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Retrospective Lectures

May 27-June 1, 1984
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american society for mass spectrometry

The Thirty-Second Annual Conference on Mass Spectrometry and Allied Topics

Retrospective Lectures

May 27 - June 1, 1984

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INTRODUCTION

A theme at the 32nd Annual Conference on Mass Spectrometry and Allied Topics held in San Antonio was the exploration of our origins. This was most evident in a series of "retrospective lectures" presented by outstanding scientists who worked through the early years of the discipline. As you will read in this special issue, they have provided us factual and anecdotal information as they "take you back in time." We are grateful to Prof. Al Nier, Dr. Richard E. Honig, Prof. Harry Svec, Seymour Meyerson, and Prof. Klaus Biemann for participating in this theme conference of ASMS and for preparing papers from their talks for this special issue of the proceedings. We think that they will be of great value to the ASMS membership today and for many years to come.

Another retrospective activity at the 32nd Annual Conference was the Vice-President's Workshop entitled "Mass Spectrometers of Yesteryear". It featured several informal papers by pioneers involved in the development of both magnetic and quadrupole-type instruments which stimulated lively discussions among those attending. R. Graham Cooks, Vice President for Programs, encouraged all those involved in the "early" days of mass spectrometry (twenty or more years ago) to share any reminiscences or anecdotes they might have with our membership by writing a short paper for this same special retrospective issue. These contributions follow the papers of our retrospective lecturers.

We would like to acknowledge the work of R. Graham Cooks who conceived and arranged the technical program for the San Antonio meeting including the retrospective lectures contained herein. We hope that you will find this special issue to be of interest and value and urge you to pass it on to your colleagues.

Bob Finnigan
Editor and Member-at-Large
ASMS Board of Directors

NOTE: This special volume is produced by the American Society for Mass Spectrometry. It is to be sent to all registrants of the 32nd Annual Conference on Mass Spectrometry and Allied Topics and to members of ASMS. A limited number of extra copies have been printed and may be purchased from the Society Office.

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MASS SPECTROMETRY IN PLANETARY RESEARCH

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ABSTRACT

The availability of rockets and space probes has made possible in situ investigations of the earth's upper atmosphere and the atmospheres of other planets and comets. Mass spectrometers are able to make both gas and isotopic analyses. They have played a major role in the study of the earth's upper atmosphere and in the investigation of the atmospheres of Mars and Venus. The results obtained have important consequences in furthering our understanding of the evolution of the solar system. Application to the exploration of the outer planets and comets promises to provide important results no one can foresee.

INTRODUCTION

Over the years the Space Science Board and other advisory committees to the National Aeronautics and Space Administration, such as the Solar System Exploration Committee, have emphasized that there should be several main goals for our exploration of the Solar System. These include: (1) to determine the origin, evolution and the present state of the Solar System, (2) to gain a better understanding of the earth through comparative planetary studies, and (3) to investigate the relationship of the solar system and the appearance of life.

Some of these goals can be met partially through use of earth-based telescopes or appropriate laboratory studies. In the main, however, true understanding can only be obtained by using properly instrumented spacecraft which are sent on exploratory missions.

Of special interest are the structure and composition of planetary atmospheres, including our own. Much can be learned by remote sensing - examining the spectra emitted or absorbed by the atmosphere when it is illuminated by sunlight, or by studying the refraction or reflection of radio or light waves. However, if a detailed understanding is to be obtained, there is no substitute for in situ measurements made with appropriate instrumentation.

To this group it should come as no surprise that the most powerful instrument one can employ for making precise measurements of an unknown gas mixture is the mass spectrometer. It is versatile, sensitive and has a very large dynamic range. It can readily discriminate between similar compounds and through identification of cracking patterns, has a built in redundancy. Finally, it can make isotope as well as gas analyses, a feature of vital importance in planetological studies.

Dozens of rocket-borne mass spectrometers have been sent into the earth's upper atmosphere. Instruments have been sent to Mars to study the planet's upper and lower atmosphere and look for organic volatiles in surface soil, and to Venus to study its atmosphere. Later in this decade a mass spectrometer will be included in the complement of instruments included on the Galileo spacecraft to be launched on a mission designed to investigate the atmosphere of the planet Jupiter.

The mass spectrometers used have accomplished their mass separations using time-of-flight methods, resonance (as in the quadrupole) and magnetic deflection. Some instruments have been designed to measure only the ionic constituents, others to measure only the neutral components of the atmosphere under investigation. In this brief presentation I will restrict my remarks to measurements made on the neutral atmosphere components.

Mass spectrometers carried on spacecraft have placed on them special restrictions not found in laboratory instruments. For example, in most applications they must be light, complete instruments, preferably weighing less than 7 kg; their power consumption must be low, preferably under 10 watts. In addition they must be able to withstand the intense vibration and mechanical shock associated with rocket launchings. This latter requirement, when coupled with the weight restriction, places severe constraints on the mechanical construction.

