

Aug. 23, 1960

F. A. WHITE
MASS SPECTROMETER

2,950,388

Filed Oct. 24, 1957

3 Sheets-Sheet 1

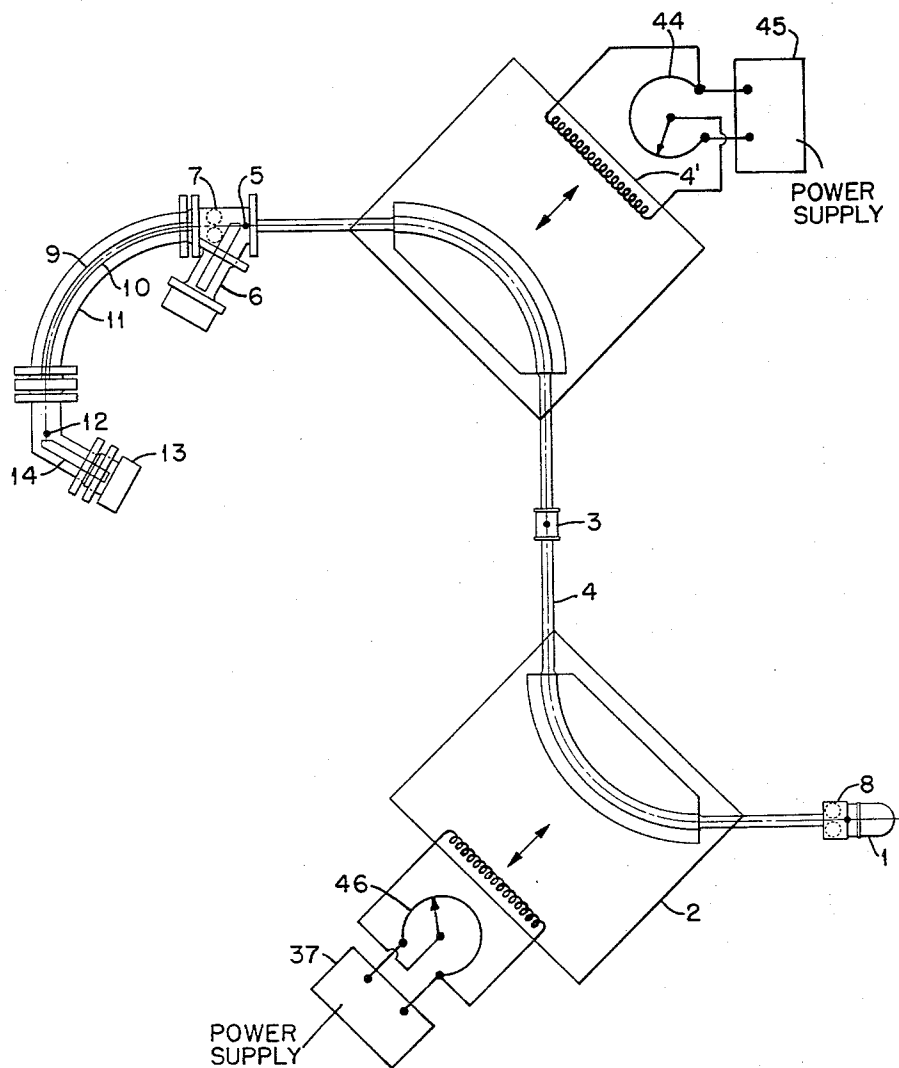


Fig. 1.

