Sept. 20, 1960 C. F. ROBINSON 2,953,680

MASS SPECTROMETER

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Fig. 1.

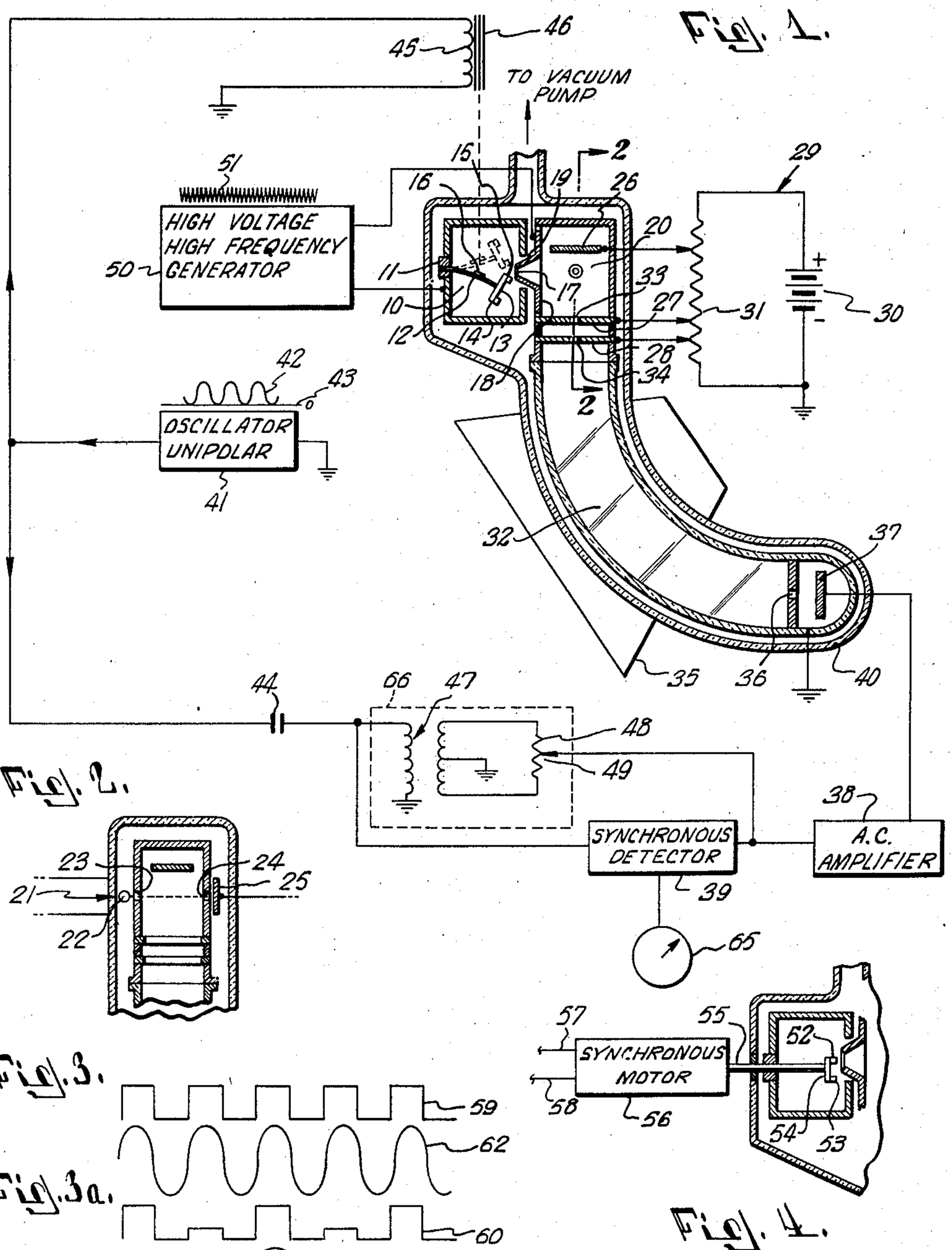

Fig. 2.

Fig. 3.

Fig. 3a.

Fig. 3b.

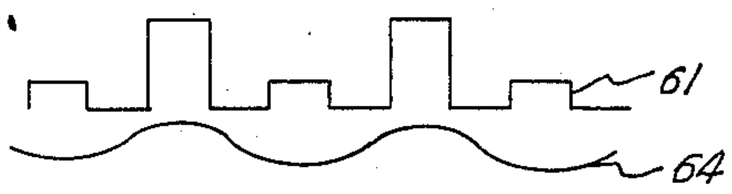

Fig. 4.