THE ATMOSPHERE EXPLORER PROGRAM

The most ambitious program to date for studying the chemistry and physics of the earth's upper atmosphere was the Atmosphere Explorer mission in which three satellites called AE-C, -D, and -E were launched in the mid-1970s [1]. Each carried a large complement of experiments including three neutral gas and one or two ion mass spectrometers. One of the neutral mass spectrometers employed an "open" source [2] and used magnetic deflection mass separation. It will be discussed in detail later. The other two had "closed" sources [3,4] and had quadrupole mass analyzers. Of these, one was intended primarily for making precise particle density measurements, the other for measuring atmospheric temperature and winds.

MISSIONS TO OTHER PLANETS

In the Pioneer-Venus mission [5] a complement of experiments was carried on the orbiter and on the several probes which descended to the surface. Included in these were three mass spectrometers for studying the composition of the neutral atmosphere. The orbiter carried a quadrupole [6], and the "bus", an instrument almost identical with the open source mass spectrometer employed in the Atmosphere Explorer Program. This instrument analyzed the Venusian upper atmosphere [7] as the bus descended toward the planet surface. The large probe had a single focusing magnetic mass spectrometer [8] designed to make measurements in the dense lower atmosphere of Venus. In the several recent Russian Venera landings on Venus, monopole mass spectrometers were employed for studying the composition of the lower atmosphere [9,10].

In the Viking mission to Mars the aeroshell of each of the two Landers carried a double-focusing instrument for studying the composition of the upper atmosphere during the

descent to the planet [11]. It differed from the instrument to be described here in that it was smaller (1.0 inch instead of 1.5 inch) and, because of weight restrictions, did not use electron multiplier detectors. The Landers themselves carried double focusing magnetic mass spectrometers for analyzing the atmosphere at the planet surface and for looking for organic compounds in the soil [12].

THE OPEN SOURCE ATMOSPHERE EXPLORER MASS SPECTROMETER

My colleagues and I at Minnesota provided the "open" source mass spectrometer. As in all of our recent work, it employed the Mattauch-Herzog [13] double focusing configuration for accomplishing the mass separation. It permits the simultaneous collection of several masses of ions and forms a compact package - a factor of great importance in avoiding mechanical damage due to vibration or shock. Since a permanent magnet is employed, the power requirements are extremely low, and contrary to popular belief, the magnet weight is not excessive.

Figure 1 is a schematic drawing of the instrument. Since the AE satellites moved in orbits whose perigees were always more than 130 km above the earth's surface, the atmospheric density was sufficiently low that ambient atmosphere could be admitted directly to the source as shown. After passing through three high transmission grids, the beam entered the ionizing region where ions are produced by a tightly collimated electron beam perpendicular to the figure, shown as a black dot between the two small bar magnets. The magnets are seen on end in the figure, appearing as small cross-sectioned rectangles.

As in conventional laboratory mass spectrometers, ions formed by the electron beam are propelled toward the mass analyzing region by an electric field directed toward the right in the figure. This field is due in part to the potential difference between grid 3 and the magnet assembly and in part to the field penetrating through the slit to the right of the electron beam, this field being due to the lower potential of the ion focusing electrodes J_1 and J_2.

In an instrument operating under normal conditions, if one designates V as the potential difference between ground G and the assembly Sh which holds the magnets M, then grid 3 has a potential of approximately 1.2 V and the J electrodes potentials of approximately 0.9 V. Mass scans are obtained by varying V. The potentials of the + and - electric analyzer plates, grid 3, and the J_1 and J_2 electrodes are proportional to V at all times. Grid 2 is kept at a small negative potential, also tracking V. This has the effect of neutralizing any positive field which may penetrate to the left of the grounded grid 1 and affect other instruments such as electron probes on the satellite.

In the atmosphere Explorer OSS instruments ions differing in mass by a factor of 8 were collected simultaneously. Galileo Electro Optics Spiraltron [14] electron multipliers in the counting mode were employed as ion detectors. For measuring signals beyond the range of the high mass multiplier, the current falling on the grid between S_4 and the multiplier was read with an electrometer.

Figure 2 is a typical spectrum obtained with the high mass collector when air was introduced into the instrument in a laboratory study. Clearly seen are the familiar molecular and fragment ion peaks, including isotopic species. Most of the CO_2 and H_2O can be attributed to residual gases in the system.

