

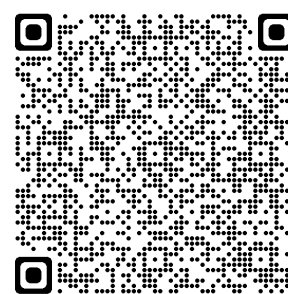


# A Retrospective Session (II) ASMS 1984 Instrument Science: The State of the Art

ASMS History Committee  
Catherine Fenselau, Barbara Larsen &  
Mariam ElNaggar

## INTRODUCTION

This poster provides synopses of invited retrospective lectures and contributed essays on the development of mass spectrometry instrumentation from the perspective of participants at the 1984 ASMS conference in San Antonio. The resulting booklet was distributed to all society members and complete contributions can be viewed at the history page of the ASMS website.



*The Introduction  
of Computers to  
Mass Spectrometry  
for Data Acquisition  
and Processing*

Klaus Biemann,  
MIT

“The symbiosis of mass spectrometers and computers is one of the earliest--and perhaps most widely applied--combinations of instruments and computers used by chemists today.”

### Meeting the Computational Demands of High Resolution Mass Measurement

- Early determinations of exact masses required manual peak matching or comparison to reference lines on a photoplate.

- Nonetheless, high resolution mass spectrometry was deemed indispensable to provide elemental compositions of natural products, and elemental compositions of fragment ions aided deduction of correct structures.

- Biemann's lab in 1964 reported using semi-automated punch cards to record a complete high resolution spectrum on an IBM 7094 computer to produce elemental composition data for all ions formed. Element maps displayed ion compositions ordered by distribution of heteroatoms.

- In 1967, Burlingame's lab reported that spectra from a double focusing scanning instrument could be digitized and read into an SDS Sigma 7, which thresholded the data and recorded peak profiles on magnetic tape for further processing on a CDC 6600 computer.

### On-line Recording of Mass Spectra of Compounds Emerging from a Gas Chromatograph (GCMS).

- GCMS work involved low resolution spectra, but rapid scan rates and rapid data acquisition. In 1967, Biemann's lab reported using an IBM 1800 computer system to directly accept the analog signal to process and store the data.

- Continuous reading of spectra of a GC effluent allowed the intensity of any ion to be recorded or reconstructed throughout the separation. These selected ion chromatograms provided specific quantitation.

### Spectral Matching Allows Rapid Sample Identification

- Library searching algorithms initially used selected sets of peaks, e.g., the two largest peaks in every 14-mass unit window and reported similarity indices. - As matching algorithms became reliable, the novice had less incentive to learn to interpret mass spectra manually.

- Consortia were formed to reduce duplication of constructed libraries, and eventually two collections evolved (from essentially the same sources), the NIH/EPA Collection (40,000) and the commercially distributed Registry of Mass Spectral Data (67,000). Increased speed and decreased size of microprocessors, and larger disc storage capacity at affordable cost have stimulated much progress in mass spectrometry and its utility in environmental analysis and quantitation in pharmacology, toxicology and clinical chemistry.



*Recollections of  
mass spectrometry  
in Britain and the USA*

John H. Beynon,  
Royal Society Research Unit,  
University College of  
Swansea, U.K.