INVENTOR.
CHARLES F. ROBINSON

BY

Christie, Parker & Hale.

ATTORNEYS.

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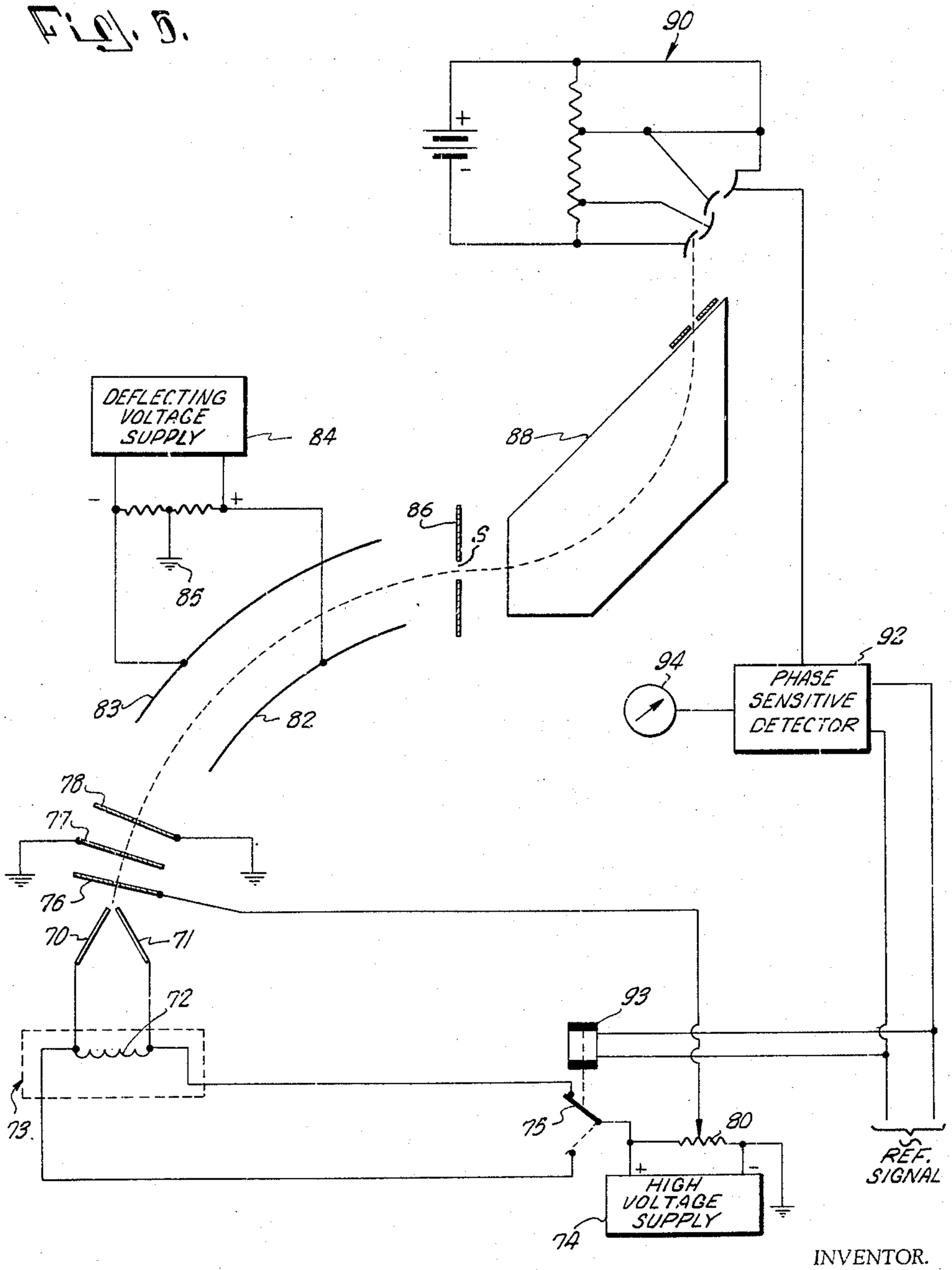
Fig. 5.