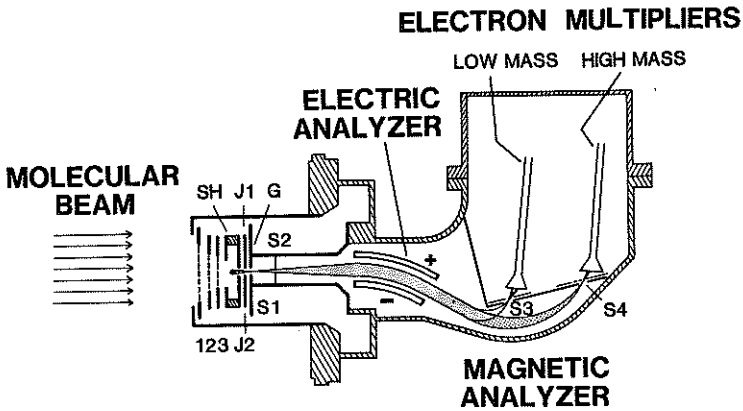


Fig. 1. Open Source Atmosphere Explorer Mass Spectrometer. The radius of curvature in the magnetic field of the ions reaching the high mass collector is 1.5 inches (3.81 cm). The magnetic field strength is 4500 gauss. The total weight of the instrument including all electronics is 16 pounds (7.3 kg).

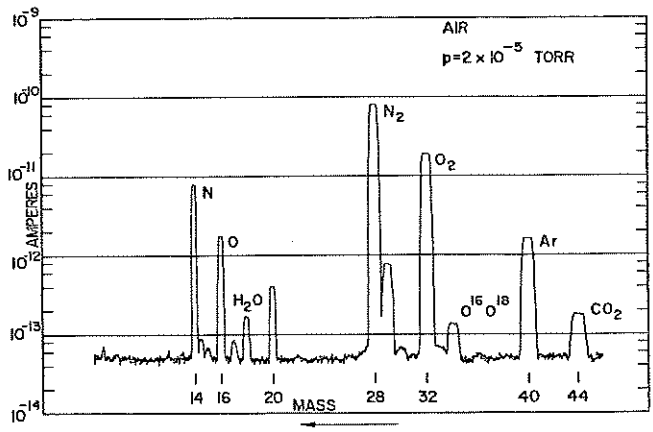
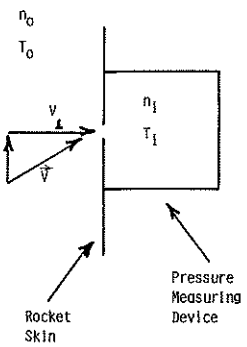


Fig. 2. Typical mass spectrum obtained when air is introduced into instrument of Fig. 1.

When mass spectrometers are carried on fast moving spacecraft for sampling ambient atmospheres, interesting effects may occur which are not encountered in normal laboratory applications. Predominant among these is a ram effect which may cause the particle density in an ion source to differ drastically from the ambient value one is attempting to measure. In Fig. 3 consider a pressure sensor moving toward the lower left with a velocity V through an ambient atmosphere in which the particle density and temperature are n_o and T_o respectively. This is equivalent to having a mass motion of gas with a vector velocity $\vec{V}$ toward the sensor. A gas beam thus enters the orifice in the pressure measuring device as shown. The molecules in the beam have a velocity distribution given by the vector velocity $\vec{V}$ superimposed on the normal omnidirectional Maxwellian velocity distribution characteristic of the temperature of the ambient atmosphere through which the device is moving. After entering the chamber and colliding with the walls, the molecules acquire an omnidirectional velocity distribution characteristic of the wall temperature. The particle density in the chamber builds up to such a value, n_i, that the number of molecules escaping by ordinary effusion from the hole in unit time equals the number entering. The equation relating the number densities inside and outside the chamber follows from a simple kinetic theory calculation with the result given in Fig. 3.



$$n_o = n_i (T_i/T_o)^{1/2} / F(S)$$

where $S = V_\perp / v_{p_o}$

and $F(S) = \left[\pi^{1/2} S(1 + \text{erf } S) + e^{-S^2}\right]$

Some typical values of F(S)

S	F(S)
0	1
1	3.6
2	7.2
-1	0.09
-2	0.0017

Fig. 3. Relation between particle density (n_o) in an ambient atmosphere and inside (n_i) of a pressure sensor moving toward the lower left with a velocity V. $V_\perp$ represents the perpendicular component of the velocity V and v_{po} the most probable velocity in the Maxwellian distribution of the ambient particles.

In the case of a spinning spacecraft where V changes sign, n_i will undergo a large modulation even when the spacecraft is moving with velocities comparable with v_{po}, the most probable velocity of the gas molecules in the Maxwellian distribution in the ambient gas. For high speed spacecraft such as earth orbiters, moving with speeds of around 8.5 km per second, the modulation becomes very large indeed. For example, when the instrument "looks" forward the value of n_i for N_2 will be approximately 60 times that in the ambient atmosphere, n_o. When the instrument "looks" backward, the n_i value will be many decades below n_o.

