A Retrospective Session (I) ASMS 1984 Applications and the ASMS Community

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 applications and of the ASMS 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 on the ASMS website.

Viewing a Moment in the History of ASMS

Mynard Hamming,
Conoco Inc.
Ponca City OK

As the Chairman of Subcommittee III on Computer Applications of ASTM Committee E-14 on Mass Spectrometry I attended an Executive Committee Meeting in Dallas, Texas, on Saturday, March 8, 1969. Chairmen were then invited to such meetings as a form of training for being an ASTM officer. To me the real thrill was being a part of a moment in history. It was a step in the transformation of ASTM Committee E-14 into ASMS. One of the ASTM officers repeated the letters "ASMS" over and over again. He said it had a good ring to it (and he was right).

The room was poorly furnished, and it was a warm sleepy Saturday afternoon in Dallas. Joe Franklin had a proposed constitution. It was discussed in great detail by the ASTM officers. Another committee chairman and I were mostly quiet, giving support with a smile or nod. All of us in that room from ASTM had a feeling the future for advancements in mass spectrometry would be brighter with ASMS.

The new society known as "The American Society for Mass Spectrometry" was expected to be voted into existence at the next meeting in May 1969 of the ASTM Committee E-14. It was voted on and is today as so many now know it to be.

Graham Cooks, V.P. Programs

Ivan Kaminsky, Jim DeCorpo (Board Treasurer) and Judith Sjoberg at the 1984 registration table.

Chemical Physics Mass Spectrometry at the Humble Oil and Refining Co.

F.H. Field,
Rockefeller University

Frank Field recounts a remarkable two decades at Humble Oil in Baytown, TX, where a group of physical chemists was assembled and supported to study ion molecule reactions. They also discovered chemical ionization. "Chemical physics mass spectrometry at Humble originated with Joe Franklin." Field credits Franklin with convincing Humble management of the value of several kinds of basic research. "Joe was a chemical engineer who was involved almost completely in engineering jobs that made money at the refinery, but he had a passion for trying to understand phenomena at the most basic level possible. Joe wanted to know more about appearance potentials.

Frank Field started a program measuring appearance potentials at the University of Texas and in 1952 was recruited to join Franklin at Humble; in 1954 Fred Lampe joined the group; in 1957 Jean Futrell came to Humble to work on related projects in radiation chemistry; in 1961 Burnaby Munson joined the group. Humble provided funds to purchase an instrument especially designed for research in chemical physics mass spectrometry in 1956, at a cost exceeding $600,000 in 1984 dollars. Field reports that he designed the instrument with high-capacity differential pumping—300 liters per second on both source and analyzer, which allowed the team higher ion source pressure than had been used previously. This extended the kinds of ion-molecule reactions that could be observed and allowed the discovery of chemical ionization.

Eventually, Franklin took an endowed chair at Rice, Field moved to Rockefeller University, Lampe went to Penn State, Futrell directed research at PNNL and then at the University of Delaware, and Munson joined the faculty at the University of Delaware.

"The total amount of money spent was relatively modest, but even at that I doubt that there was a direct payout to Humble on the investment in terms of profitable new processes discovered …whatever the benefit to the Humble Company, society as a whole profited."

Observations of some of the Events leading to The Formation of ASTM E-14 Twenty Years Ago

Harold F. Wiley,
Consolidated
Electrodynamics Corp.,
Pasadena, CA

- Because of wartime restrictions, developments in mass spectrometry were kept secret. The most outstanding example is the Manhattan project. Instrument manufacturers of the time were Consolidated Instruments Corporation (CEC), General Electric and Westinghouse, selling primarily to petroleum companies and government laboratories.

- CEC developed the first commercial mass spectrometer used to monitor refining aviation fuel. In 1942, the first CEC model 21-101 was delivered to Atlantic Refining Company of Philadelphia.

- The first meeting of 10 mass spectrometry users was in Pasadena, California in spring of 1944; the next meeting occurred at the ACS meeting in NYC in September 1944; a third meeting was held in Philadelphia in December 1945 with attendance growing to 37 practitioners representing 16 laboratories. CEC unveiled a computer for solving twelve simultaneous linear equations there.

- From then on CEC organized annual meetings in different parts of the country. CEC Group Reports were circulated, which included service hints and landmark papers. The primary contributors were the users. Some were subsequently published in technical journals.

- The suggestion for the formation of the ASTM Committee E-14 for Mass Spectrometry was made in 1951 by E.B. Tucker of American Oil. An organizing conference was held at the ASTM headquarters in January 1952.

- The first meeting sponsored by E-14 occurred at the 1952 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. Twenty-one papers were presented in three sessions. Jack Sharkey presided over the first session and the first paper, given by Al Nier, was entitled "Recent Developments in Mass Spectrometry."

- Elected officers of this newly formed organization were Bill Young, Jack O'Neal of Shell, Fred Mohler of NBS, Harold Kelley of Dupont, and Harold Wiley of CEC.

