# United States Patent [19]

**Merren**

[11] **3,770,337**

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[54] **MASS SPECTROMETRY**


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[73] Assignee: **Associated Electrical Industries Limited,** London, England



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[30] **Foreign Application Priority Data**

June 17, 1970 Great Britain ..... 29,499/70

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[51] **Int. Cl.** ..... **B01d 59/44,** H01j 39/34

[58] **Field of Search** ..... 250/41.9 ME, 41.9 D



[56] **References Cited**

UNITED STATES PATENTS

3,242,333 3/1966 Yamamoto ..... 250/41.9 D

FOREIGN PATENTS OR APPLICATIONS

1,161,432 8/1969 Great Britain ..... 250/41.9 ME



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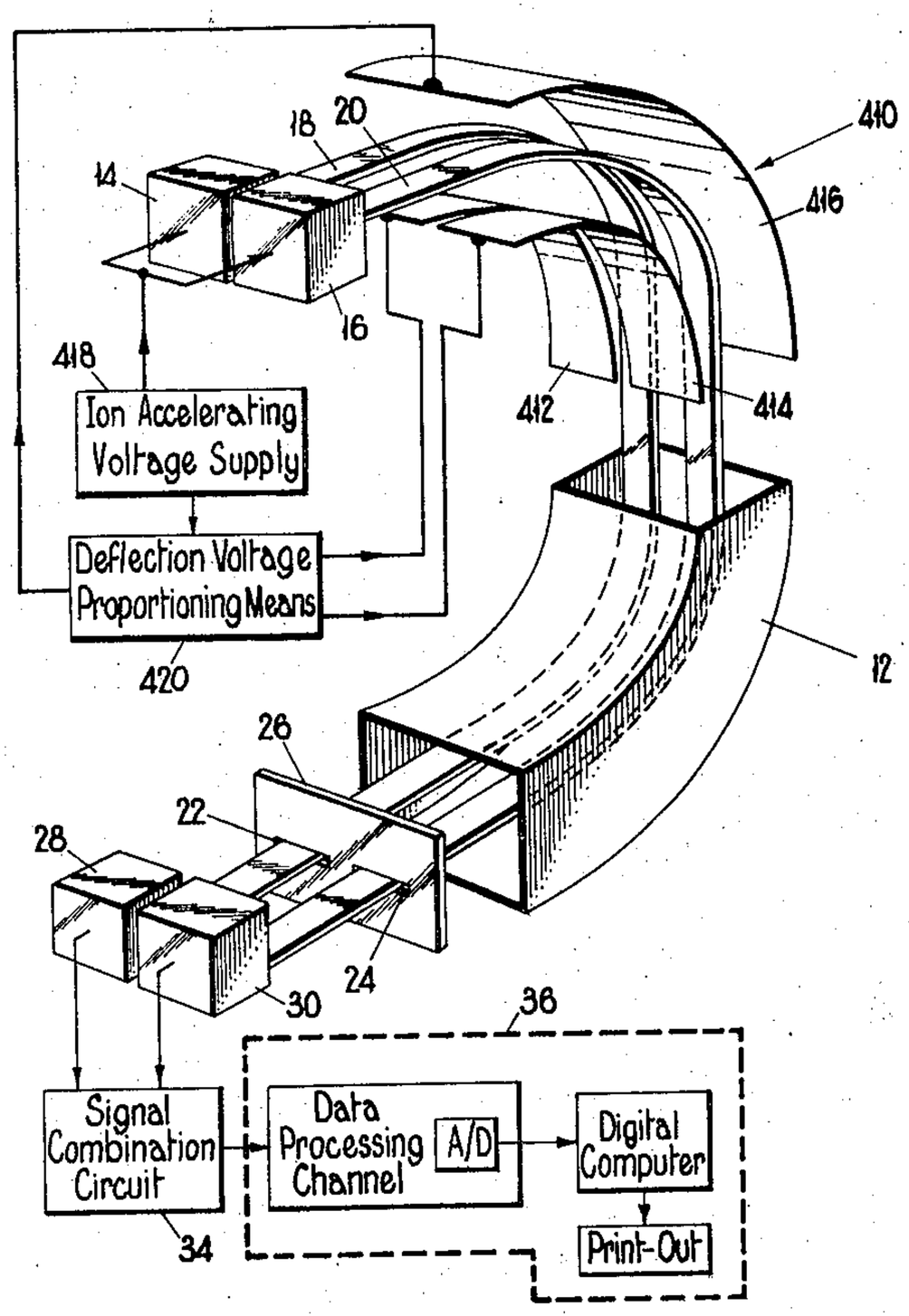
*Assistant Examiner*—C. E. Church
*Attorney*—Watts, Hoffmann, Fisher & Heinke



[57] **ABSTRACT**

In a double-beam mass spectrometer, the two spectral outputs are given a small relative time displacement and superimposed without any peaks overlapping. Only a single data processing channel is required with only a single analogue-to-digital converter for computer processing of the results.