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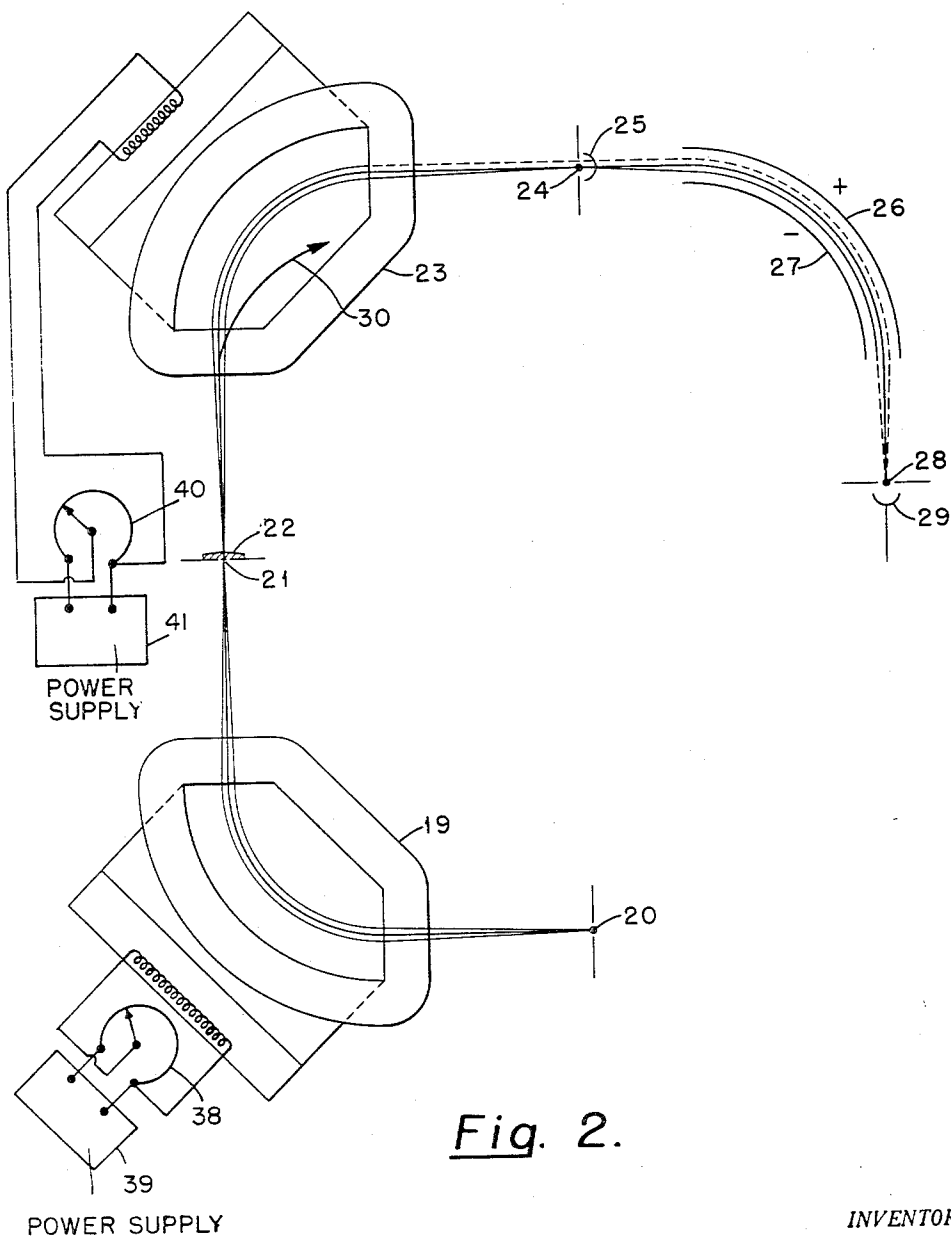


Fig. 2.