In deriving the relation given in Fig. 3 it is assumed that the orifice in the measuring device is small so that molecules entering will make many collisions and achieve thermal equilibrium before escaping. This condition is satisfied in closed-source instruments such as NACE (neutral atmosphere composition experiment) flown on the Atmosphere Explorer spacecraft AE-C, -D, and -E [3]. On the other hand, if the ion source is more open as in the OSS instrument (open-source mass spectrometer) flown on the same spacecraft [2], the situation is less clear, and laboratory calibrations with a molecular beam facility [15] are required to determine how much the conditions differ from the ideal case of a small entry orifice. Surprisingly, with a geometry closely resembling that shown in Fig. 1, the equation shown in Fig. 3 is almost satisfied and only a small correction need be applied. Apparently the grid structure and its accompanying supports is almost as effective in thermalizing particles as is a closed box.

From earth-based spectroscopic observations atomic oxygen has long been known to be an important constituent in the earth's atmosphere above 100 km. Schaefer and Nichols [16] made the first in situ measurements of this species, using an open source mass spectrometer. Because atomic oxygen is highly reactive, they and other early investigators [17,18,19] felt that with an open source structure, one had a better chance of measuring it than with a closed-source instrument where multiple collisions on ion source surfaces would cause recombination and hence loss of the constituent. Nevertheless some collisions were unavoidable so quantitative measurement of atomic oxygen using open source instruments have been open to question.

On the other hand, atomic oxygen, when it recombines, forms molecular oxygen, and this can be used in closed-source mass spectrometers as a quantitative measure of atomic oxygen above 200 km in the earth's atmosphere where the ambient concentration of O_2 is low, and an ambiguity does not arise. The method has been used effectively in experiments with the NACE instrument as well as in other investigations [20].

In the case of an open-source mass spectrometer carried on a fast moving vehicle such as an earth satellite, the ambient atmosphere appears as a stream of particles having a speed of approximately 8.5 km/sec, or an equivalent energy of about 0.37 eV/amu. In other words, atomic oxygen atoms reaching the instrument appear to have an energy of 6 eV, oxygen molecules, 12 eV, etc. Use may be made of this fact to distinguish between true ambient molecules and ones created on instrument surfaces or appearing as a residual background. If, in Fig. 1, grid #3 and the focusing electrodes J_1 and J_2 are connected electrically to the structure Sh holding the magnets M, there will be no electric field to draw ions out of the electron beam when they are formed. Ambient particles which have struck the ion source and have become thermally accommodated have an energy of less than 0.1 eV. This energy is not enough to overcome the negative space charge potential holding ions in the electron beam. Only fragment ions which acquire kinetic energy in the dissociation process can overcome the potential well of the electron beam. This number can be reduced by using as low as possible electron accelerating potentials. Ambient particles which have not struck surfaces retain their full energy with respect to the instrument. As stated above, they have more than a few electron volts of kinetic energy, and carry this energy with them after ionization and readily escape from the electron beam region into the ion accelerating region to the right of J_1 and J_2 in the figure.

In the Atmosphere Explorer spacecraft the Open-Source Mass Spectrometer is mounted on the "equator" and "looks" radially outward. The spacecraft can be operated in either a despun or spinning mode. In the latter case the spin period is nominally 15 seconds and the spin axis is perpendicular to the plane of the orbit. As a result the mass spectrometer "looks" alternately "forward" and "backward".

The instrument itself has a number of modes of operation, including several peak-stepping modes. For oxygen studies the instrument switches back and forth between masses 16 and 32 at intervals of 1/16 second. Figure 4 shows the results obtained at two different altitudes in orbit 1165 of satellite AE-C as the instrument opening passes through the forward direction [21]. The data show a number of interesting features. First of all, definite sharp maxima occur as the instrument rotates through the forward direction. It is disappointing that the fall off was not greater for large angles. It seems likely that this was due to imperfect rejection of slow particles, that is, incoming particles which have struck ion source surfaces and were not fully accommodated. Had it been possible to apply a slight retarding potential, this background would undoubtedly have been lower.

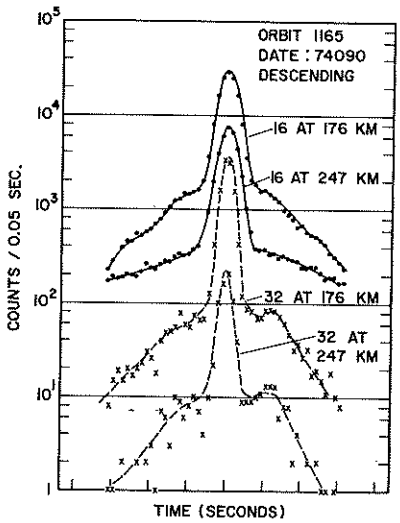


Fig. 4. Mass spectrometer electron multiplier output for masses 16 and 32 as the instrument in fly-through mode looks "forward" on the spacecraft which is spinning with a period of 15 seconds. The spin axis is perpendicular to the plane of the orbit.