- The meeting was again held jointly with the Pittsburgh Conference in 1953. After that Committee E-14 sponsored the Annual conference through 1968.

…"may your filaments burn brightly forever and forever and forever."

Reminiscences of the early days of Mass Spectrometry in the Petroleum Industry

S. Meyerson,
Standard Oil Company,
Whiting IN

Early Days of Instrumentation
- The first commercial instrument CEC 21-101 (Dempster geometry, 180-degree analyzer) was built for analysis of low-boiling liquids. It was sold to Atlantic Refining Company instrument and installed in 1942.
- The second instrument was purchased by Standard Oil company for $19,500.
- Early operation required manual adjustment of the filament-current potentiometer to maintain constant ionizing current.
- Sensitivity instability was usually cured by flowing butene through the instrument overnight. Jack Sharkey and Gus Friedel eventually attributed the problem to sample oxygenation of impure tungsten filaments.

MS Community
- Annual users' meetings were initiated by CEC in 1944, with the first one held on the West Coast for 10 people.
- In the decade 1944 to 1954 CEC released 108 MS group reports about instrumentation, calculations, and various applications, with 75% of the reports submitted by the petroleum industry.
- In 1944, the National Bureau of Standards announced a group of 15 hydrocarbon standards of known purity for calibrating analytical instrumentation. The American Petroleum Institute also contributed reference compounds. A joint API-NBS effort began making reference spectra available in 1947.
- In 1952 the groundwork was laid for a single mass spectrometry meeting as Committee E-14 of the American Society for Testing Materials (ASTM) with the objective defined as the "promotion of knowledge and advancement of the art of mass spectrometry."
- An independent professional organization, the American Society for Mass spectrometry, was formed in 1969.

Structure/Reaction Mechanisms of Organic Molecules
- Quantitative analysis of gaseous mixtures, light hydrocarbons and fractions from distillation was the main activity at the petroleum companies.
- Ionization and appearance potentials were determined in both petroleum and university laboratories
- John Hipple at Westinghouse defined the origins of the diffuse signals that we know as metastable peaks, and Alois Langer, also at Westinghouse, published a collection of rearrangement peaks.
- Meyerson studied spectra of multiple alkylbenzenes and other small molecules and concluded that "the molecular events underlying mass spectra are networks of competing and consecutive chemical reactions." Myerson found many parallels between ion reactions in his mass spectrometer and organic chemistry, and he directed many of his papers to organic chemists.

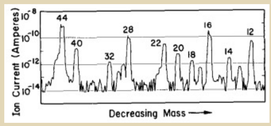
Mass Spectrometry in Planetary Research

Alfred O. Nier,
University of Minnesota,
Minneapolis, MN

Space Science Board goals
- determine the origin and evolution of the solar system
- better understand the earth through comparative planetary studies
- investigate the of the solar system and the appearance of life.

Earth's Atmospheric Exploration
- designed a double-focusing magnetic sector instrument with an open-source design meeting requirements 1.5", light-weight 7.3 kg, low power (10 watts), shock resistant.
- determined the components of the earth's atmosphere (atomic oxygen and nitrogen).

Mars Viking Landers 1975-76
- traveled with a GCMS to look for organic compounds in the soil. None was observed at the ppb level.
- found the atmospheric ratio of Ar to CO_2 was less than 2%, in contrast to an earlier conclusion from the Russian Mars 6 exploration.
- observed the presence of NO with a small satellite peak at m/z 29 and determined the $^{15}N/^{14}N$ ratio to be 60% higher than on earth.
- produced the (below) famous mass spectrum of the Martian atmosphere
- resulted in alternative hypotheses about differences between the atmosphere of Mars and that of earth.



Mass spectrum of the Martian atmosphere taken from the first Mars lander at 140 km altitude

Venus Pioneer Mission 1978
- identified the principal atmospheric gases as CO_2, CO, N_2, O, N and He, with large variations observed between day and night measurements.
- used a single focusing wedge magnet with high resolution and a mass range of 1-208 u.
- $^{22}Ne/^{20}0$ Ne ratio was 0.07, which lies nearer to solar wind than a terrestrial value. C and O isotope abundance ratios are similar to terrestrial values.
- upper limits for He, Kr, O_2, SO_2, H_2O, Cl and Hg were determined.

Conclusions in 1984
" Eventually, any comprehensive theory for the evolution of the solar system will have to reconcile the results obtained for meteorites and lunar samples with those found in in situ studies of the planets themselves."

"Early" Days at Humble, Circa 1960

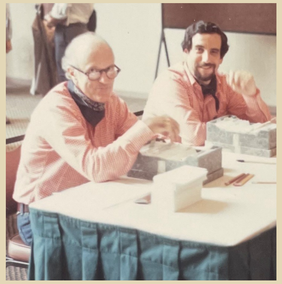
Thomas Aczel,
Exxon Research and Engineering Co.