**8 Claims, 4 Drawing Figures**



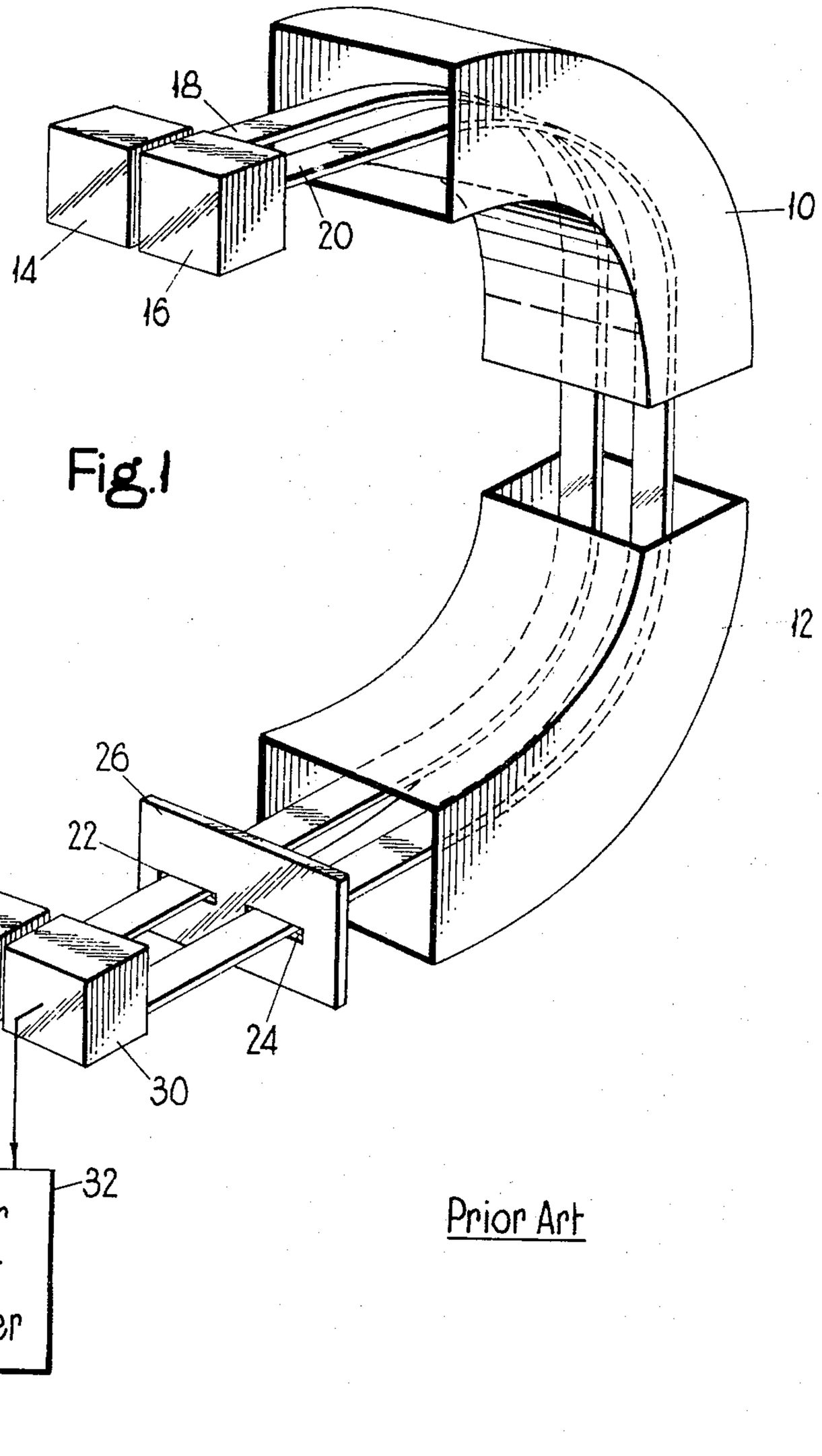



Fig.1