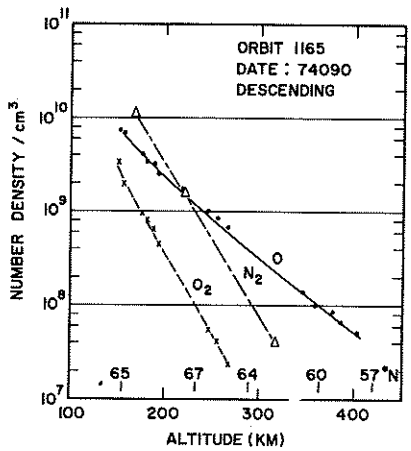


Fig. 5. Number densities for atomic and molecular oxygen deduced from data such as shown in Fig. 4. The number density curve for N_2 was obtained while the instrument was in its normal mode of operation, the source responding as one which is closed.

It is interesting to note that the 32 peak falls off with altitude much more rapidly than the 16. This is as it should be since the scale heights in the atmosphere differ by a factor of two. By means of calibration techniques involving original laboratory data as well as operation in other modes during flight, it was possible to put data such as shown in Fig. 4 on an absolute basis. The final result for the descending mode of the orbit is shown in Fig. 5. It is gratifying to see that the O_2 profile closely parallels that for N_2 and is drastically different from that for O. The mass 32 peak is thus a true measure of the O_2 concentration in the atmosphere. The use of this method, called the "fly-through" or retarding potential method, made it possible to measure O and O_2 simultaneously in the lower thermosphere where their abundances are roughly comparable. Notable, also, was the fact that when the instrument was operating in the normal mode, the 32 peak above 200 km, then being produced almost entirely from recombination of atomic oxygen in the instrument, had the same slope as the 16 peak in the fly-through mode.

Another feature of the data is the difference in widths of the 16 and 32 peaks at the sharply forward position. While a small part of the width is caused by the acceptance angle of the instrument itself [22], the major part comes about because the ambient particles reaching the instrument have a velocity distribution made up of a unidirectional component of about 8.5 km/sec upon which is superimposed an omnidirectional Maxwellian distribution having a maximum of roughly 1 km/sec for gas at the temperature of the atmosphere, about 950°K. Hence as the spacecraft spins, the instrument accepts particles arriving at different angles. Because of the higher maximum velocity for lighter particles, one should expect the mass 16 peak to be broader than that for mass 32 as is indeed the case. A detailed study of peak shapes such as shown in Fig. 4 has made it possible to make in situ determinations of thermospheric temperature [23,24].

The power of mass spectrometry in helping elucidate complex problems is well illustrated by its direct identification of atomic nitrogen as a constituent of the earth's thermosphere. Its presence had been predicted from considerations of the chemical reactions which would take place between the various neutral and ionic constituents in the presence of the sun's radiation [25]. Optical spectroscopic observations indeed established its existence qualitatively. The first quantitative determinations were made mass spectroscopically [26] by observing the mass 30 peak in the OSS instrument at high altitudes - 400 km and above. At these altitudes the amount of ambient NO was far too low to account for the mass 30 peak observed. It was concluded that NO was formed in the instrument as a result of collisions of incoming N atoms with atomic O residing on instrument surfaces. Confirmation was obtained at low altitudes where the mass 14/mass 28 abundance ratio was higher than expected if due only to the dissociation of molecular nitrogen or the formation of doubly charged ions by electron impact in the instrument. This study, together with a series of subsequent investigations, established many interesting facts about the behavior of atomic nitrogen in the earth's upper atmosphere.

As a result of numerous rocket flights, of a number of satellite flights and of incoherent scatter radar data, a large body of data on atmospheric composition, density and temperature has been accummulated. Based on these data a number of empirical models have been developed, giving the composition and temperature of the earth's thermosphere as a

function of altitude, latitude, time, magnetic activity, etc. Among recent models is the ESRO 4 [27]. A more comprehensive model having a much larger data base, a large part of which was obtained with the mass spectrometers on the Atmosphere Explorer satellites, has also been developed [28,29,30].

THE VIKING MISSION TO MARS

One of the most ambitious space progrms to date was the Viking mission to Mars [31]. The purpose of the mission was to learn as much as possible about the atmosphere and surface of Mars and to see if life did or could exist. Two identical spacecraft were launched toward Mars in the summer of 1975, arriving at Mars about 10 months later. Upon reaching the planet the spacecraft went into orbit and at an appropriate time released Landers which decended to Mars. The part of the spacecraft which remained behind was called the Orbiter. It carried three experiments, a camera for photographing the surface of Mars, an infrared sensor for measuring the temperature of the Martian surface and an infrared sensor for measuring water vapor in the Martian atmosphere.

To slow down the Lander as it approached the planet, an aeroshell provided a braking force until a parachute and retro-rockets could take over the final descent. The aeroshell carried a neutral mass spectrometer for studying atmospheric composition, a retarding potential analyzer for studying electron and ionic distribution, and pressure and temperature sensors for investigating atmospheric structure during the descent.