INVENTOR.
CHARLES F. ROBINSON

BY

Christie, Parker & Hale

ATTORNEYS

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MASS SPECTROMETER

Charles F. Robinson, Pasadena, Calif., assignor, by mesne assignments, to Consolidated Electrodynamics Corporation, Pasadena, Calif., a corporation of California

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9 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometer and particularly to methods and apparatus for detecting trace amounts of substances in a solid sample being analyzed by mass spectrometry. The invention overcomes the difficulty in analyses for traces of certain materials which are present in the mass spectrometer background.

In the analysis of solids, particularly metals, emission spectroscopy rather than mass spectroscopy is sometimes used. Emission spectroscopy has two main difficulties:

(1) Interferences are more common than not. The intensity of the radiation from one substance will depend, sometimes markedly, on the presence or absence of unrelated materials. In particular, the radiation from some materials is so easily suppressed that they are usually regarded as unmeasurable. Unfortunately, there are many such materials; emission spectroscopy is usually considered limited to some 70 of the elements, the missing ones including I, Br, Cl, S, Se, O, N, H, P, He.

(2) The spectra are very complex. Typical spectra consist of hundreds or thousands of lines; some materials, notably the heavy metals such as tungsten and the rare earths may have hundreds or thousands of lines in the visible portion of the spectrum.

The difficulties mentioned above are negligible in mass spectrometers for the analysis of solids because the enormous interferences common in emission spectroscopy do not occur in mass spectrometers and the spectra are comparatively simple, consisting of at most a few dozen lines. In solid mass spectrometry, however, a problem sometimes arises in analyses for traces of materials present in the mass spectrometer background.

A mass spectrometer is essentially an apparatus for producing ions and sorting them according to the ratio of their mass to their charge, i.e. according to their specific mass.

One method of producing ions from a solid sample is to vaporize the sample in a vacuum with a spark. The vapor is allowed to diffuse in an ionization chamber where the vapor is ionized by electron bombardment. The resulting ions are then propelled into an analyzer as an unsorted beam and in the analyzer are sorted under the influence of a magnetic or electrical field, or both, into groups, say into divergent beams of ions, having the same specific mass. The sorted ions are collected and discharged and the quantity of each kind of ion is measured by the magnitude of the electrical current produced by discharge of the ions.

Another method of producing ions from a solid source also involves a spark source, the spark itself producing the ions which are analyzed. This type of source is used in the double focusing Mattauch type instrument which is described in considerable detail in my co-pending application Serial Number 626,860, filed December 7, 1956, and which is now U.S. Patent 2,851,608, granted September 9, 1958.

The use of a spark presents problems not heretofore solved when a mass spectrometer is employed to detect

elements present in trace quantities in the sample. The intense heat generated by the spark causes materials occluded in the walls of the chamber surrounding the spark source to be released and thereafter ionized along with the same materials vaporized from the sample. An error of indeterminate amount is thus injected in the analysis of such materials in the sample. This problem is particularly acute for traces of materials such as nitrogen, oxygen and carbon which are often occluded in the walls of the chamber containing the spark source and thus form an error-producing mass spectrometer background.

I have discovered that the foregoing difficulty may be overcome, at least in part, by alternately drawing a spark from a sample and a standard of known composition so that bursts of vapor or ions are alternately produced from the two. The vapor bursts are successively ionized and sorted, and the ions of a given specific mass originating respectively in the sample and the standard either directly as ions or indirectly as subsequentially ionized vapor are alternately collected and their charges measured. The measurement of the respective charges shows qualitatively any difference in the relative abundance of a constituent present in both sample and standard and represented by the particular type of ions collected, even though a substantial amount of the constituent is present in the mass spectrometer background.

I prefer to form the alternate bursts of vapor from sample and standard by moving these alternately and periodically into sparking range of an electrode, for example by mounting both sample and standard on a vibrating reed, a revolving turret, or other carrier. However, the same results may be accomplished by moving the electrode alternately into sparking range of the sample and the standard or by employing two electrodes, one disposed within sparking range of the sample and the other within sparking range of the specimen, and alternately energizing the two spark gaps thus formed.

However the bursts of vapor are formed, they are alternately ionized, say thermionically or by a stream of electrons. Bursts of the ions from the two sources are propelled alternately in an analyzer chamber or the like and there sorted on the basis of mass-to-charge ratio, i.e. specific mass. The ions of a given specific mass from the two sources are focused on a collector and discharged to produce an ion current which may be recorded conveniently by a galvanometer as a series of peaks on a chart. If the peaks of ion current are all of equal height, it will be apparent that the constituent being measured is of the same abundance or concentration in both the sample and the standard. If alternate peaks representing the sample are taller than those representing the standard, the constituent is more abundant in the standard, and vice versa.