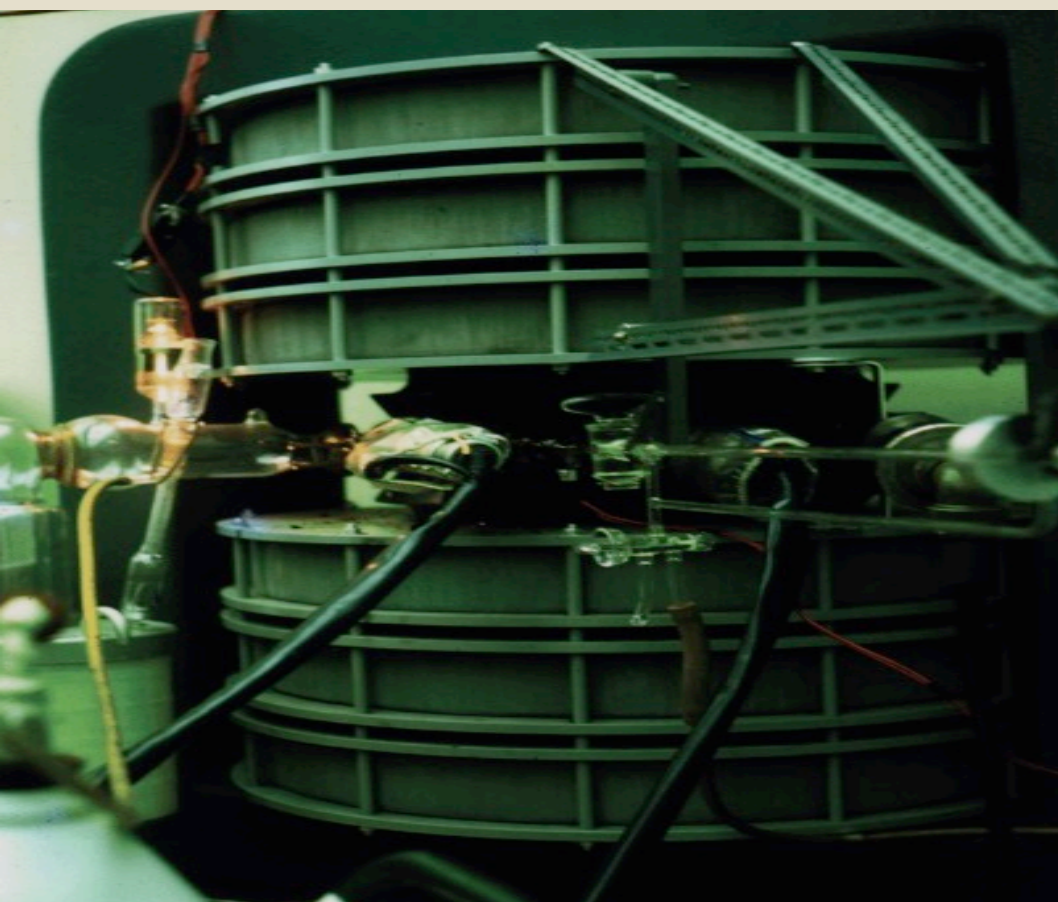
In 1947 John Beynon went to work in the research department at Imperial Chemicals Inc. (ICI) where he was given the assignment to build a mass spectrometer. ICI wanted to use the technology to follow isotope tracers in gas samples from studies of metabolism of potential pharmaceutical products.

His design was based on a paper published by Graham, Harkness and Thode, basically a glass instrument, with a manually variable exit slit, magnetic scanning, and a Faraday cup detector. Resolution was about 250 and ions m/z up to 200 could be transmitted at full accelerating voltage. The instrument proved to be useful for qualitative identification of organic compounds and soon this was the major application. Initially the magnetic field was scanned by hand. Two people were required to produce a spectrum. One scanned the magnet slowly and called out the peak heights and the sensitivity factors. The other wrote down these values and normalized the spectrum using a mechanical calculator. Peaks were seen as deflections on a galvanometer.

By 1953 steady improvement of the ICI instrument provided resolution of 600, which resolved simple doublets such as CH<sub>4</sub> and O, with mass accuracy of 25 ppm for molecular ions. With expanded characterization of organic compounds in mind, they approached Metropolitan Vickers to build a double focusing instrument with Neir-Johnson geometry. The instrument (called MS-8) was delivered in 1955 with resolution of 13,500. Subsequently, Metropolitan Vickers commercialized a larger version, the MS-9.

In 1955 Beynon participated in the third annual meeting of ASTM Committee E-14 on Mass Spectrometry, held in San Francisco. He reports that 200 scientists participated in the 4-day conference. Sixty-nine papers were presented, each in 20 minutes. There was to be no publication, however photography was allowed. Hospitality suites and subcommittee meetings were part of the activity, as well as an exhibition of mass spectrometers and associated equipment.