The Lander itself carried a number of experiments: facsimile cameras to study the terrain, active biological experiments to look for living organisms in soil samples, a gas chromatograph mass spectrometer combination, GCMS, to look for organic compounds in the soil and to measure atmospheric composition, a meteorological station, a seismometer to look for Mars quakes and an X-ray fluorescence analyzer for determining the inorganic composition of soil samples. These, together with a small magnet for looking for magnetism in soil samples and radio experiments completed the complement of investigations.

For many years the composition of the Martian atmosphere was a source of wild speculation and many believed it might resemble our own. However, following the 1965 fly-by of the Mariner 4 spacecraft and subsequent earth-based spectroscopic measurements it appeared that it was composed primarily of CO_2 with small traces of CO, H_2O, and O_2. The radio occulation experiments on the Mariner 4 spacecraft indicated that the surface pressure lay near 6 mb. Then, in 1974, before the launch of the Viking spacecraft, a disturbing development took place. The Russian interplanetary station Mars 6 descended on Mars. It carried a mass spectrometer pumped with a sputter ion pump. Housekeeping data transmitted during the parachute descent indicated an abnormally high sputter ion pump current which was attributed to the presence of argon [32,33]. The amount was estimated to be as much as 35 percent of the atmosphere. This caused great consternation in the Viking program as the GCMS mass spectrometer was also pumped with a sputter ion pump which might have failed if an atmospheric analysis was attempted with so much argon present. Were such a test conducted soon after the landing, as was planned, and the instrument failed, a look for hydrocarbons in the soil might not be possible. An investigation of the soil was one of the high priority items in connection with the search for life on Mars.

The Upper Atmosphere Mass Spectrometer (UAMS) mounted on the aeroshell had been regarded as one of the minor instruments in the mission. However, on the morning of July 20, 1976, as the first Viking Lander descended to the planet, it had its moment of glory as all eyes were on the data as it came out of the Jet Propulsion Laboratory computer.

Figure 6 is the mass spectrum of the atmosphere observed as the Lander descended and passed the 140 km altitude [34]. It is clear from the relative 40 and 44 peaks that the Ar/CO_2 mixing ratio must be less than 2 percent. This is confirmed from the relative 20 and 22 peaks when use is made of the laboratory calibrations. A detailed examination of the peaks showed that N_2, O_2, CO, O and NO, in addition to Argon, were present. The 18 and 17 peaks are attributed to water, present in the apparatus as a residual impurity. The discovery of N_2 was of great interest because of the role nitrogen plays both in the history of volatiles and in biology.

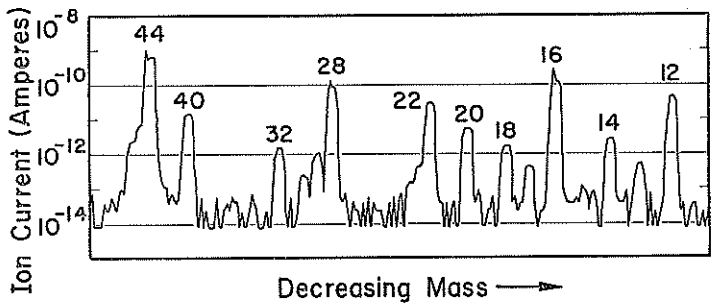


Fig. 6. Mass spectrum of the Martian atmosphere at 140 km altitude as found by UAMS on Viking 1. CO_2, Ar, N_2 and O_2 are clearly evident. Large 16 peak is due mainly to atomic oxygen (not measured quantitatively in the experiment). Careful analyses of 28, 29, and 30 peaks indicated presence of NO and $^{15}N/^{14}N$ ratio 60 percent greater than on earth.

An examination of the relative 46, 45, and 44 peaks led to the conclusion that the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ isotopic abundance ratios agreed within a few percent with terrestrial values and hence by inference so would the $^{17}O/^{16}O$ ratio. Of more interest were the 30, 29 and 28 peaks. These are shown in Fig. 7 schematically in a linear block diagram for a typical spectrum. From an analysis of the relative 44, 28, 14 and 12 peaks one can determine the part of the 28 peak due to N_2 and the part due to CO (as a fragment of CO_2 and as ambient CO). From this one can construct 29 or 30 peaks assuming the C and O isotope abundances are terrestrial. The excess 30 peak is attributed to NO in the Martian atmosphere, not previously observed.

The 29 peak is more interesting. It appears that the $^{15}N/^{14}N$ ratio on Mars is approximately 60 percent higher than on the earth. The most reasonable explanation is that as a result of photochemical reactions in the Martian thermosphere [35,36,37] atomic N is lost with the rate of loss of ^{14}N being greater than that of ^{15}N. It follows that in earlier days Mars must have had much more nitrogen in its atmosphere, a conclusion of profound planetological significance.

