10th Annual Conference • 1962 • New Orleans, LA, Jung Hotel

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

Society Growth

By 1962, the size of the meeting had grown considerably, both in attendance and number of papers presented; 81. The last session was Friday morning, so the program easily accommodated the number of papers with a single oral session running through the week. Thus, attendees did not have to face the conflict of wanting to be at two different papers at the same time.

There was still an emphasis on petroleum chemistry, but other areas of study were making inroads. For instance, "Mass Spectra Correlations and Appearance Potentials of the Major Tobacco Alkaloids" by a group at Philip Morris Research Center and "Spectra of Compounds of Biological Interest" by K. Biemann and J. McCloskey from MIT were placed towards the end of the Hydrocarbon Studies II session. The future was on the horizon. The sessions and their chairs are listed below.

Session	Title	Chair	# Papers
Monday Morning	Hydrocarbon Studies I	Klaus Biemann	10
Monday Afternoon	Hydrocarbon Studies II	Ralph Brown	10
Tuesday Morning	Analytical Techniques I	A. Hood	10
Tuesday Afternoon	Analytical Techniques II	Harry Svec	9
Wednesday Morning	Instrumentation I	Maurice Testerman	10
Wednesday Afternoon	Instrumentation II	Al Nier	6
Thursday Morning	Negative Ion Symposium	C. E. Melton	5
Thursday Afternoon	Collision Processes	Fred Lampe	10
Friday Morning Solids	Techniques	C. M. Stevens	11

High Resolution/Accurate Mass Studies

Alfred Nier reported in a 1955 paper in Science that the high resolution instrument he and his co-workers had developed for determination of the accurate masses of isotopes could be potentially useful in a general purpose analytical application.

> "Molecules having the same mass numbers, but differing in weight by an amount determined only by the difference in binding energies of the nuclear particles can be clearly resolved . . . Extension of the use of the instrument [Nier-Johnson double focusing mass spectrometer] to the resolution of heavy hydrocarbons should prove fruitful."
>
> *A. O. Nier, "Determination of Isotopic Masses and Abundances by Mass Spectrometry," Science, 121 (1955) 740.*

This concept was followed up on by John Beynon, then at Imperial Chemical Industries, and he charged Metropolitan Vickers with the task of creating a mass spectrometer with sufficient resolving power to test the concept proposed in Nier's publication. The instrument they delivered, the MS-8, was one of a kind. With it, Beynon showed that accurate mass determination by high resolution mass spectrometry could provide information regarding elemental composition. The MS-8 was followed by the MS-9 which had a long and glorious history. By 1962, all of the major instrument companies were working on improving the resolving power of their instruments.

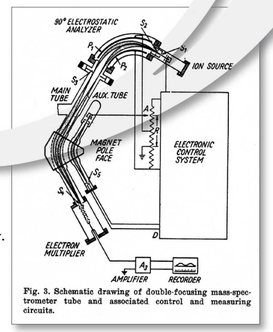
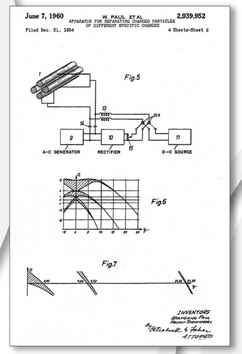


Fig. 3. Schematic drawing of double-focusing mass-spectrometer tube and associated control and measuring circuits.

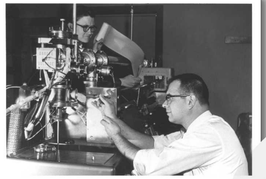
Reprinted with permission from Science, 121 (1955) 739.

There's More Than One Way to Separate Masses

Prior to 1962, a variety of different principles for the separation of ions by mass had been explored and developed other than by magnetic sector. These included the Bennett radio frequency, the omegatron, the cycloidal, and the quadrupole mass spectrometers. However, the only commercially viable instruments in 1962 were those based on magnetic (and electrostatic) sectors and time-of-flight.