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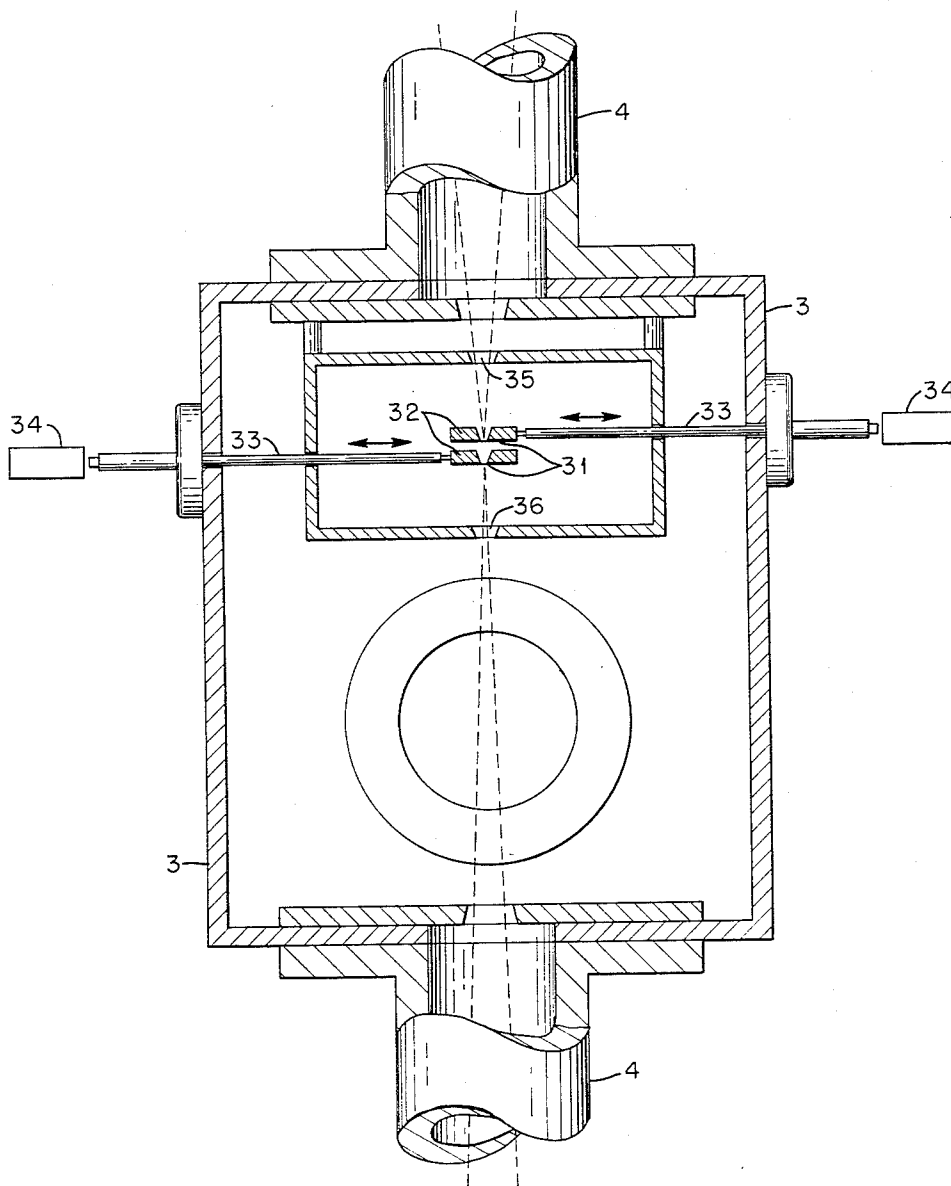


Fig. 3.

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2,950,388

MASS SPECTROMETER

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7 Claims. (Cl. 250—41.9)

The present invention relates to a method for generating atomic ions, and more especially to a novel method of and means for obtaining pure atomic spectra and eliminating therefrom molecular ions of the same charge and the same mass. The invention has particular application to the field of mass spectrometry.

In a mass spectrometer ion source, electrons from a filament serve to ionize a gas and the ions are withdrawn from the region of their formation and accelerated into a beam. Both molecular ions and atomic ions may be present in large numbers in the beam. In a conventional analytical mass spectrometer, the resolution is insufficient to resolve the mass differences between ions such as Na-23 and $\text{Li}^{17}\text{O}^{16}$, for example, which have substantially the same mass-to-charge ratio M/E . Hence there is no way for the mass spectrometer operator to determine which type of ion is being received at the collector.

Accordingly it is an object of this invention to provide a novel method of and means for resolution or differentiation between atomic and molecular ions having identical mass-to-charge ratios. Another object of this invention is to provide a beam solely of atomic ions by generating in a source both molecular and atomic ions, focussing the ions into a mixed beam, dissociating the molecular ions in flight, and refocusing the resulting atomic ions together with the atomic ions already present by passing them through an analyzing system. Still another object is to provide a method for identifying a complex ion present as an impurity. Yet another object is to improve ratio measurements in the presence of impurities. These and other objects of this invention will be best understood by reference to the following detailed description, when read in conjunction with the appended drawings, wherein:

Fig. 1 illustrates one form of apparatus suitable for providing and measuring a beam of atomic ions;

Fig. 2 illustrates schematically the paths taken by atomic and molecular ions in passing through an alternative embodiment of the novel apparatus of Fig. 1; and

Fig. 3 illustrates a suitable slit assembly including the foil, frame, and slits for use with the above apparatus.