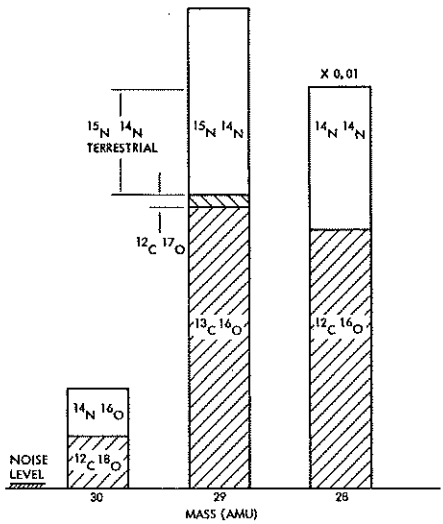


Fig. 7. Block diagram representing to scale the relative heights of the mass peaks at 28, 29 , and 30 amu in a spectral scan near 140 km altitude during the descent of Viking 1. The contributions of the various isotopic combinations are shown. For reference the noise level of the amplifier which measured the ion currents is also shown.

Figure 8 summarizes the measurements made with the Viking Upper Atmosphere Mass Spectrometer during the descent of the Viking 1, the first Lander. The profiles for Viking 2, which landed on September 3, 1976, were similar except that they were less steep due to the lower atmosphere temperature at the time and place. Measurements could only be made in the approximate altitude range 110-200 km. Lack of sensitivity of the instrument above 200 km prevented obtaining reliable data at higher altitudes. Below 110 km the atmospheric pressure was so high that the instruments ceased to function properly. Since the turbopause level in the Martian atmosphere lies near 120 km, the relative mass spectrometer-determined number densities at 120 km represent essentially the relative number densities for the bulk atmosphere, that at the surface of the planet.

The mass spectrometer carried on the Lander employed an electron multiplier detector and hence had a considerably higher sensitivity than the aeroshell mass spectrometer. Moreover, it was a somewhat larger instrument and could resolve masses up to 200 amu. Gas volatilized from soil samples at temperatures as high as 500°C was passed through the GC column with the hope of detecting organic compounds, if present in the soil. None were found although the sensitivity was sufficient to detect most compounds in the parts per billion range [38].

The study of the atmosphere was much more rewarding. Direct analyses could be made and by means of an inlet system which removed CO_2, CO and H_2O the inert gases could be enriched, with the result that the sensitivity for them was enhanced [39]. The existence of

N_2 was confirmed, as was its anomalous isotopic abundance ratio. Also confirmed were the "normal" isotopic ratios for oxygen and carbon.

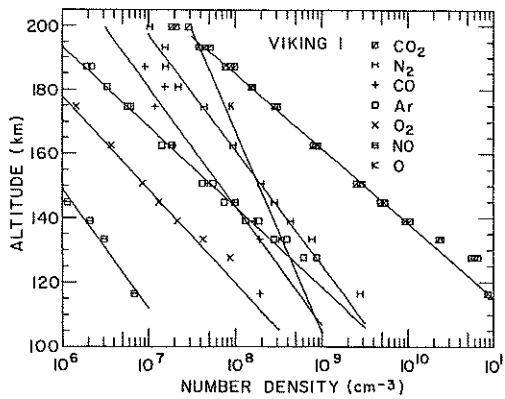


Fig. 8. Number densities of CO , N_2, CO, O_2, NO and O in the Martian atmosphere as determined during the landing of Viking 1 on July 20, 1976. The lines drawn are the least squares fit of a straight line to the data above 140 km. The atomic oxygen line was determined from the retarding potential analyzer also mounted on the aeroshell of the spacecraft.

^{36}Ar which could not be detected with the UAMS was shown to exist with an $^{36}Ar/^{40}Ar$ about 10 percent that on earth. Neon, krypton, and xenon were detected, with very low abundances as was a trace of ozone. Figure 9 shows mass spectra obtained for Kr and Xe. Except for the abnormal 80 peak, attributed to the high pressure of argon in the instrument, the krypton appeared to terrestrial-like. On the other hand, the xenon appeared to contain much more ^{129}Xe than observed in the terrestrial atmosphere.

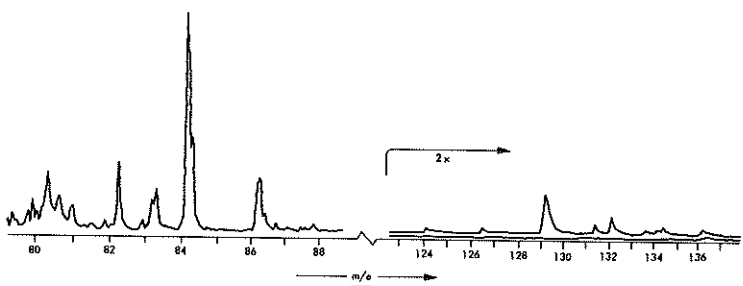


Fig. 9. Mass spectra for Kr and Xe as found with mass spectrometer on surface of Mars. The spectra shown are the averages of 9 scans. The lower line shown in the xenon spectrum is the average of three background scans. The abundances of Kr and Xe in the Martian atmosphere were estimated to be 0.3 and 0.08 ppm, respectively.