Prior Art

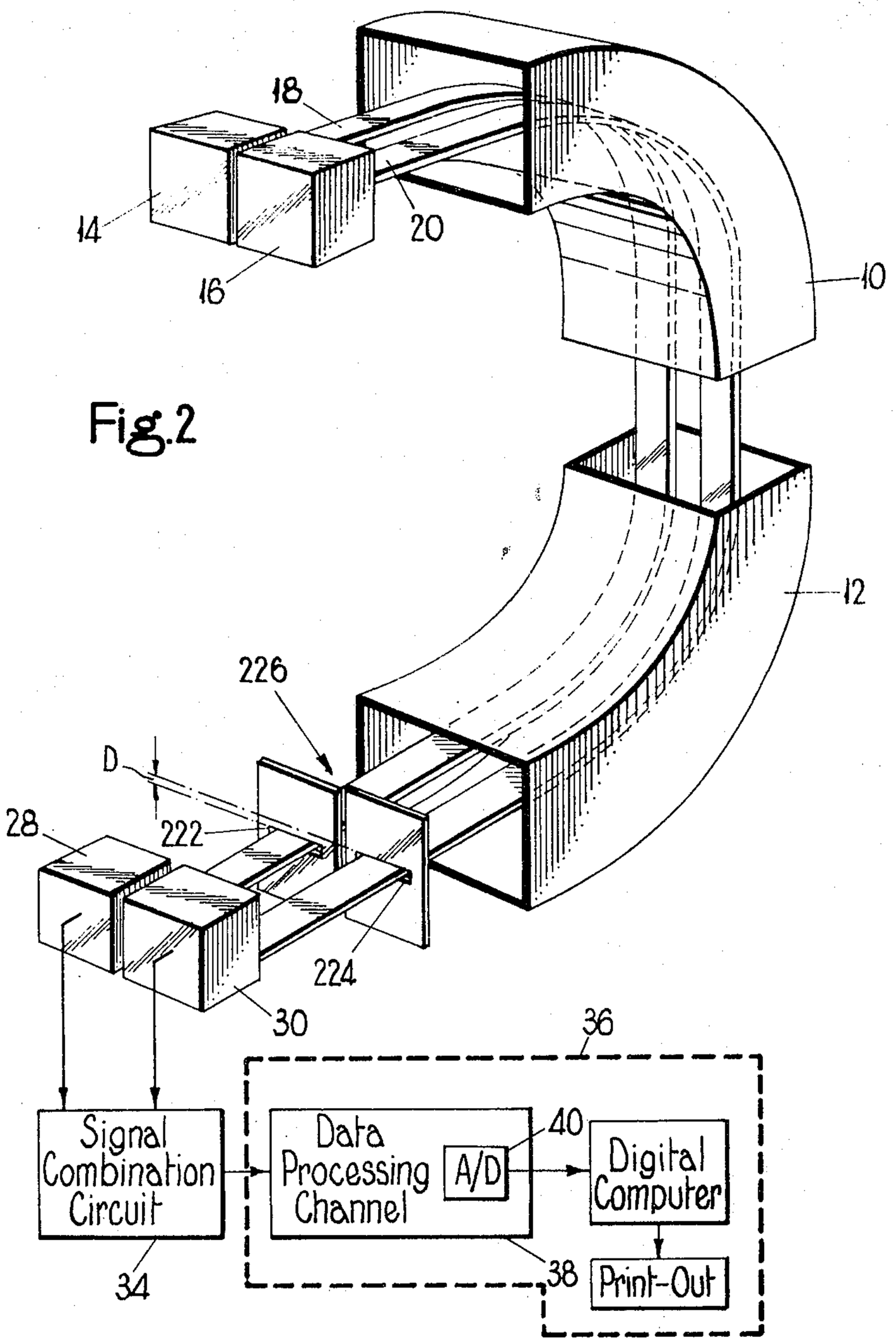
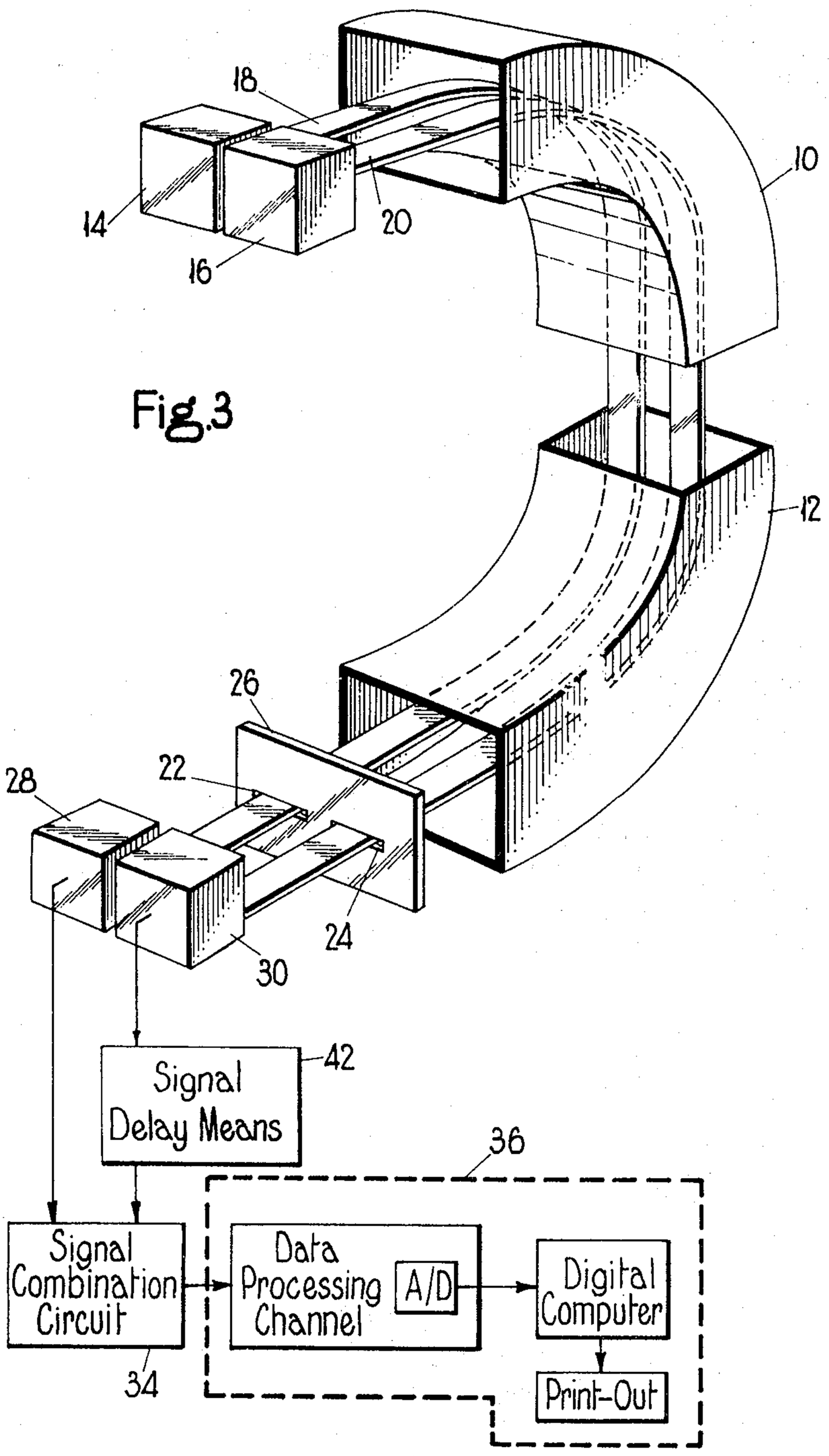