Wolfgang Paul and co-workers had conceived of the quadrupole mass filter in a paper published in 1953 and in the years following, he filed patents on the concept in several countries in Europe and in the United States. While the underlying physical principles for mass separation by magnetic sector and time-of-flight could be grasped by someone with a solid foundation in high school physics, the mass separation principle of the quadrupole mass filter was much more abstruse. Nevertheless, interest in creating a commercial instrument based on the quadrupole concept was strong and in 1961, Atlas-MAT used a quadrupole mass filter as a residual gas analyzer; the AMP 3. Although not widely distributed, others saw the need for a low-cost mass spectrometer and towards the end of the 60's, Finnigan Instruments Corporation was producing a successful commercial instrument based on the quadrupole mass filter.



Roland Gohlke of Dow Chemical Company working on the interface between the gas chromatograph and a Bendix time-of-flight mass spectrometer. Gohlke's 1959 Analytical Chemistry paper "Time-of-flight mass spectrometry and gas-liquid partition chromatography" was the first successful demonstration of the combination of the two instruments. The vacuum system, open source design and rapid scanning capability of the Bendix instrument made it a natural choice for combined GC/MS. In the background, Dr. Fred McLafferty displays the mass spectrum from an oscillographic chart recorder; the standard data acquisition technology for mass spectrometry for many years.

It's Combo Time!

In the previous decade, the irrefutable logic of connecting the outlet of a gas chromatograph to the inlet of a mass spectrometer was apparent to any number of gas chromatographers and mass spectrometrists. However, the seemingly insurmountable task of accommodating the one atmosphere pressure difference in the operating conditions of the two instruments discouraged all but the most dedicated researchers. It is generally accepted that the first demonstration combining the two instruments in an analytically useful tool was by Roland Gohlke at Dow Chemical in 1959 using a Bendix time-of-flight mass spectrometer. His approach was a split connection such that the majority of the GC column effluent was vented to atmosphere while a small fraction entered the mass spectrometer. Others quickly entered the field and a variety of "carrier gas separator" designs were developed to increase the amount of analyte reaching the mass spectrometer while simultaneously preferentially disposing of the GC carrier gas, usually helium.

Three major concepts for interfacing the two instruments by means of such separators appeared in short order: the molecular effusion design proposed by J. Throck Watson and Klaus Biemann at MIT, the jet separator design proposed by Ragnar Ryhage at the Karolinska Institute in Sweden, and the molecular effusion design proposed by Peter Llewellyn, then at Varian.

In the ensuing decade, most commercial mass spectrometer manufacturers offered a combined GC/MS instrument featuring a variation of one or the other of these interface designs. Eventually, the use of low flow rate fused silica capillary columns and the concomitant design of differentially pumped mass spectrometer vacuum systems with high pumping speed ion source housings obviated the need for these interfaces, although the jet separator is still in use today.

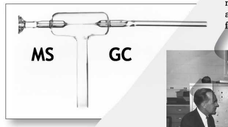
Molecular Effusion Separator

The operation of this device depends upon establishing conditions for molecular flow inside the fritted glass tube connecting the GC to the MS. Under these conditions, the mean free path of the gas is larger than the interior diameter of fritted glass tube and the lighter helium molecules in the GC effluent will preferentially diffuse out of the tube to be pumped away, while the analyte molecules enter the mass spectrometer.

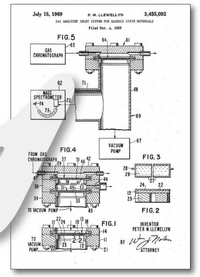
Gregory Tobias, Philadelphia

Jet Separator

By establishing conditions for supersonic flow for the GC effluent exiting the nozzle, the lighter helium molecules will expand away from the nozzle preferentially while the heavier analyte molecules will remain on the flow centerline. The skimmer opposite the nozzle will pass the majority of the analyte molecules on the centerline flow into the mass spectrometer.



Ragnar Ryhage and Chuck Sweeley in front of the LKB 9000 gas chromatograph-mass spectrometer delivered to Dr. Sweeley's laboratory at Michigan State University. Dr. Ryhage of the Karolinska Institute in Sweden was instrumental in developing the jet separator for interfacing the LKB 9000 with a gas chromatograph. This commercial instrument was readily accepted by those in the biological community and was the 'industry standard' for biological mass spectrometry for a number of years.