Below: Magnet from a CEC 103 instrument  
with direct probe and gas inlet systems



*Mass Spectrometers of  
Consolidated Engineering  
Corp and its Successors*

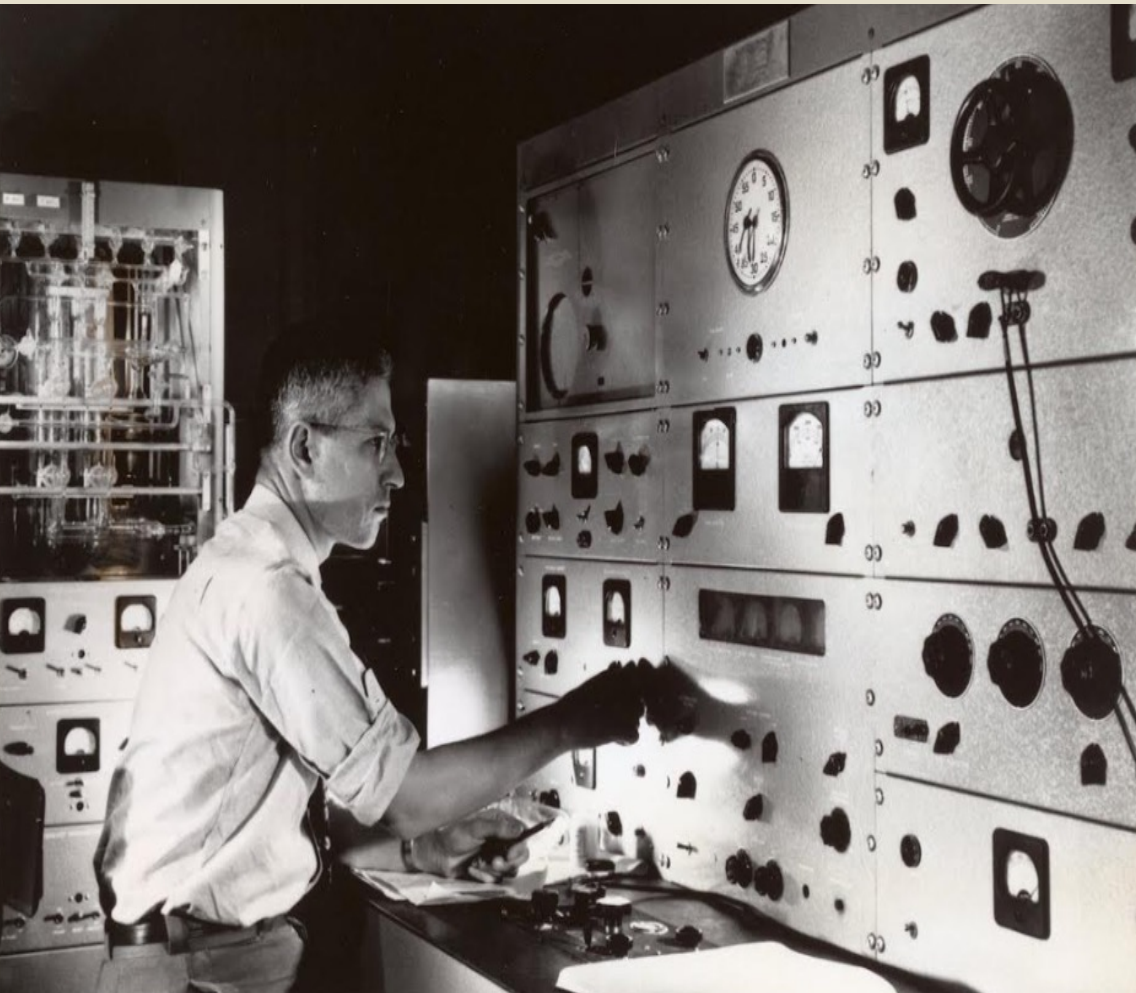
Charles M. Judson,  
University of Kansas,  
Lawrence KS  
(Director of Engineering  
in the Analytical Instruments  
Division of Consolidated  
Engineering Corp. 1963-1970)

“Consolidated Engineering Corp., a geophysical exploration company, undertook in the late 1930s the development of mass spectrometers to analyze mixtures of hydrocarbon gases, initially with the goal of seeking petroleum deposits by analysis of the gases evolved from the ground. The problems of obtaining reproducible spectra were at length resolved, the analysis was found to be of no value in petroleum prospecting, but an urgent problem in hydrocarbon gas analysis was found.” Mass spectrometry had a role to play in the production of aviation fuel.