18
14
20
16
10
12
226
D
28
222
224
30
36
Signal Combination Circuit
Data Processing Channel
A/D
40
Digital Computer
Print-Out
34
38

Fig. 2


18
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Signal Delay Means
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Signal Combination Circuit
Data Processing Channel
A/D
Digital Computer
34
Print-Out

Fig.3

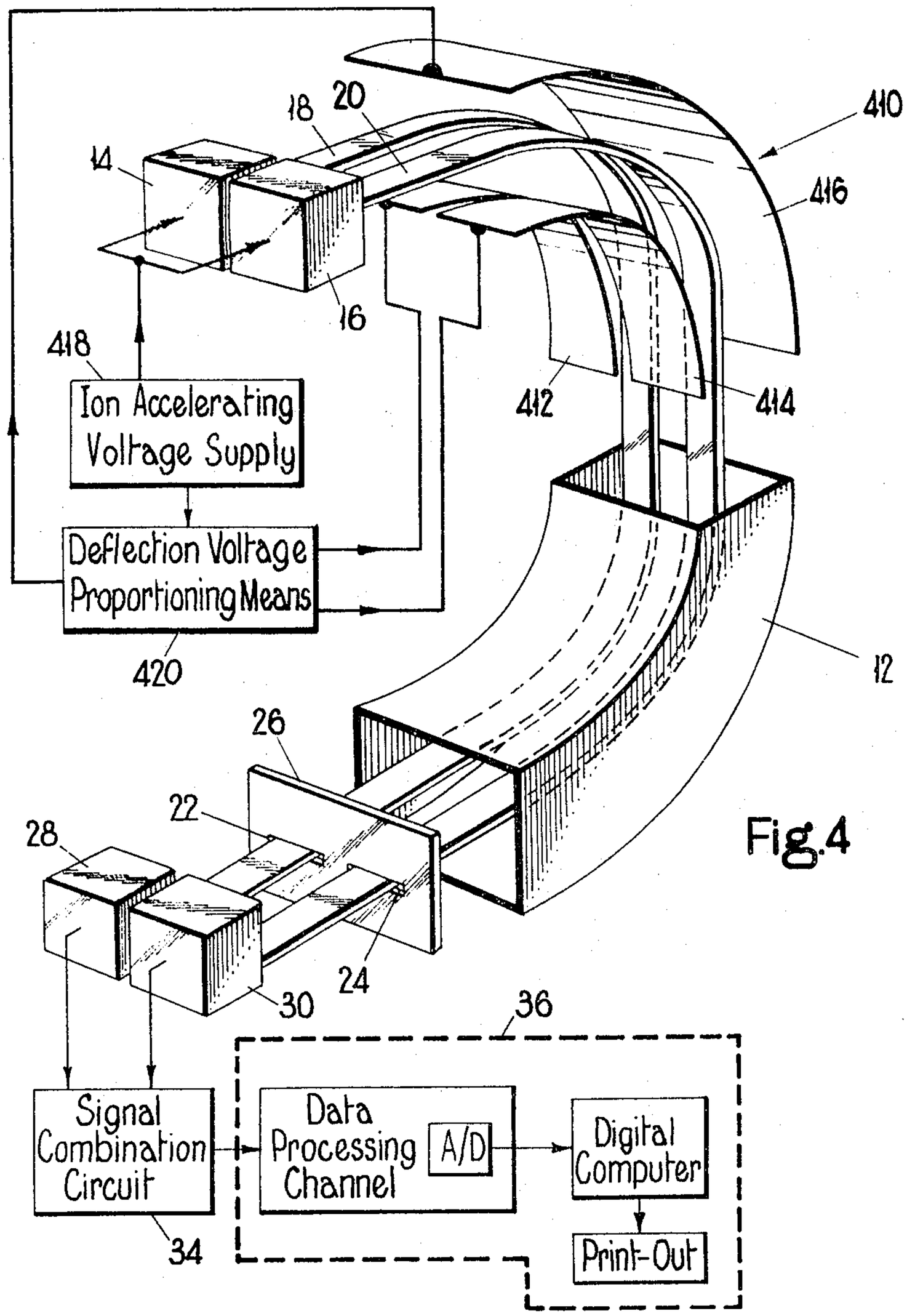
410
18
20
14
416
16
418
Ion Accelerating Voltage Supply
412
414
Deflection Voltage Proportioning Means
420
12
26
22
28
24
30
36
Signal Combination Circuit
Data Processing Channel
A/D
Digital Computer
Print-Out
34