According to the invention, ions are generated in an ion source and focused into a beam which is then accelerated into a magnetic analyzer and bent through 90° . Ions of a single M/E ratio emerging from the analyzer are dissociated, preferably by focusing them on a thin foil, which a significant fraction pass through due to the high accelerating voltage (about 30 kev. or greater). The beam may be alternatively partially dissociated by raising the local pressure in the analyzing tube, near the region of the focal point of the analyzer, as by differential pumping, without use of the foil, but the foil gives much more complete dissociation and is preferred for low mass elements. The foil serves to dissociate substantially all of the molecular ions into their atomic constituents. I have found that a significant fraction of

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these ions lose only a small amount of their kinetic energy and retain their charge, so that they can be refocused and detected. The ions passing through the window are then bent through 90° by another magnetic analyzer, and may be counted by means such as an electron multiplier at the focal point. They are further bent through 90° in an electrostatic analyzer and collected on an electron multiplier at the focal point of the electrostatic analyzer. In this manner a pure atomic spectrum can be generated. In mass spectrometry, impurities can be detected and identified by dissociating complex ions into their component elements and observing the mass of the resultant ions. In isotopic ratio measurements, the removal of impurity ions in the described manner avoids large possible errors due to impurities of equal mass with one of the elements, such as $\text{Li}^{17}\text{O}^{16}$ in a Na-23/Na-24 measurement, or a tungstate ion at mass 202 in Pb-202 measurement. Much better isotopic analyses are possible, even at high masses, using dissociation by residual gas molecules in the analyzer.

Referring now to Fig. 1, a conventional electron bombardment type of ion source 1 may be used to bombard molecules fed thereto. Ions produced are accelerated from the ion source into a magnetic analyzer 2. The magnetic field strength is adjusted by means of a conventional rheostat 44 in the power supply 45 therefor so that particles of the desired mass-to-charge ratio are focused on source slit 3 in analyzer tube 4. A thin foil, which may be mounted on a metallic frame, is placed adjacent the slit 3 to intercept the beam. The frame may be made removable from the beam by a small hand magnet external to the vacuum system, to avoid opening the system. Ions passing through the slit 3 are focused by a second magnetic analyzer 4' at a focal point 5. In the absence of the foil across slit 3, the mixed beam will be detected at point 5 by an electron multiplier 6 attached thereto. The system may be evacuated through suitable diffusion pumps 7, 8 in the conventional manner. Reference is made to "Applied Spectroscopy," Nov. 1954, pp. 169-173 for a description of a two-stage magnetic analyzer without the foils. After the foil is inserted to intercept the beam through slit 3, the strength of magnetic analyzer 4' is varied by means of a conventional rheostat 46 in the power supply 37 therefor. Multiplier 6 will detect an ion beam at a lower field strength than that previously required to focus the mixed beam at point 5, because of the degradation of energy suffered by the atomic ions in passing through the thin window.

Further positive identification of the ions may be made with the electrostatic analyzer which includes a pair of curved parallel plates 9, 10 inside a Pyrex pipe 11. It is arranged to focus the beam at point 12 at the entrance to electron multiplier 14. Amplifier 13 may further amplify the current from the multiplier and may be connected to a suitable display device such as a chart recorder or meter. It will be apparent that by using three separate analyzers, errors due to elastic scattering of ions is greatly reduced. Resolution achieved with this arrangement is so great that measured contribution of the Na-23 beam at the mass 23.5 position (at focal point 12) was only one part in 10^{11} , for example. I have found that the electrostatic analyzer should be the last path for the beam, so that ions of only a single mass enter the electrostatic analyzer at one time. When the electrostatic analyzer is instead placed adjacent the ion source 8, large beam currents of ions or neutral atoms tend to build up an insulating coating on the deflecting plates, interfering with proper operation of the analyzer. While the plates 9, 10 could be formed of

metal, the plates preferred are formed of Pyrex glass coated with platinum or gold.