War-time use of mass spectrometers was restricted to laboratories engaged in petroleum analysis. Even with unrestricted sales after the war, applications continued to be mainly in the petroleum field until the mid-1950's when heated inlet systems became available and spectra could be obtained of all kinds of volatile organic compounds. The company changed its name to Consolidated Electrodynamics Corp. and continued to be known as CEC. Two hundred of its 21-101/102/103 instruments were sold over a 25-year period. More than 100 patents limited competition in the U.S. until the 1960s.

In the early 1960s the company introduced a Mattauch-Herzog double focusing instrument, designed to be a high-resolution organic instrument or, alternatively, a spark-source instrument for trace inorganic analysis. Its photoplate acquisition provided high resolution analyses before computerized data acquisition was available. About 100 of these instruments were sold. The company's last product was the 21-490/491/492 with a 4-inch radius 90-degree analyzer, the successor to the 21-100 series. About 200 instruments of this model were sold, 50 by CEC and the rest by the Dupont Company, which bought CEC in 1970.

Below: A CEC 101 in operation circa 1943



*How I Got into  
Mass Spectrometry*

Amos S. Newton,  
Lawrence  
Berkeley  
Laboratory



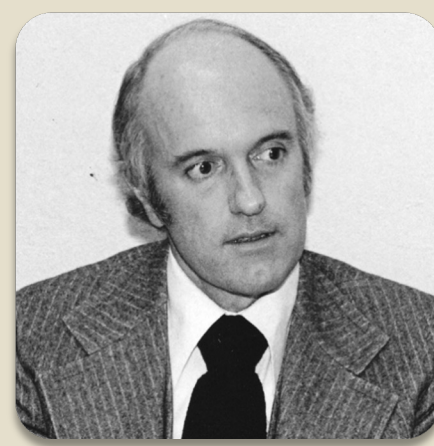
Dr. Newton worked at the Lawrence Berkeley Lab (LBL) during and after the WWII as a radiochemist concerned with the analysis of gaseous radiation chemical products and lower vapor pressure liquid products. He says the former was difficult and the latter virtually impossible in 1948. So, he undertook to purchase a mass spectrometer for the lab that would provide analysis of gaseous radiation mixtures. He took a test sample to GE in Schenectady and one to CEC in Pasadena.

The test sample was H<sub>2</sub> = 22.1%, C<sub>2</sub>H<sub>6</sub> = 24.4%, ethylene oxide = 13.4%, n-C<sub>4</sub>H<sub>10</sub> = 17.0 %, and i-C<sub>4</sub>H<sub>10</sub> = 23.2 %. He reports that Sybil Rock, who was in charge of the analytical laboratory at CEC, made a provisional analysis in two hours and returned a correct analysis by the end of the workday after she consulted by phone with some of her customers about the mass 28 ions.

A few months later CEC installed a model 21-102 system with magnet #73 at LBL. The instrument had a sealed ion source which had to be returned to Pasadena for cleaning and filament replacement. A small earthquake in Berkeley snapped the all-glass inlet system, which Dr. Newton's lab then successfully redesigned to be earthquake-proof.

*Early Developments  
of the Quadrupole  
Mass Spectrometer*

Robert E. Finnigan,  
Finnigan Corporation,  
San Jose CA



Bob Finnigan clarifies that the quadrupole mass spectrometer (QMS) was invented independently and virtually simultaneously in the early 1950s by Wolfgang Paul (Univ of Bonn, FRG) and Richard Post (Univ. California, Berkeley). In both cases the analyzer was developed to support particle accelerator experiments. By 1960, work by K.R. Shoulders and others at Stanford Research Institute (Menlo Park, CA) had produced a practical QMS with a mass range of 1 to 500 Da, which used radiofrequencies approximately equal to most of those used in commercial QMS systems in 1984.

Finnigan came to SRI in 1962 to co-found and lead a process controls research group. He quickly identified the QMS as potentially an excellent detector for measurement and feedback control of industrial processes. In 1963 he moved to Electronics Associates Inc. to develop and produce QMS-based residual gas analyzers. Their residual gas analyzers sold well.