Fig.4

# MASS SPECTROMETRY

## CROSS-REFERENCE TO RELATED APPLICATIONS

"Plural Beam Mass Spectrometer for Conducting High and Low Resolution Studies"
Serial No. 638,133; filed May 12, 1967 by Patrick Powers and now U.S. Pat. No. 3,573,452.
"Plural Beam Mass Spectrometer"
Ser. No. 73,072; filed Sept. 17, 1970 by Brian Noel Green.
"Multiple Slit Assembly for Mass Spectrometers"
Ser. No. 119,250; filed Feb. 26, 1971 by Brian Noel Green and Robert Alexander McDowell and now abandoned.

## BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to mass spectrometers and more particularly to double beam mass spectrometers of the kind described in the above reference Powers and Green applications.

2. Description of the Prior Art

In the analysis of substances with a mass spectrometer, ions of a substance being analysed are generated in an ion source and then expelled from the ion source as an ion beam. The beam passes through a magnetic analyser in the case a single-focusing mass spectrometer; and through an electrostatic analyser and then a magnetic analyser in the case of a double-focusing mass spectrometer.

During a given analysis, the ion accelerating voltage or the magnetic field in the magnetic analyser may be varied to cause a scanning effect which causes ions of different mass-to-charge ratios to be collected by the ion collector of the mass spectrometer. The collection of ions of different mass-to-charge ratios during a scan causes the spectrometer to produce an output which is a mass spectrum of the substance being analysed.

In the above referenced Powers and Green applications, there are disclosures of, amongst other things, the use of two ion sources which simultaneously and independently produce two ion beams which can be of different substances. The two ion beams are passed through a common analyser system and separately collected by two independent ion collectors to produce two mass spectra. The use of a common analyser ensures that ions of the same mass-to-charge ratio in each of the beams are given identical deflections. Thereby the two mass spectra may be mutually correlated to a very high degree of accuracy.

Amongst many other advantages, a double beam mass spectrometer provides the very important capability of chemical mass marking. In chemical mass marking, one of the ion beams is formed from a reference substance, such as perfluorokerosene, which provides a spectrum containing peaks at several known mass-to-charge ratios. Since the reference spectrum is accurately correlated with the spectrum of the unknown substance, the reference peaks act as accurate markers forming a calibrated scale from which the mass-to-charge ratios of peaks of the unknown substance can be interpolated. (In non-chemical mass marking, the relatively difficult and inaccurate process of analytical field measurement is necessary).

There is an ever increasing tendency to employ compouter processing of mass spectrometric analyses,



with the attendant advantages of speed, accuracy, and the elimination of tedious manual calculation and interpretation of results. The dual outputs of a double beam mass spectrometer may be recorded for later processing by a computer, or utilised in real time. Owing to the simultaneous occurrence of the two outputs, they would require separate treatment in prior art arrangements. When converting the analogue outputs to digital signals compatible with the computer, two analogue-to-digital converters would be required. This would double the cost and operating difficulties of a significant part of the system.

## SUMMARY OF THE INVENTION

The present invention provides a method and apparatus for combining signals representative of the simultaneous spectral analysis of two substances, thereby permitting single channel processing of the combined signal.

In accordance with one aspect of the present invention, a double beam mass spectrometer is provided for simultaneously enabling the mass spectral analysis of two substances such as an unknown and a reference substance. The two mass spectra produced by the analysis are given a small relative time displacement so that they can be combined without any peaks overlapping. The resulting single composite signal has no loss of spectral data compared to the two signals before combination, and the composite signal requires only a single analogue-to-digital converter for conversion to a digital form suitable for real-time processing in a digital computer.

