258 and 2.460 respectively. From Equation 1 it is apparent that the value of these last two coefficients

is of no significance where β approaches zero as in a surface ionization source.

Therefore, without altering the instrument geometry, I am able to secure maximum resolving power for any given conditions of ionization by changing the radius of curvature of the entrant faces of the magnet poles. This is simply accomplished by the use of removable pole faces as illustrated.

I claim:

1. A mass spectrometer comprising an ion source, an electrostatic compensator, means including spaced magnetic pole pieces forming a magnetic field, means for causing ions formed in the source to travel serially through the electrostatic compensator and the magnetic field, the entrant faces of the magnetic pole pieces being convex in the direction of ion entry, and means for sensing ions passing through the magnetic field.

2. A mass spectrometer comprising an ion source, an electrostatic compensator, means including spaced magnetic pole pieces forming a magnetic field, means for causing ions formed in the source to travel serially through the electrostatic compensator and the magnetic field, an apertured electrode disposed between the compensator and the magnetic field, the entrant faces of the magnetic pole pieces being convex in the direction of ion entry, and means for sensing ions passing through the magnetic field.

3. A mass spectrometer comprising an ion source, an electrostatic compensator, means including spaced magnetic pole pieces forming a magnetic field, means for causing ions formed in the source to travel serially through the electrostatic compensator and the magnetic field, face plates removably attached to the entrant faces of the magnetic pole pieces, the outer surface of the face plates being convex in the direction of ion entry, and means for sensing ions passing through the magnetic field.

4. A mass spectrometer comprising a spark source of ions, an electrostatic compensator, means including spaced magnetic pole pieces forming a magnetic field, means for causing ions formed at the spark source to travel serially through the electrostatic compensator and the magnetic field, face plates removably attached to the entrant faces of the magnetic pole pieces, the outer surface of the face plates being convex in the direction of ion entry, and means for sensing ions passing through the magnetic field.

5. A mass spectrometer comprising an ion source, an electrostatic compensator, means including spaced magnetic pole pieces forming a magnetic field, the entrant faces of the pole pieces being convex, means causing ions to flow from the source through the compensator and magnetic field, means for sensing ions passing through the magnetic field, the dimensions of the instrument being determined from

$$\frac{r_e}{r_m} = -1.7\frac{d}{r_m} + 0.3 = \frac{1}{2}\sqrt{\left(3.4\frac{d}{r_m} - 0.6\right)^2 + 44\frac{d}{r_m}}$$

and

$$\gamma = -\frac{3.2 + r_e/r_m}{0.3(r_e/r_m)^2 + (d/r_m)(r_e/r_m)}$$

where:

r_m = the radius of curvature in the magnetic sector;

r_e = the mean radius of curvature in the electric sector;

d = sector separation;

$$\gamma + 1 = \frac{r_m}{\rho}$$

ρ = radius of curvature of entrant face of magnetic pole pieces.

6. A mass spectrometer comprising an ion source, an electrostatic compensator, means including spaced magnetic pole pieces forming a magnetic field, the entrant faces of the pole pieces being convex, means causing ions to flow from the source through the compensator and

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magnetic field, means for sensing ions passing through the magnetic field, the dimensions of the instrument being determined from

$$\frac{r_s}{r_m} = -1.7 \frac{d}{r_m} + 0.3 + \frac{1}{2} \sqrt{\left(3.4 \frac{d}{r_m} - 0.6\right)^2 + 44 \frac{d}{r_m}}$$

and

$$\gamma = 2.8 \left(\frac{r_m}{r_s} \right)^2$$

where:

r_m = the radius of curvature in the magnetic sector;

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r_e = the mean radius of curvature in the electric sector;
 d = sector separation;

$$\gamma = 1 - \frac{r_m}{\rho}$$

and

ρ = radius of curvature of entrant face of magnetic pole pieces.

(6) 10

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UNITED STATES PATENT OFFICE
Certificate of Correction

Patent No. 2,851,608

September 9, 1958

Charles F. Robinson

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 37, for " (r_e/o_m) ", which is the last quantity of the denominator of the equation, read $-(r_e/r_m)$ — and this equation should be designated as —(5)—; column 4, line 59, Table 1, last column thereof, for "1.3" read —1.32—; same column, line 74, Table 2, last column thereof, for "10.92" read —10.9—; column 5, lines 53 and 54, the equation

$$\gamma = 2.8 \left(\frac{r_m}{r_e} \right)^{2.7}$$

should be designated as —(6)—; column 6, lines 65 to 68, claim 5, for

$$\gamma + 1 = \frac{r_m}{\rho} \quad \text{read} \quad \gamma = 1 - \frac{r_m}{\rho}; \text{ and}$$

Signed and sealed this 2nd day of December 1958.

[SEAL]

Attest:

KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.