In the practice of my invention, if the abundance of the constituent being measured is the same in sample and standard, the ion current developed at the collector will alternate at a frequency of $2f$, where f is equal to one complete cycle of the sparking involving the sample and the standard. If, however, the two abundances are unequal, the ion current will contain a Fourier component of frequency f, and the phase of this component will depend upon which abundance is greater. Thus, if the concentration of the constituent in the sample is greater than in the standard the Fourier component of frequency f will be 180 degrees out of phase with the Fourier component produced when the concentration of the constituent is greater in the standard than in the sample.

In a preferred form of my invention this phase relationship is determined by a synchronous detector. An alternating voltage of frequency equal to the frequency of al-

ternation of the samples is used as the gating signal in a synchronous detector and the ion discharge current after suitable amplification is fed into the synchronous detector as a modulating signal. The signal of the output of the detector indicates the relative abundance of the element of interest in the known and in the sample.

In the practice of my invention it is possible to detect slight differences in the abundance of a given element in a standard of known composition and a sample of unknown composition, even through a quantitive analysis for a given element would show substantial abundance in both the standard and the sample due to the mass spectrometer background.

The invention will be more fully understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic view of one form of the mass spectrometer of the invention;

Fig. 2 is a section taken on the line **2—2** of Fig. 1;

Figs. 3, 3A and 3B show the wave forms of current measured at the collector electrode of the spectrometer of Figs. 1 and 2;

Fig. 4 is a fragmentary view of a mass spectrometer like that of Fig. 1, but provided with a different form of sparking device; and

Fig. 5 is a schematic view of a Mattauch type mass spectrometer illustrating the practice of the invention.

The mass spectrometer illustrated in Fig. 1 has a spark chamber **10** with metallic walls to the rear of which a reed support **11** is attached conductively. The reed support holds one end of a conductive reed **12** which extends forward in the spark chamber. The free end of the reed **12** carries a head **13** on which a sample **14** to be analyzed and a moving standard **15** are held in spaced relation. Affixed to the reed approximately at its midpoint is a magnetic button **16**. Opposite the reed clamp the spark chamber has an aperture **17**. A fixed electrode **18** has a hollow conical projection **19** which extends into the aperture in the spark chamber and forms a conduit between the spark chamber and an adjacent ionization chamber **20**. The fixed electrode is insulated from the spark chamber by suitable spacing around the aperture. In the ionization chamber vapors formed in the spark chamber are ionized in conventional manner by electron bombardment.

At one side of the ionization chamber an electron gun **21** (see Fig. 2) is mounted and directs an electron beam **22** across the chamber through apertures **23, 24** in opposite walls of the chamber. A catcher electrode **25** is placed behind the aperture **24** to discharge electrons passing through the chamber. Within the ionization chamber are a repeller **26** and accelerating electrodes **27, 28**. The repeller and accelerating electrodes are connected through suitable leads to a D.C. voltage supply circuit **29**. The voltage supply circuit consists of a battery **30** connected across a slide wire resistor or voltage divider **31** to which the several electrodes in the ionization chamber are connected.

When the voltage divider is properly set, high potentials between the repeller and accelerating electrodes are developed to propel ions from the ionization chamber into an analyzer **32** through slits **33, 34** in the accelerating electrodes. An electromagnet **35** (only one pole face is shown) is placed around the central portion of the analyzer to provide a magnetic field. Under the influence of the magnetic field the ions propelled into the analyzer are sorted into divergent beams according to the specific mass of the ions. By adjustment of the potentials applied to the repeller and accelerating electrodes, the ion beam of interest, i.e. that consisting of ions having a given specific mass, may be focused upon a resolving slit **36** in the end of the analyzer chamber opposite the ionization chamber. A collector electrode **37** is placed behind the resolving slit and is connected to an alternating current amplifier **38** whose output is fed into one side of a synchronous detector **39**.

The spark chamber, the ionization chamber and the analyzer are all contained within an envelope **40**. A vacuum pump, not shown, is connected to the envelope to produce a high degree of vacuum within the envelope.