Mass Spectrometry was practiced in the industrial laboratory of Humble Oil and Refining Company (later known as Esso, Enjay and Exxon Research). The instrument was a CEC 21-103c which was adapted with a heated glass inlet for solids introduction which was ultimately adopted by several manufacturers. The data were acquired on photographic charts which were retrieved through the side panel by the operator wearing a black sleeve. The chart was transported to a dark room where the chart was manually folded like an accordion and immersed in the developing solution. If the folds didn't come in contact with the solution, there would be blank spots in the spectrum. The wet spectrum had to be dried on a hot, sizzling rotating drum.

Peak numbers or mass numbers were manually counted out with the hydrocarbons as mileposts every 14 mass units. The peak heights were measured with a ruler- fifty to a hundred per spectrum with many spectra acquired per day. The laborious work was enhanced by the use of a transparent ruler with amplifications of 1,3,10 and 30 as a galvanometer to eliminate the multiplication.

High resolution instrumentation, introduced into the lab in 1963-66, used a UV Visicorder which eliminated the need to develop the spectra. The pattern recognition required 1-2 inches per unit mass, which made the spectrum of m/z 60-700 50 to 100 feet long! Using the ^{13}C isotope peak, the molecular masses could be determined to 20-30 ppm mass accuracy.

Each mass spectrum contained several hundred to a thousand molecular ions, which were measured and manually input into a computer program to determine concentrations. Prior to the high-resolution spectrometer, the concentrations of the components were determined using simultaneous equations using a Frieden calculator. The calculations were checked using calibration spectra and up to twenty components could be determined by this method. Eventually advances with computer acquisition obsoleted many of these manual manipulations.



Bob Finnigan (Board Member-at-Large), who organized the 1984 Retrospective and Harry Hertz (Board Secretary)

The Singing of "The Eyes of Texas"

Earle Lumpkin,
Humble Oil and Refining Co.

"Before there was an ASMS, organized in 1969, and before there was an ASTM E-14 Committee, organized in 1952, most of the practicing mass spectroscopists in the U.S. met annually for the Consolidated Engineering Corporation Group Meeting. These meetings were inaugurated in 1945, and I attended my first in 1946 in Houston. There was the presentation of formal papers, an instrumental clinic, and a banquet on Wednesday night preceded by a mixer."

We sang at the mixer and CEC hired an accordionist to accompany us. Early on the attendees were composed mostly of petroleum company employees, and many were from Texas. So, we sang a song all Texans know—The Eyes of Texas. Even when the sing-song session was abandoned, several of us--myself, Archie Hood, Chuck Robinson-- made sure to sing our song. Joe Franklin and Burnaby Munson (both Texans) joined us, and we "selected men with robust, if not melodious, voices and declared them Honorary Texans. Notable among these are John Beynon, Fred McLafferty, and Thomas Aczel." The tradition continues! In 1984 I led ALL the attendees in singing The Eyes of Texas at the Wednesday night ASMS barbeque at the Lone Star Brewery in San Antonio in the Lone Star state. "Keep it up!"

The social event at the 1984 Conference was a Western Barbeque. Past President Burnaby Munson introduced visiting scientists from Japan and Europe

Line dancing with Pamela Craine, Jim Lehman, Catherine Fenselau, (President), Bob Cotter, and Sue Weintraub

Reflections

Ed Emery
Balzers,
Hudson NH

"Life in mass spectrometry in those very early days was a challenge, and a real treat. The wisdom of spectra and interpretation lay in the hands and minds of so relatively few, compared to the fine compilations now available…..The modern, diverse application front finds increasing numbers of scientists pursuing their volumes of terminal printout of complicated spectra."

Ed was introduced to mass spectrometry in 1952 by R.W. Law and R.C. Childs at Allied Chemical and Dye Corporation in Glenolden, PA. He observes that in 1954 C.E.C. had eleven sales and service offices across the country including Philadelphia, and remarks that it was "common to have several upper echelon of C.E.C. drop in [on service calls], take off their coats and help". He reports that the introduction of mass spectrometry for analysis of coal and coal-tar chemicals (previously defined by melting points and refractive indexes) revealed many unknown impurities among their 'pure' reference samples.

In 1956 he relocated to Colgate-Palmolive-Peet Co. in Jersey City, where he ventured into soaps, fats, essential oils, and detergents. He tells how he made a believer out of one doubter of the capability of mass spectrometry by showing that a (commercial?) sample of "dodecylbenzene" was a mixture of chain lengths with many different masses, and that the spectrum of a second sample, synthesized and purified by the doubter, showed a single molecular mass consistent with purity.

Ed illustrated his reflections with a copy of a portion of an oscilographic record and a picture of a C.E.C. 21-103C installed in 1956 and still running in mint-condition in 1972.