The relative displacement can be accomplished in a number of ways. A preferred method is to displace one of the two conventional collector slits of the mass spectrometer in the plane of deflection of the ion beam. Thus ions of the same mass-to-charge ratio in the different beams are collected at slightly different times during a scan. Alternatively the electrical signals representing one of the spectra can be given a time delay, or both spectra could be delayed by different amounts. As a further alternative, the two ion beams could be passed through different electrostatic fields in the electrostatic analyser. These different electrostatic fields can be achieved by splitting one or both of the sectors forming the electrostatic analyser in a plane midway between the planes of the two ion beams, and applying slightly different voltage to the part sectors.

Accordingly, it is the principal object of the present invention to provide novel and improved methods and apparatus for combining into a composite signal the spectral analyses of a plurality of substances.

Other objects and a fuller understanding of the invention may be had by referring to the following description and claims taken in conjunction with the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic perspective diagram of a prior-art double beam mass spectrometer;

FIG. 2 is a schematic perspective diagram of a preferred embodiment of the invention;

FIG. 3 is a schematic perspective diagram of another embodiment of the invention; and

FIG. 4 is a schematic perspective diagram of a further embodiment of the invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIG. 1 there is shown in highly schematic form the general layout of an M.S. 30 double-beam mass spectrometer as sold by AEI Scientific Apparatus Inc. The M.S.30 mass spectrometer is a double-focusing mass spectrometer, and in common with single-beam double-focusing mass spectrometers, possesses an electrostatic analyser **10** and a magnetic analyser **12.** Two ion sources **14** and **16** each produce a respective ion beam **18** and **20** (represented diagrammatically in the drawing) which are then directed through the analysers **10** and **12** for deflection and mass separation in known manner. One of the ion beams contains ions of a reference substance producing peaks of accurately known mass numbers. After leaving the magnetic analyser **12,** the ion beams **18** and **20** each pass through a respective collector slit **22** and **24** in a collector slit assembly **26** thereafter to impinge on respective ion collectors **28** and **30.** The outputs of the ion collectors **28** and **30** are amplified in known manner by electron multipliers and applied to a paper chart printer **32** of known type.

When the magnetic field in the magnetic analyser **12** is scanned, the output of the printer **32** is a chart bearing two traces, each of which is a mass spectrum of the substance from which ions are formed in the respective one of the ion sources **14** and **16.** Owing to the indentity of the analysing fields to which the ion beams **14** and **16** are subjected, the electric signals supplied by the ion collectors are such that at any time throughout the scan, both signals represent the same mass number in each spectrum. The advantage of the spectral correlation is mitigated by the necessity for providing dual data processing channels, each with its own analogue-to-digital converter, as a spectrometer/computer interface if on-line computer processing of results is required, in a manner often employed with single-beam mass spectrometers. In FIGS. **2, 3** and **4** and the following description, applicant shows how this disadvantage may be overcome. In these Figures those parts which correspond to like parts in FIG. **1** are given like reference numerals.

(As aforesaid, FIG. **1** is highly schematic, and many features and details of the M.S. 30 mass spectrometer have been omitted both for clarity and since they are not part of the invention nor are they require for an understanding of the invention).

Referring now to FIG. **2,** the basic M.S. 30 mass spectrometer is employed, but with a modified collector slit assembly **226** wherein two collector slits **222** and **224** have relatively different positions in the respective planes of deflection of the ion beams **18** and **20.** The positional difference "D" between the slits **222** and **224** has the effect that during a scan, ions of any given mass-to-charge ratio in one of the ions beams reaches its respective ion collector at a slightly different time that that at which ions of the same mass-to-charge ratio in the other ion beam reach the other ion collector. A suitable time difference is between 1.5 and 10 milliseconds for a ten second scan, depending on the resolutions of the two beams. (An ideally suitable slit assembly is disclosed in the above referenced Green and McDowell application).

The outputs of the ion collectors **28** and **30** are combined in a suitable signal combination circuit **34** which performs scalar addition of the two signals to produce a single composite signal which resembles the output of a single-beam mass spectrometer when analysing a substance producing frequent peaks. This single signal is then processed in a DS30 data processing unit **36,** as sold by AEI Scientific Apparatus Inc., to produce an output indicative of the substances being analysed. Only a single data processing channel **38** is required, the channel **38** needing only one analogue to digital converter **40.**



Thus, entirely contrary to what might have been expected to be required, the invention enables single-beam data processing equipment to be employed with a double-beam mass spectrometer. The invention also enables mass measurement to be carried at low resolution. This is a feature which is unique to plural beam systems.