The triple analyzer above described, but having no foil across the slit 3, may be used for determining simultaneously the ratio of ions of different masses present in a beam to be analyzed. One very useful measurement is that of the ratio of uranium-235 to uranium-238 in a gaseous diffusion cascade. The lighter ion may be measured by the detector 6 while simultaneously the heavier ion is measured by the detector 14 after it has been passed through the electrostatic analyzer. The complex ion $6K_{39}$, having a mass of about 234 may be present, and could be removed by a very thin foil which leaves sufficient residual kinetic energy in the ions for subsequent analysis.

Referring now to Fig. 2, ions of many masses are assumed to originate at a point source 20. Both atomic and molecular ions are accelerated out of the source and passed through a magnetic analyzer 19, adjustable by means of rheostat 38 in power supply 39 therefor. The analyzer will bring the ions into focus along different points in the focal image plane depending upon their respective mass-to-charge ratios. Ions having the same mass-to-charge ratios will be bent on the same radius of curvature and focused on point 21. The thin foil 22 is disposed at the focal point 21. As the molecular ions and neutral particles in the beam penetrate the foil, most of the molecules will be dissociated. The foil may be considered to provide uncorrelated forces which act on the various atoms of the molecule and break the weak molecular bond. The atomic ions are brought to focal point 24 with a radius of curvature smaller than that in the analyzer 19 because of the loss of energy in the foil. The neutral fragments resulting from dissociation will not bend in the magnetic analyzer 23, but will continue along the path from foil 22. The lighter fragments of the molecule, if they are charged, will have a quite different radius of curvature as shown by the arrow 30, from that which the molecules had in the first analyzer. For example, an O-16 ion broken off a water molecule would cause a difference in radius of curvature of 16 mass units. The strength of the second analyzer 23 may accordingly be adjusted by rheostat 40 in the power supply 41 therefor to focus the light fragments upon the point 24, where they may be detected by an electron multiplier 25.

The sorted ion beam is then passed through an electrostatic analyzer including plates 26, 27, to which a suitable potential difference is applied. The resulting beam is focused at point 28 and detected by suitable electron multiplier or other detector 29. By using the electrostatic analyzer in addition to magnetic analyzer 23, the effect of the energy spread due to ions passing through the foil 22 can be minimized. Therefore a sharp spectrum of pure atomic ions may be observed at the image point 28. The first magnetic analyzer may be oriented as shown in Fig. 2 or as shown in Fig. 1, its direction with respect to the analyzer 23 being a matter of choice. The electrostatic analyzer, however, should be oriented as shown.

Referring now to Fig. 3 thin foils 31, 31 are mounted on the underneath side of rectangular metal frames 32, 32, and disposed between variable slits 35, 36, which form a rectangular box within slit assembly 3 and communicate with analyzer tube 4. A small hand magnet 34 may be used to move the frame, to avoid opening the system, by means of extension rods 33, 33 which support the frames. The rods are provided with nickel ends so that they may be moved by the magnet to withdraw or insert them from or into the beam.

Table I indicates some of the molecules and atoms which have been analyzed in the spectrometer, using a very thin film (No. 1) and a thicker film (No. 2). It will be noted that with a thicker film, higher voltages

are required and a greater energy degradation (ΔE) in the film results.

Table I

Film No.:		Accelerating High Voltage (kilovolts)	Magnetic Field (gauss)	ΔE (kilovolts)
1	H ₂ O	29.2	2,067	4.0
2	H ₂ O	36	2,255	4.6
1	CO ₂	51	2,682	7.9
1	Li ⁷	45	3,946	5.0
1	Li ⁷	32	1,348	2.04
1	Na ²³	37	2,596	2.4
1	K ³⁹	50	3,899	6.5
1	Rb ⁸⁵	31.2	4,522	9.3
1	O ¹⁶	46.5	2,417	7.7
2	A ⁴⁰	50	3,946	12.7
2	He ⁴	50	1,245	4.6
2	H ¹	50	630	4.0

One suitable thin foil was prepared from a nickel foil by removing the thick copper backing on which nickel had been electrostatically deposited. A nickel foil about 250 A. thick should be satisfactory for many applications. A second foil was made by evaporating aluminum on an organic film. A preferred foil was an organic resin film about 100 A. thick, prepared as described in Canadian Journal of Chemistry 33, 15 (1955). To allow low energy ions to penetrate the foil, it is made as thin as possible. A foil substantially 100 A. thick will dissociate virtually any complex ion. The accelerating voltage required to propel the ions through the foil increases with the mass of the ion and foil thickness.