However, in 1967 he left EAI to form the Finnigan Instruments Corporation (with Roger Sant, T.Z. Chu, Mike Story and W.J. Fies) with the intention to develop, manufacture and market a gas chromatograph/mass spectrometer system utilizing the QMS. At that time the only GC/MS commercially available was the Swedish LKB 9000.

The company's first GC/MS system, the model 1015, was delivered to the Stanford Medical School Genetics Department in January 1968. The gas chromatograph was interfaced using a single-stage glass jet separator, the design for which was given to Bob Finnigan by Einer Stenhagen of the Univ. of Goteborg, Sweden.

Below: Sybil M. Rock, Acting Manager for  
Applications Service, CEC with a computer  
she developed to process mass spectra



*The Development  
of Secondary Ion  
Mass Spectrometry  
(SIMS): A Retrospective*

Richard E. Honig,  
RCA Laboratories,  
Princeton, NJ



“Contrary to common opinion, secondary ion mass spectrometry (SIMS) has been with us for more than half a century under various guises, the most recent reincarnation being FAB (fast atom bombardment).”

### Earlier History of secondary ion Mass Spectrometry

- The earliest references to Secondary ion emission were made by J.J. Thomson (1910), J.S. Thompson (1931), K.S. Woodcock (1931) and R.H. Sloan and R. Press (1938).

- (1949) A discharge source was designed by Herzog and Viebock to produce primary ions of Fe, Ni, Cu, Al with which to bombard various targets.

- (1951) A double mass spectrometer was designed at RCA laboratories to study oxide-coated cathodes by secondary ion emission.

- (1958) Eliminating the primary ion selector allowed for sputtering of surfaces with low energy ion beams.

### More Recent Developments (1960-1984) including organic samples

- Instruments were developed using high primary current density to obtain concentration profiles in depth and to identify trace impurities.

- High primary current density was combined with high lateral ion sources to construct ion microscopes (Castaing and Slozian) and ion microprobes (Liebl), which were of particular interest to the electronics industry.

- Liquid metal sources (e.g. Ga), offered lateral resolution down to 0.3 μm.

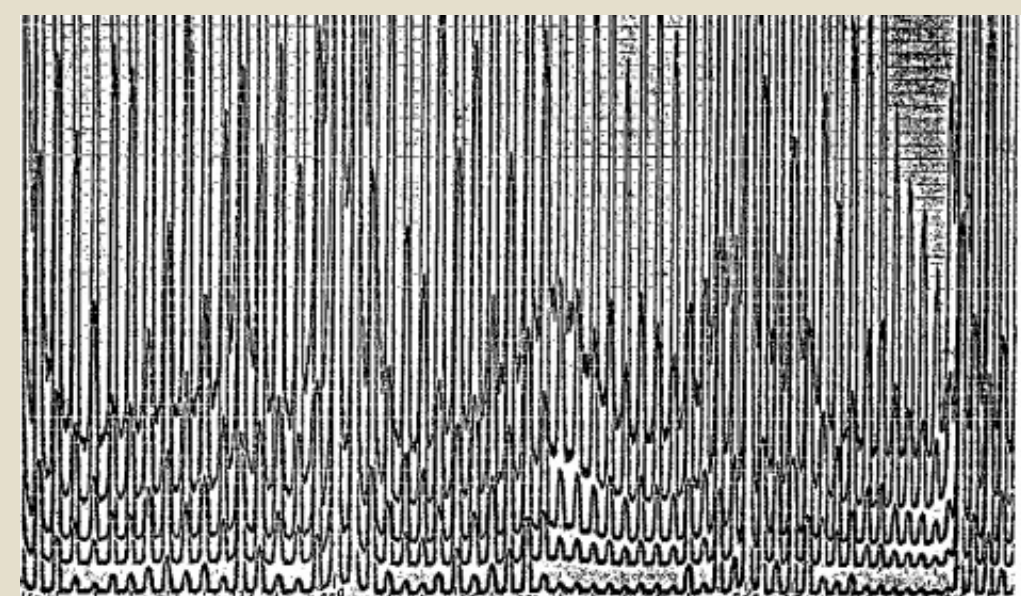
- Low primary current density in large beams (static SIMS) allowed the first forays into analysis of intact organic molecules.