Outside the envelope a unipolar oscillator **41**, which produces a signal having a wave form shown by reference character **42**, is connected to one side of the synchronous detector through a coupling condenser **44** and to an electromagnet **45** having a magnetic core **46**, thereby forming a magnetic field about the coil. This field fluctuates at the frequency of the oscillator output. In this circuit it is important that the oscillator be unipolar as evidenced by the relation of wave **42** to a zero reference **43** to avoid frequency doubling by the magnet **45**.

Connected in parallel with the synchronous detector is a transformer **47**. One coil of the transformer is connected to the lead carrying the oscillator output and grounded. The other coil of the transformer is center-tapped to ground and bridged by a slide wire resistor **48** having a cursor **49**. The cursor is connected to the output of the A.C. amplifier.

A high voltage high frequency generator **50** has an output illustrated by reference character **51**. The output is impressed between the head and the fixed electrode so that a spark is developed when either the sample or the moving standard is directly above the conical extension of the fixed electrode.

An alternative form of the spark chamber of my invention is shown in Fig. 4 in which a sample **52** and a standard **53** are attached to opposite ends of a head **54**. The head is rotated on a shaft **55** of a synchronous motor **56**. The shaft is aligned so that the sample and the standard will alternately be in sparking range of the fixed electrode as the shaft is rotated. In order that the motor may be placed outside the envelope (as shown), the shaft must be suitably sealed to prevent leakage of air where the shaft goes through the envelope. Leads **57, 58** on the synchronous motor are connected to the output of the oscillator. The output current of the oscillator causes the motor to complete one revolution at the frequency of the output of the oscillator. In all other respects the form of the apparatus of my invention shown as a fragmentary view in Fig. 4 corresponds with the form shown in Figs. 1 and 2.

In the operation of the instrument of Fig. 1 a spark is produced alternately from the sample and from the moving standard. The reed carrying the head to which the sample and the standard are attached is caused to swing between the position shown in solid lines and the position shown in dotted lines by the action of the magnetic field of the electromagnet upon the magnetic button attached to the reed. The magnetic field is formed intermittently when the electromagnet is energized by the output-current pulse from the oscillator. The frequency of the swing of the reed is equal to the signal generated by the oscillator.

A high frequency high voltage is impressed between the head and the fixed electrode so that a spark is developed when either the sample or the standard is directly above the conical extension of the fixed electrode. The head is conductively connected to the spark chamber so that the sparks drawn from the sample and the standard will be cut off once the sample or standard swings beyond the aperture in the spark chamber. As the reed swings back and forth between the two positions shown in Fig. 1 sparks are produced alternately from the sample and from the moving standard. These vaporize the sample and the standard alternately at intervals.

The modified form of my invention shown in Fig. 4 in which the head is rotated likewise alternately produces sparks from the sample and the moving standard and

vaporizes the sample and the standard alternately at intervals. The alternate bursts of vapor thus formed diffuse from the spark chamber into the ionization chamber where they are ionized and propelled into the analyzer. In the analyzer the ions follow a trajectory which is a function of the specific mass of the particular ion if the magnitude of the accelerating potential and the strength of the magnetic field are held constant. In practice the accelerating potential and the magnetic field strength are selected so that ions of a given specific mass will be focused through the resolving slit and discharged on the collector electrode. Discharge of the bursts of ions on the collector electrode produces a measurable current having a configuration similar to one of the square waves shown in Figs. 3, 3A or 3B.

The wave form illustrated by reference character **59** in which the peaks are of equal magnitude occurs when the abundance of the element or molecule of interest is the same in both the sample and the standard. The wave form designated by reference character **60** shows such abundance to be greater in the sample than in the standard while the wave form **61** shows the abundance to be less in the sample than in the standard. In each of the square waves **59**, **60** and **61**, the first peak represents the ion current of the element of interest in the sample and the second peak represents the ion current of the same element in the standard. Sine-wave Fourier components **62**, **63**, **64** of each square wave are shown directly beneath the corresponding square waves of Figs. 3, 3A and 3B.

The relative abundance of the element of interest in the sample and the standard may be compared conveniently by the synchronous detector. The trigger signal or oscillator output having a frequency f is fed into one side of the synchronous detector as a carrier signal. The amplified ion current is fed into the other side of the synchronous detector. The output of the synchronous detector is indicated by a meter **65**.