At pressures of about 10^{-6} mm. Hg in the analyzing tube in the region of slit 3, I have observed that some ions dissociate on impact with the residual gas molecules in the tube, and with increased pressure in that region, the amount of dissociation increases. With a CO₂⁺ beam, for example, the C-12⁺ and O-16⁺ ions have been observed after dissociation. Since energy losses only a few volts are caused by such dissociation, its applicability to high mass analysis is apparent.

It will be apparent to those versed in the art that I have discovered improved means for generating atomic spectra of special importance to mass spectrometry.

Having described the invention, what is claimed as novel is:

1. In a mass spectrometer including an ion source which produces both atomic and molecular ions, means for forming said ions into a beam, magnetic means for resolving the ion beam into beams of selected masses, an ion detector, and means to measure the current at said detector, the improvement which comprises: additional means for resolving the ion beam from said magnetic means into beams of selected masses disposed in spaced relation to said magnetic means, means disposed in the path of said beam between said magnetic means and said additional means to dissociate molecular ions in flight, means to adjust said magnetic means to focus ions of selected mass at a focal point between said magnetic and said additional means, and means to adjust said additional means to focus ions of selected mass on said detector.

2. In a mass spectrometer including an ion source which produces both atomic and molecular ions, means for forming said ions into a beam, magnetic means for resolving the ion beam into beams of selected masses, an ion detector, and means to measure the current at said detector, the improvement which comprises: additional means for resolving the ion beam from said magnetic means into beams of selected masses disposed in spaced relation to said magnetic means, a thin foil disposed in the path of said beam between said magnetic means and said additional means to dissociate molecular ions incident thereon, means to adjust said magnetic means to focus ions of selected mass on said foil, and means

to adjust said additional means to focus ions of selected mass on said detector.

3. In a mass spectrometer including an ion source which produces both atomic and molecular ions, means for forming said ions into a beam, magnetic means for resolving the ion beam into beams of selected masses, an ion detector, and means to measure the current at said detector, the improvement which comprises: additional means for resolving the ion beam from said magnetic means into beams of selected masses disposed in spaced relation to said magnetic means, an analyzer tube connecting said source with said detector and disposed within the resolving fields of said magnetic and said additional resolving means, respective means to adjust said magnetic and said additional means to focus ions of selected masses at a focal point between said magnetic and said additional means and upon said detector, respectively, and means to control the pressure within said tube in the region of said focal point to dissociate molecular ions in said beam.

4. In a mass spectrometer including an ion source which produces both atomic and molecular ions, means for forming said ions into a beam, first magnetic means for resolving the ion beam into beams of selected masses,

an ion detector, and means to measure the current at said detector, the improvement which comprises: second magnetic means for resolving the ion beam from said first means into beams of selected masses disposed in spaced relation to said first means, a thin foil disposed in the path of said beam between said first and second magnetic means to dissociate molecular ions incident thereon, respective means to adjust said first and second magnetic means to focus ions of selected masses, and a third means for further resolving the ion beam from said second means into beams of selected masses disposed in spaced relation to said second means, said detector being disposed adjacent said third means to receive the ion beam.

5. The device of claim 2 wherein said foil is an organic resin film at least substantially 100 angstrom units thick.

6. The device of claim 2 wherein said foil is nickel of greater thickness than 100 angstrom units.

7. The device of claim 4 wherein said third means comprises a pair of oppositely charged, curved, spaced apart plates forming an electrostatic analyzer.

No references cited.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,950,388

August 23, 1960

Frederick A. White

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 1, line 36, for "idential" read -- identical --;
column 4, line 10, Table 1, third column thereof, first line,
for "29.2" read -- 29.5 --.

Signed and sealed this 11th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents