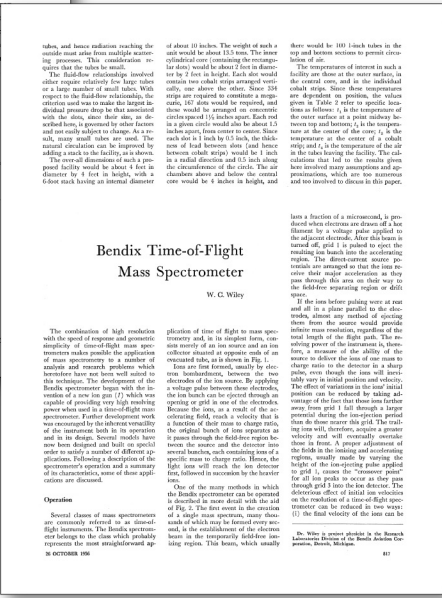


The Bendix Time-of-Flight Mass Spectrometer

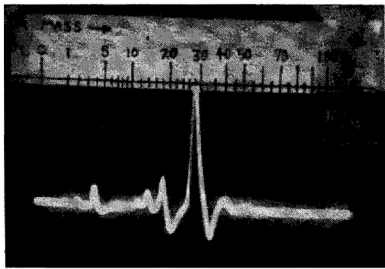
Michael A. Grayson, Washington University in St. Louis
American Society for Mass Spectrometry

In a time not that long ago and a place not too far away, a time-of-flight mass spectrometer for commercial sale was introduced by the Cincinnati Division of Bendix, an automotive, aerospace and industrial company. This was the first successful commercial instrument that was not based on magnetic sector analyzer technology. Preceding the introduction of the instrument, William C. Wiley, then at the Bendix Aviation Corporation Research Laboratories, and his

co-worker Ian H. McLaren reported on the development of the instrument in the *Review of Scientific Instruments and Science*.



Earlier Work

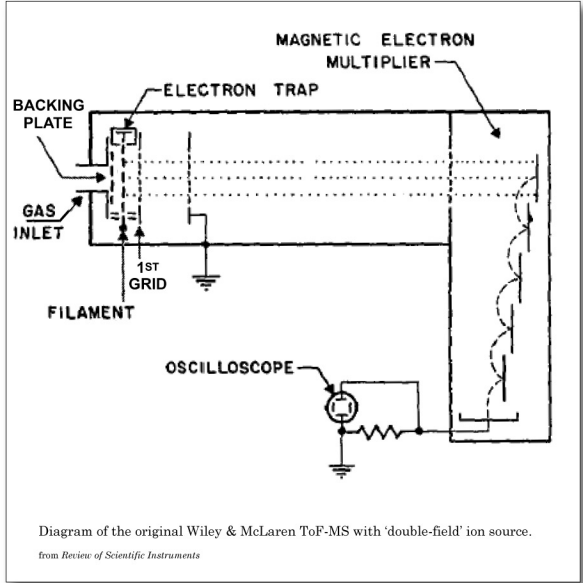


Mass spectrum of atmospheric gases and helium showing ion peaks ascribed to H⁺, H₂⁺, He⁺, C⁺, N⁺, H₃O⁺, N₂⁺, and A⁺.

Stephens of the University of Pennsylvania reported on a linear time-of-flight instrument at the April meeting of the American Physical Society in 1946 and followed that with a paper in *Review of Scientific Instruments* in 1953.

The idea for a mass spectrometer based on the difference in time that it would take ions of different mass to traverse a field-free region given the same kinetic energy was explored for over a decade before the Bendix instrument was introduced. Mass spectrometry was an important tool in the Manhattan Project and while sector instruments designed by Nier were used extensively, other mass analyzer technologies were explored as part of the Project. William

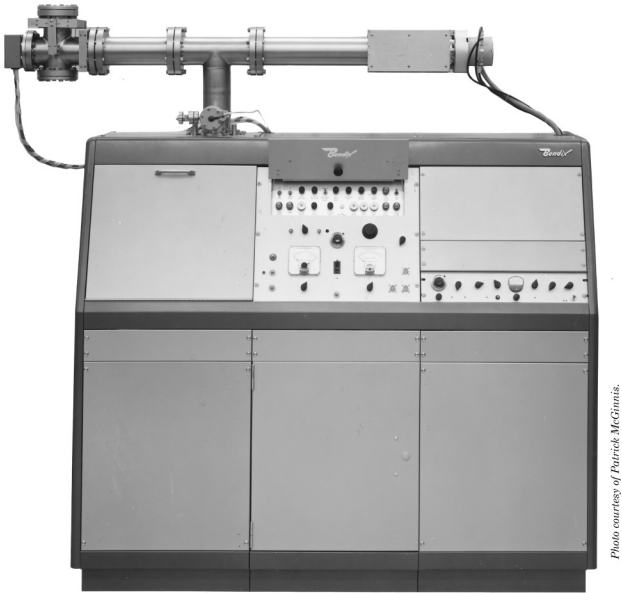
The problem that Wiley and McLaren saw as limiting the development of a commercial time-of-flight instrument was the need to accelerate discrete ion bunches to kilovolt energies using the state-of-the-art electronics available at that time. Instead of trying to accelerate the ion bunch in a ‘single-field’ source by pulsing a grid through a large potential difference, thousands of volts, they devised the ‘double-field’ source which had fixed high voltages and applied a low voltage pushout pulse on the grid at the back of the ion formation region.



In addition, the ‘double-field’ source enabled the use of an ion focusing technique that the authors called ‘Time-Lag Energy Focusing’; known today as delayed extraction. By varying the time between the pulse of ionizing electrons and the pushout pulse, the conditions for combined space and energy focusing could be optimized for ions over a select mass range.

Detection

Ion detection presented a serious challenge as well. In particular, ion packets arriving at the detector had peak widths on the order of 10 nsec and contained an extremely small amount of charge. An electron multiplier with 100 MHz response and amplification on the order of a million or more was required. Bendix developed their own electron multiplier using continuous dynodes immersed in an orthogonal magnetic field. This device was capable of providing both the frequency response and gain necessary to obtain mass spectra from the instrument.



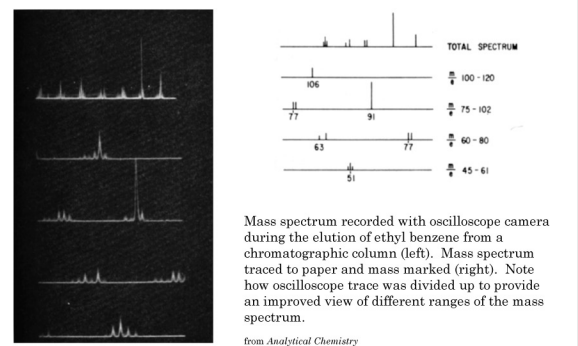
Bendix Model 12-101A; ca 1961

Design

GC/MS

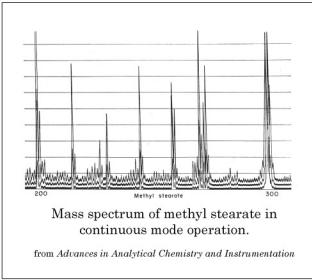
The coupling of a gas chromatograph to a mass spectrometer was demonstrated in 1957 by Holmes and Merrill for a magnetic sector instrument. However, they could only observe a 16 mass unit portion of the spectrum on an oscilloscope. Gohlke also reported a GC/MS combination instrument based on the Bendix ToF-MS in 1957 followed by a more detailed description in 1959. While mass spectra were still displayed on an oscilloscope, the mass range was as broad as the instrument could produce, typically 6000 amu with the instrument operating at a frequency of 2 kHz.

The subsequent development of the output scanner (see maintext) provided a means of oscillographic recording the complete mass spectrum of individual GC peaks in real time, on the order of several seconds per spectrum. This was a significant improvement over any other combined GC/MS instrument of the time since sector instruments took at least an order of magnitude longer to scan the mass spectrum.



Recording

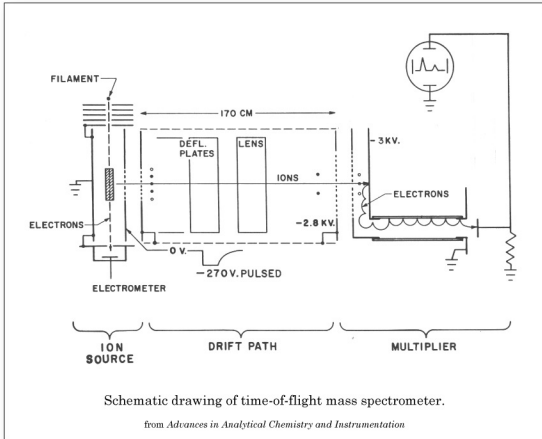
Initially, the primary output of the instrument was the oscilloscope display. Permanent records of the spectrum could be obtained with the use of an oscilloscope camera, but this was not an optimum recording medium. To remedy this problem, an output scanner, based on the concept of a ‘boxcar integrator’, was designed such that it would integrate the output of the electron multiplier for a small fraction of each spectrum. By continuously shifting the integration period to later portions of subsequent spectra, a signal, comparable to that from sector instruments, could be obtained for oscillographic recording.



Mass spectrum of methyl stearate in continuous mode operation.

After a series of prototype designs, one of which was placed into service in Fred Mc Lafferty's lab at Dow Chemical in Midland Michigan, the Model 12-101 was produced and marketed. Don Damoth described this instrument in 1965 in *Advances in Analytical Chemistry and Instrumentation*.

It had a 1.7 m field-free region and operated at an accelerating potential of 2.8 kVdc. The ion source was at ground potential and the field-free region was maintained at accelerating potential by means of a cylindrical screen with glass standoffs inserted inside the vacuum envelope. It had both a lens and a set of deflection plates in the field-free region to focus the ions onto the detector. The instrument operated at a fixed frequency of 10kHz and had a mass range of ~1800 u. It used an electron ionization source with trap current regulation. Under these design conditions, the instrument produced hydrocarbon mass spectra very similar to those of contemporary magnetic sector instruments. This was an important goal for Bendix as one of the primary applications of commercial mass spectrometers was in the field of petrochemistry.



Schematic drawing of time-of-flight mass spectrometer.

Demise

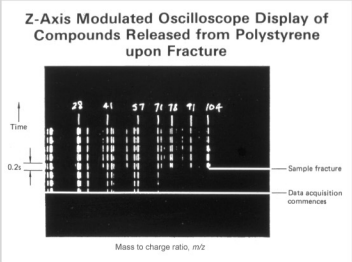
Even though the Bendix ToF-MS was well-suited for application as a GC/MS instrument and had been used to develop the technique, sales of the instrument declined in the early ‘70s. With the introduction of the quadrupole mass filter by Finnigan Corporation as an analytical mass spectrometer, sales of Bendix instruments began to drop off. Quads took over a larger and larger share of the ‘fast scanning’ instrument market after Hewlett Packard began marketing their quadrupole mass filter and eventually Bendix became part of Consolidated Vacuum Corporation, a manufacturer of vacuum systems and components. Interest in the analytical instrument part of CVC waned and eventually died out. By the mid ‘70s most people in the community considered mass analyzers based on the time-of-flight concept to be completely forgotten and useless; never to be heard from again!

“... a modified Bendix Time-of-Flight mass spectrometer ...”

While the Bendix instrument was not well-received in the community of sector instrument users, its unique ability to produce spectra on the millisecond time scale was attractive to a different community of scientists. An added feature that may or may not have been intentional in the instrument design was the large open ion source and the easy accessibility to the ion source housing which hung over the end of the instrument chassis. Simple vacuum flanges that could be easily modified to accommodate new and unusual experiments made the instrument particularly popular for those adventurous souls wanting to apply mass spectrometry to new areas of chemistry.

More often than not, abstracts of journal articles and conference proceedings would contain the phrase “a modified Bendix Time-of-Flight mass spectrometer was used to . . .” or “a Bendix time-of-flight mass spectrometer has been modified to . . .”. Besides the development of GC/MS, the instrument was applied to a wide variety of problems:

- Investigation of thermodynamic properties of inorganic compounds by modifying the ion source to accommodate a Knudsen cell
- Studies of photochemical oxidation
- Studies of ion-molecule or neutral particle-molecule interactions
- Investigation of noble gas compounds
- Chemical-ionization reactions in high-temperature hydrocarbon oxidation
- Determination of chemical species prevalent in a plasma jet
- Analysis of ablator blow-off gases from space-craft heat shields
- Investigation of reactions driven by flash photolysis
- Studies of ion-molecule reaction cross-sections
- Laser ionization of organic solids
- Thermal decomposition behavior of perchlorate oxidizers studied by flash mass thermal analysis
- Fast-flow kinetic studies of methane reactions with atomic oxygen at room temperature
- Investigation of compounds produced during polymer fracture



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MASS SPECTROMETRY

1946

Stephens describes physical principle of time-of-flight mass spectrometer at American Physical Society meeting in Cambridge

1948

Goudsmit of Brookhaven National Laboratory describes a helical ToF-MS immersed in a magnetic field

1952

Stephens patents a mass spectrometer based on the principle of separation by Time-of-Flight

1956

Wiley of Bendix Aviation describes ToF-MS in *Science*

1959

Gohlke publishes combined GC/MS instrument using Bendix ToF-MS in *Analytical Chemistry*

1962

Studier of Argonne National Laboratories uses a modified Bendix ToF-MS to study the surface chemistry of uranium

1964

Lampe and Hess use a Bendix ToF-MS to study the specific reaction rate of the second-order formation of Ar₂⁺

1968

Futrell and co-workers investigate ion-molecule reactions at elevated pressures with a modified Bendix ToF-MS
Vastola and Pirone perform ionization of organic solids by laser irradiation

1973

Modica performs shock tube studies of sulfur hexafluoride and sulfur chloride using a quadrupole mass filter as the mass analyzer

1979

EPA proposes methods for environmental analysis by GC/MS using a quadrupole mass filter as the mass analyzer

1984

The EPA methods for environmental analysis are published in the Federal Register