Where the ion current peaks are of equal magnitude; i.e. the abundance of the element of interest is the same in both sample and the standard, the frequency of the oscillator output will be f and the lowest frequency present in the ion current will be $2f$ and the synchronous detector will have a zero output. However, if the ion current peak from the sample is greater than that from the standard as shown in Fig. 3A, the ion current will contain a Fourier component of frequency f as illustrated by reference character **63**.

If the ion current peak from the sample is less than that from the standard as shown in Fig. 3B, the ion current will contain a Fourier component of frequency f as illustrated by reference character **64**. The wave form **64** is 180° out of phase from the wave form **63** shown in Fig. 3A. When an ion current corresponding to that shown in Fig. 3A is fed into one side of the synchronous detector and the oscillator output is fed into the other side, the meter will indicate an output from the synchronous detector. When an ion current corresponding to that shown in Fig. 3B is fed into one side of the synchronous detector, and the oscillator output fed into the other side, the meter will again indicate an output from the synchronous detector. However, the output will be of opposite sign to the indicated output of the synchronous detector when an ion current corresponding to that shown in Fig. 3A is fed into the synchronous detector as a modulated signal.

In the event any amount of the given element exists in the mass spectrometer background such amount will be represented by an ion current of constant magnitude whether the spark is being drawn from the standard or the sample.

To compensate for any discrepencies in spark intensity between that drawn from the moving standard and that drawn from the unknown, a small amount of the carrier signal, which is the output signal of the oscillator, can be

fed into the modulated signal from the collector electrode by means of the balancing network **66** consisting of the center tapped transformer and the slide wire resistor. The amount of the signal to be fed in from the trigger source is determined by setting the instrument to analyze the amount of an abundant element such as iron which would exist in approximately equal concentrations in the unknown if the intensity of the spark from the sample and the standard were equal. Under such circumstances unequal spark intensities would register as an output of the synchronous detector. By an adjustment of the slide wire resistor an amount of the carrier signal is fed into the signal from the collector electrode until the output from the synchronous detector is at zero, thereby compensating for differences in spark intensities throughout the mass spectrum for the sample and the standard then being compared.

The alternative form of mass spectrometer shown schematically in Fig. 5 is characterized by production of ions directly in a spark developed between two electrodes. In accordance with the present invention, these two electrodes are composed respectively of the material of the standard and the solid sample to be analyzed. The instrument includes an ion source, in this instance spark electrodes **70** and **71** connected at opposite ends to the secondary winding **72** of a transformer **73**. The transformer coil is connected to the positive side of a high voltage supply **74** through a switch **75** by means of which the high voltage supply is alternately connected to one and then the opposite side of the coil.

First, second and third apertured electrodes **76**, **77** and **78** are arranged serially in alignment with the spark gap, electrode **76** being connected through a suitable voltage divider **80** to the high voltage supply and serving as an accelerating electrode to propel ions from the spark source as a beam through the electrodes **77** and **78**.

An electrostatic deflector constituting curved plates **82**, **83**, is arranged serially with respect to the electrodes, the beam issuing from the electrode array and entering the deflector as shown. The two plates of the deflector are connected to opposite sides of a deflecting voltage source **84** and as illustrated both plates are at a pre-assigned potential with respect to ground **85**. A fourth apertured electrode **86** may be disposed adjacent the exit end of the electrostatic deflector. Electrode **86** has an aperture S 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.

A transverse magnetic field is formed in a conventional manner by a pair of magnetic poles, one of which, pole piece **88**, 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 **88** to form a magnetic field therebetween transversely of the direction of the ion travel into the magnetic field. Ion sensing means such as an electron multiplier **90** is employed for collecting ions focused thereon. For the accomplishment of the present invention an alternating reference signal from an oscillator (not shown) is applied both to a phase sensitive detector **92** and to a solenoid **93** operative to alternately interconnect the positive side of the high voltage supply **74** to opposite sides of transformer coil **72**. An output sensing device **94** of any conventional nature is connected to the phase sensitive detector.

The function of the apparatus for carrying out the objectives of the invention is substantially identical to the operation of the apparatus of Fig. 1 as previously described, and is further apparent from the illustrated circuitry.

Thus, by my invention it is possible to detect slight differences in the abundance of a given element in a standard and in an unknown even though the mass spectrometer may show substantial abundance of the element in both the standard and the unknown due to

the existence of the element in the mass spectrometer background.