- Variations in instrumentation and sample preparation allowed for the desorption of heavy organic molecules, including laser desorption, (LDMS), <sup>252</sup>Cf plasma desorption (PDMS) and fast atom bombardment (FAB).

- A puzzle still to be understood is how high energy bombardment can desorb large organic molecules without destroying them in the process.

Honig notes with surprise that for different desorption methods the mass spectra obtained are similar. And he predicts (in 1984) that SIMS (in all its form) publications will soon exceed 1000 per year.

Below: Oscillograph recording awaiting  
manual peak assignments



*Mass Spectroscopy –  
Ways and Means –  
A Historical Prospectus*

Harry J. Svec,  
Ames Laboratory-USDOE  
and Iowa State University



- Nineteenth century studies of discharge tubes provided an understanding of the relationships between discharge beams, gas pressure, magnetic fields, electrical fields.

- Those studies provided recognition of the electron and the words “electron” and “ions”.

- Around 1900, J.J. Thomson turned his attention from cathode rays to anode rays (cations) and drove the evolution of discharge tubes towards mass spectrometry. He developed photographic plates to record ion trajectories.

- W.F. Aston extended the study of positive rays in the Cavendish Lab and obtained (~1915) conclusive evidence for the existence of isotopes of stable elements, including Ne and Cl. He mapped “mass defects” of nuclides from whole numbers, improved vacuum systems and perfected electric discharge ionization.

- In 1918, A.J. Dempster (Univ. of Chicago) described an instrument for ionizing solids that had post-ionization acceleration and electrometric detection. He also improved electron bombardment sources.

- In 1935 Dempster measured the last of the elemental isotopes, Pt and Ir, and Aston announced that “mass spectroscopy had served its purpose and would die away as a field for research”

- Dempster established the relationship m/z = [H<sup>2</sup>-r<sup>2</sup>]/2E for ion optics that combined kinetic energy and momentum selection.

- In 1936, J. Mattauch and R. Herzog demonstrated an ion optic system with first order focusing over the length of a photoplate detector.

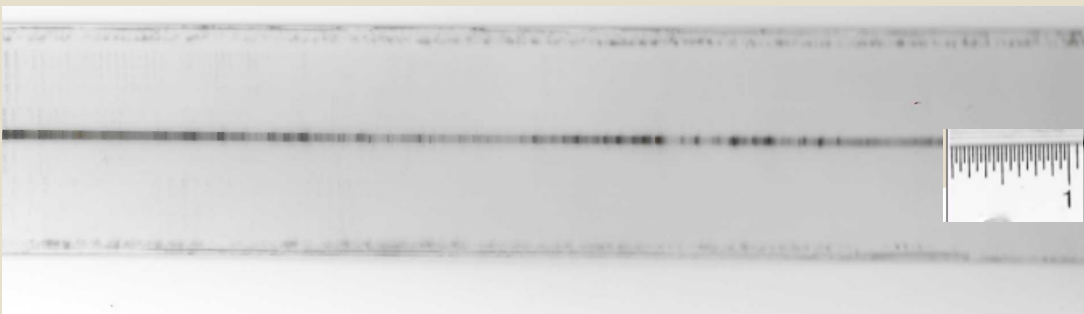
- Velocity selection experiments led to time-of-flight analyzers by W.E. Stephens (1946), A.E. Cameron and D.F. Eggers (1948) and W.C. Wiley and I.H. McLaren (1955). Wiley and McLaren's design was commercialized by Bendix and could scan from m/z 1 to 600 with 10,000 spectra per second.

- J. Hipple, H. Somer, and H. Thomas described an omegatron (1948) based on the cyclotron principle, which GE commercialized. Beckman commercialized a velocity selector based on the principle of the linear accelerator.

- A.O. Nier, E. Johnson and colleagues constructed double focusing instruments (1953) with electrometric detection. Using an extended magnetic field, K. Ogata and H. Matsuda (1955) constructed a system with a resolution of 1 part in 500,000.

- N.S. Hanney described a spark source mass spectrograph in 1954 with Mattauch Herzog ion optics and photoplate detection. Metropolitan-Vickers commercialized a similar instrument.

- W. Paul introduced the quadrupole mass filter (1958).



Above: Photoplate detector, developed  
and awaiting manual peak assignments