The invention is based on the fact that when dealing with samples having peaks with mass numbers not exceeding about **300,** the actual mass displayed by a peak produced by ions of a fraction of nominal mass number N (where N is, of course, an integer) seldom lies outside the range $N - 0.1$ and $N + 0.35$. In these circumstances it is possible to displace the reference spectrum so that its peaks lie in the free zones between actual masses $N + 0.35$ and $N + 0.9$, thus keeping the reference peaks clear of the sample peaks and thereby indentifiable without confusion.

Collector slit displacement is not the only way of achieving the objects of the invention.

FIG. **3** shows an alternative embodiment wherein a standard MS30 mass spectrometer is again employed. The electrical output of one of the ion collectors, (**30**) is time delayed in a suitable signal delay means **42,** and then combined with the undelayed output of the other ion collector (**28**) in the signal combination circuit **34,** the resulting signal being passed to the DS30 data processing unit (**36**) as before. The signal delay means **42** may take any known form, for example an electrical delay line, or (particularly for longer delays and/or slower scans) an ultrasonic delay line. A known form of continuous loop tape recorder with relatively displaced record and playback heads could be utilised as the delay means **42.** For a 10 second scan, a delay of between 1.5 and 10 milliseconds is suitable, depending on the resolutions with which the two beams are collected.

FIG. **4** shows a third alternative embodiment of the invention for achieving spectral displacement. The MS30 mass spectrometer is provided with a dual electrostatic analyser **410** wherein the normally unitary inner electrostatic sector is spit into two sectors **412** and **414** which together with the normal unitary outer sector **416** effectively forms two side-by-side electrostatic analysers. The standard electrostatic analyser (**10**) is normally supplied from the ion accelerating voltage supply via a potentiometric chain of resistors (not shown), and for the purposes of the FIG. **4** embodiment, the ion accelerating voltage from a supply **418** is passed through a delfection voltage proportioning means **420** which delivers correctly proportioned deflection voltages to the sectors **412, 414** and **416.** The correct proportioning of the deflection voltages ensures that as in the FIG. **2** embodiment, ions of a given mass-to-charge ratio in one beam reach the respective ion collector at a slightly different time during a scan than ions of the same mass-to-charge ratio in the

other beam reach the other ion collector. The resulting signals are combined and processed as before.

The proportioning means **420** may take the form of a relatively standard potentiometric chain modified by the provision of a further tap, slightly displaced from the tap for supplying the normal inner sector. As an alternative to splitting the inner sector, the outer sector may be split; or both inner and outer sectors may be split.

Other modifications and variations may be made to the invention.

Although the invention has been described in its preferred form with a certain degree of particularity, it is understood that the present disclosure of the preferred form has been made only by way of example and that numerous changes in the details of construction and the combination and arrangement of parts may be resorted to without departing from the spirit and the scope of the invention as hereinafter claimed.

I claim:

**1.** A double-beam mass spectrometric analytical system comprising variable analytical field producing means to produce a variable analytical field; ion source means to produce two ion beams and direct them through the analytical field; two ion collectors each disposed to collect one of the ion beams; spectral signal producing means to produce a spectral signal from each of the ion collectors in dependence upon the mass-to-charge ratios of collected ions; spectral signal time displacement means to produce a relative time displacement between those parts in each of the spectral signals corresponding to the collection of ions of the same mass-to-charge ratios by the respective collectors, said spectral time displacement means comprising a collector slit assembly defining two collector slits, one in the path of each beam, the slits being relatively displaced such that ions of the same mass-to-charge ratio in each beam pass through their respective collector slit at different times during a scan; displaced spectral signal combination means to combine the relatively displaced spectral signals to form a combined spectral signal wherein peaks from one spectrum lie in the inter-peak spaces of the other spectrum; a single data processing channel including a single analogue-to-digital converter to process and convert the combined spectral signal into a digital computer compatible signal; and a digital computer adapted to receive said compatible signal, said computer being adapted and programmed to act upon data received to interpolate the mass numbers of peaks of one spectrum from the mass numbers of peaks of the other spectrum.

**2.** A double-beam mass spectrometric analytical system comprising variable analytical field producing means to produce a variable analytical field; ion source means to produce two ion beams and direct them through the analytical field; two ion collectors each disposed to collect one of the ion beams; spectral signal producing means to produce a spectral signal from each of the ion collectors in dependence upon the mass-to-charge ratios of collected ions; spectral signal time displacement means to produce a relative time displacement between those parts in each of the spectral signals corresponding to the collection of ions of the same mass-to-charge ratios by the respective collectors, said spectral displacement means comprising differential ion deflection field producing means to produce differential deflection of ions of the same mass-to-charge ratio in the different beams such that during a scan, ions of the mass-to-charge ratio in the different beams pass through the mass spectrometer at different times; displaced spectral signal combination means to combine the relatively displaced spectral signals to form a combined spectral signal wherein peaks from one spectrum lie in the inter-peak spaces of the other spectrum; a single data processing channel including a single analogue-to-digital converter to process and convert the combined spectral signal into a digital computer compatible signal; and a digital computer adapted to receive said compatible signal, said computer being adapted and programmed to act upon data received to interpolate the mass numbers of peaks of one spectrum from the mass numbers of peaks of the other spectrum.