I claim:

1. In a mass spectrometer for analyzing a solid, said mass spectrometer having an analyzer in which ions produced from the solid are sorted according to their specific mass and a collector electrode for collecting the ion current, the combination comprising a chamber communicating with the analyzer, a sample and a standard disposed in the chamber, means for alternately drawing a spark from the sample and from the standard to alternately produce bursts of ions from the two, means for propelling the alternate ion bursts into and through the analyzer and means connected to the collector electrode to indicate the relative abundance of a given type of ion in the sample and the standard.

2. In a mass spectrometer for analyzing a solid, said mass spectrometer having an analyzer in which ions produced from the solid are sorted according to their specific mass and a collector electrode for collecting the ion current, the combination comprising a chamber communicating with the analyzer, a sample and a standard disposed in the chamber, an alternating current source, means energized by said alternating current source for alternately drawing a spark from the sample and from the standard to alternately produce at a multiple of the frequency of the alternating current bursts of ions from the two, means for propelling the alternate ion bursts into and through the analyzer and means connected to the collector electrode and to the alternating current source to indicate the relative abundance of a given type of ion in the sample and the standard.

3. In a mass spectrometer for analyzing a solid, said mass spectrometer having an analyzer in which ions produced from the solid are sorted according to their specific mass and a collector electrode for collecting the ion current, the combination comprising a chamber communicating with the analyzer, a sample and a standard disposed in the chamber, means for alternately drawing sparks from the sample and from the standard at a given frequency to alternately produce bursts of ions from the two, means for propelling the alternate ion bursts into and through the analyzer, a synchronous detector, and means connected to the collector electrode for supplying its output to the synchronous detector to modulate the carrier wave.

4. In a mass spectrometer having means in a chamber for vaporizing a material to be analyzed, means for ionizing the vapor thus produced, and means for sorting and collecting the ions thus produced according to their respective specific masses, the combination which comprises an electrode disposed in the chamber, a carrier disposed in the chamber, a solid sample piece mounted on the carrier, a solid standard piece mounted on the carrier and spaced from the sample piece, means for moving the carrier to cause the sample piece and the standard piece to pass alternately and periodically into close proximity with the electrode, and means conductively connected to the sample piece and the standard piece to set up an electrical potential for generating a spark when either of the pieces is in close proximity with the electrode to produce alternate bursts of ions from the sample piece and the standard piece in the chamber.

5. In a mass spectrometer having means for vaporizing a material to be analyzed in a chamber, means for ionizing the vapor thus produced, and means for sorting the ions thus produced according to their respective specific masses, and means for collecting the sorted ions, the combination which comprises an electrode disposed in the chamber, a carrier disposed in the chamber, a solid sample piece mounted on the carrier, a solid standard piece mounted on the carrier and spaced from the sample piece, means for moving the carrier at a given frequency to cause the sample piece and the standard piece to pass alternately and periodically at said frequency into close proximity with the electrode, means connected to the electrode and to the sample piece and the standard piece for setting up an electrical potential for generating a spark when either of the pieces is in close proximity with the electrode to produce alternate bursts of ions from the sample piece and the standard piece in the chamber, a synchronous detector, means for supplying to the detector a carrier wave of said frequency, means connected to the ion collection means and to the detector for modulating the carrier wave with the output of the ion collector means.

6. In a mass spectrometer for analyzing a solid and including an analyzer in which ions produced from the solid are sorted according to their specific mass and a collector electrode for collecting the sorted ions to produce an ion current, the combination which comprises a chamber communicating with the analyzer, a solid sample and a solid standard disposed in the chamber, means for alternately sparking the sample and the standard at a given frequency and thereby producing alternate bursts of ions from the sample and the standard at said frequency, a synchronous detector, means for producing in the synchronous detector an alternating carrier potential of said frequency, means connected to the collector electrode for modulating the carrier potential with the ion current, and means for measuring phase change of the modulated carrier potential.

7. Apparatus according to claim 6 provided with an electrode in the chamber, electromagnetic means for alternately moving the sample and the standard in and out of sparking range of the electrode and also provided with an oscillator which powers the electromagnetic means and also provides the alternating carrier potential to the synchronous detector.

8. Apparatus according to claim 7 in which the electromagnetic means includes an electromagnet and a reed disposed in the chamber and vibrated by the magnet and carrying the sample and the standard.

9. Apparatus according to claim 7 in which the electromagnetic means includes a motor, and the sample and the standard are mounted on a turret disposed in the chamber and rotated by the motor.

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