Solution-Diffusion Separator

If the effluent from the gas chromatograph comes in contact with an organo-silicon rubber membrane, then the analyte molecules will dissolve into and diffuse through the membrane at a higher rate than the helium molecules. The rate difference is so great that, even though the ratio of helium to analyte molecules in the GC effluent is extremely high, there will still be a useful enrichment affect.

MASS SPECTROMETRY

1954

High-resolution mass spectrometry is developed at Imperial Chemical Industries in the United Kingdom for the study of organic compounds.

1955

Consolidated Engineering Corporation changes its name to Consolidated Electrodynamics Corporation.

1956

Proton affinity determinations are made by mass spectrometry.

Fred McLafferty proposes a mechanism for γ-hydrogen transfer that becomes known as the McLafferty rearrangement.

Steroids are first analyzed using mass spectrometry.

1957

Amoco researcher Seymour Myerson confirms the existence of the tropylium ion.

Trimethylsilyl esters are used as derivatives for mass spectrometry.

GC-MS is first demonstrated at the Phillip-Morris Company.

1958

CEC introduces Mascot, the first commercial mass spectrum digitizer.

The Bendix time-of-flight mass spectrometer is introduced, and multiple ion monitoring is demonstrated.

The first mass spectrometer measurements of the Earth's atmosphere are made by quadrupole mass filter by the U.S. Naval Research Laboratory.

1959

Mass spectrometry is used at MIT for peptide and oligonucleotide sequencing.

A gas chromatograph is interfaced to a time-of-flight mass spectrometer at Dow Chemical.

1960

Mass spectrometers analyze and monitor air quality in submarines.

Bendix Corporation introduces the first direct insertion (solids) probe at the Pittsburgh Conference.

CEC introduces its Model 21-110 high-resolution double-focusing mass spectrograph.

1961

Atlas-MAT introduces the first residual gas analyzer based on the quadrupole design.

The first proceedings of Committee E-14 are published for the ninth annual conference by ASTM.

1962

Associated Electrical Industries delivers its MS-9 mass spectrometer to Shell Laboratories in Amsterdam.

A secondary ion mass spectrometry ion microscope is described by researchers in France.

Mass spectrometry is first used at MIT to study the structure of nucleosides.

HISTORY

1954

The U.S. Supreme Court rules that racial segregation is unconstitutional in the case Brown v. Board of Education of Topeka.

Roger Bannister runs a mile in less than four minutes.

Rosa Parks is arrested for refusing to give up her seat to a white passenger on a city bus in Montgomery, Alabama.

1955

Albania, Bulgaria, Hungary, East Gemany, Poland, Romania, Czechoslovakia and the Union of Soviet Socialist Republics form the Warsaw Pact.

1956

Egypt nationalizes the Suez Canal, leading to war with Israel, France, and Britain.

Democratic reforms in Hungary prompt a Soviet invasion.

The United States sends military advisers to South Vietnam.

1957

The Soviet satellite Sputnik I becomes the first human-made object to orbit Earth.

President Dwight Eisenhower sends federal troops to Little Rock, Arkansas, to enforce public school desegregation.

1958

Egypt and Syria form the United Arab Republic.

The National Aeronautics and Space Administration (NASA) is created.

1959

Fidel Castro comes to power in Cuba.

Louis and Mary Leakey unearth the first Homo habilis fossils in Olduvai Gorge, Tanzania.

The Soviet space probe Lunik 2 is the first craft to land on the Moon.

The first xerographic photocopiers are sold commercially.

The International Geophysical Year begins.

1960

The Belgian Congo becomes the independent nation of Zaire.

Theodore Harold Maiman develops the first laser.

The first communications and weather satellites are sent into orbit.

1961

Yuri Gagarin becomes the first person to travel in space.

East and West Berlin are divided by the infamous Berlin Wall.

1962

Rachel Carson publishes *Silent Spring*, which ultimately leads to the banning of DDT in the United States.

The world narrowly escapes nuclear war during the Cuban missile crisis.

Algeria gains independence from France.

The Beatles score their first hit (in the United Kingdom) with "Love Me Do."