**3.** A method of operating a double beam mass spectrometer comprising ion source means to produce two ion beams, a common ion beam analyser producing an ion analysing field, an ion collector slit assembly including a pair of ion collector slits which are relatively displaced, and two ion collectors producing ion impingement dependent signals, comprising the steps of:

a. forming one of the ion beams from a substance to be analysed;

b. forming the other ion beam from a reference substance;

c. passing both beams through the analyser while scanning the ion analysing field so that the beams impinge upon the collectors to produce signals indicative of the presence in the beams of ions of mass-to-charge ratios dependent on the instantaneous value of the analysing field and over the duration of the scan producing two mass spectra each respectively indicative of the composition of the substances from which the ion beams were formed, each spectrum comprising one or more peaks each indicative of a particular specific mass;

d. giving the two spectra a relative time displacement by passing the two ions beams through the pair of relatively displaced collector slits before they impinge upon the collectors, such that peaks in one spectrum occur during inter-peak spaces in the other spectrum; and,

e. combining the relatively time displaced spectra to form a single composite spectrum.

**4.** A method of operating a double beam mass spectrometer comprising ion source means to produce two ion beams, a common ion beam analyser producing an ion analysing field, an electrostatic analyser, and two ion collectors producing ion impingement dependent signals, comprising the steps of:

a. forming one of the ion beams from a substance to be analysed;

b. forming the other ion beam from a reference substance;

c. passing both beams through the analyser while scanning the ion analysing field so that the beams impinge upon the collectors to produce signals indicative of the presence in the beams of ions of mass-to-charge ratios dependent on the instantaneous value of the analysing field and over the duration of the scan producing two mass spectra each respectively indicative of the composition of the substances from which the ion beams were formed, each spectrum comprising one or more peaks each indicative of a particular specific mass;

d. giving the two spectra a relative time displacement by subjecting the ion beams to different electrostatic fields within the electrostatic analyser, such that peaks in one spectrum occur during inter-peak spaces in the other spectrum: and

e. combining the relatively time displaced spectra to form a single composite spectrum.

**5.** A method of analysing a first substance comprising the steps of:

a. ionising the first substance and forming a first ion beam therefrom;

b. ionising a second substance and forming a second ion beam therefrom;

c. passing the first and second ion beams through a common analytical field wherein ions in each of the beams are deflected according to the mass-to-charge ratios of the ions;

d. passing the first and second ion beams through an ion collector slit assembly including a pair of ion collector slits which are relatively displaced;

e. collecting at any instant ions of a single mass-to-charge ratio in each of the beams;

f. varying the analytical field to vary the mass-to-charge ratios of collected ions and thereby form two relatively time displaced mass spectra one of each of the substances being analysed, each spectrum comprising one or more peaks, each peak representing the presence in the respective ion beam of ions of a mass-to-charge ratio proportional to the instantaneous analytical field at the respective time of collection of the ions, the peaks in the spectrum of the first substance constituting a first series of peaks, the peaks in the spectrum of the second substance constituting a second series of peaks the relative time displacement between the two spectra being such that the first series of peaks occur during inter-peak spaces in the second series of peaks;

g. combining the relatively time displaced spectra to form a single composite spectrum; and

h. interpolating the mass numbers of the first series of peaks from the second series of peaks to provide an analysis of the constitution of the first substance.

**6.** The method of claim **5** wherein said second substance is a reference substance and said second series of peaks are reference peaks occurring at known mass numbers.

**7.** A method of analysing a first substance comprising the steps of:

a. ionising the first substance and forming a first ion beam therefrom;

b. ionising a second substance and forming a second ion beam therefrom;

c. passing the first and second ion beams through an electrostatic analyser, and subjecting the ion beams to different electrostatic fields within the electrostatic analyser;

d. passing the first and second ion beams through a common analytical field wherein ions in each of the beams are deflected according to the mass-to-charge ratios of the ions;

e. collecting at any instant ions of a single mass-to-charge ratio in each of the beams;

f. varying the analytical field to vary the mass-to-charge ratios of collected ions and thereby form two relatively time displaced mass spectra, one of each of the substances being analysed, each spectrum comprising one or more peaks, each peak representing the presence in the respective ion beam of ions of a mass-to-charge ratio proportional to the instantaneous analytical field at the respective time of collection of the ions, the peaks in the spectrum of the first substance constituting a first series of peaks, the peaks in the spectrum of the second substance constituting a second series of peaks, the relative time displacement between the two spectra being such that the first series of peaks occur during inter-peak spaces in the second series of peaks;

g. combining the relatively time displaces spectra to form a single composite spectrum; and,

h. interpolating the mass numbers of the first series of peaks from the second series of peaks to provide an analysis of the constitution of the first substance.

**8.** The method of claim **7** wherein said second substance is a reference substance and said second series of peaks are reference peaks occurring at known mass numbers.

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