The investigators concluded that the data were consistent with two possible hypotheses: (1) The volatile inventory of Mars is similar to the earth's but either an early catastrophic event removed 90% of the atmosphere or Mars never degassed as much as the earth, or (2) Mars is deficient in most volatile elements, when compared with the earth, and degassing is not so complete.

It is clear that additional studies with improved instruments in future missions would be very valuable in elucidating the history of the planet.

THE PIONEER-VENUS MISSION

Twenty-five years ago little was known about the atmosphere of Venus other than that it contained CO_2 and traces of other gases. Indeed, many thought it might have an atmosphere resembling our own. Improved infrared astronomy and radio telescope data greatly enhanced our knowledge, but it was not until 1962 when Mariner 2 flew by the planet and shortly thereafter, when the Russian Venera Series of spacecraft began to land on the planet, that our knowledge made substantial strides. Today we know that there is a very dense atmosphere consisting primarily of CO_2 and that at the surface the pressure and temperature lie near 100 atmospheres (earth) and 500°C, respectively.

Thanks to the mass spectrometers carried on the orbiter and on the probes in the 1978 Pioneer-Venus Mission much has been learned about the composition of the atmosphere. For example, the orbiter instrument obtained quantitative data on the principal gases CO_2, CO, N_2, O, N and He observed in the thermosphere in the altitude region 150-250 km [40]. Large day-night differences were observed along with strong orbit-to-orbit variations in the night side atmosphere. Unfortunately, due to the presence of impurities, argon could not be measured.

The neutral mass spectrometer (BNMS) carried on the bus made careful density measurements of CO_2 and He as the bus passed through the altitude range 100-200 km during the descent [41]. The homopause level was measured, and concentrations of N_2 and CO were found near 150 km. The isotopic composition of argon could not be determined except that mixing ratios for ^{36}Ar and ^{40}Ar relative to CO_2 were found to have maximum values of 9×10^{-6} and 20×10^{-6}, respectively [42].

The large probe mass spectrometer (LNMS) was more complex and designed to operate in the high pressure region of the lower atmosphere [43]. Because it was intended to operate over a large pressure range, it employed a variable-speed pumping system using a combination of ion pumps and chemical getters. Although only a single-focusing wedge magnet instrument, it had relatively high resolution and covered the entire mass range 1-208 amu. Measurements were made from 62 km altitude to the surface [44].

Except for N_2 which was found to have a mixing ratio of 0.04 relative to CO_2, other constituents had abundances measured in the ppm range. The $^{22}Ne/^{20}Ne$ ratio was found to be 0.07 ± 0.02 which lies nearer to the solar wind than the terrestrial value. Carbon and oxygen isotope abundance ratios appeared similar to terrestrial. Small traces of H_2S and C_2H_6 may have been present. Upper limits were set for He, Kr, O_2, SO_2, H_2O, Cl, and Hg.

Of special interest were the argon measurements. Unlike Mars, where the $^{36}Ar/^{40}Ar$ was found to be 1/3000, and the earth, where it is 1/300, the LNMS instrument found the

Venusian value to be close to unity, and as on Mars and earth the $^{36}Ar/^{38}Ar$ ratio was approximately 5. A comparison was made between the total amounts of argon reported in the several experiments. Included in the comparison were the Pioneer-Venus gas chromatograph measurements and the Russian Venera 11 and 12 results [45]. The agreement is only fair, the BNMS giving a considerably lower value.

EXPLORATION OF THE OUTER PLANETS

The terrestrial, or inner, planets - Mercury, Venus, Earth and Mars have solid surfaces. Except for Mercury, all have atmospheres. The outer gas-giant planets - Jupiter, Saturn, Uranus and Neptune - appear to be vast blobs of gas with no measurable core. The principal constituent in each case has been shown to be H_2. Molecules observed or believed to be present in various amounts include: He, H_2O, CH_4, NH_3, H_2S, PH_3, HCl, Ar, Ne and some light hydrocarbons such as C_2H_6, C_2H_2, etc.

These planets have moons, some of which have atmospheres. Titan, a moon of Saturn, is particularly interesting. Its substantial atmosphere appears to be made up of about 82% N_2, 12% Ar, 3% CH_4, and traces of light hydrocarbons, CO_2, CO, and cyanogen compounds.

Our knowledge of the outer planets comes from ground-based astronomy or from the highly successful Pioneer and Voyager fly-bys. Later this decade a probe, the Galileo, will be sent to Jupiter and will penetrate its atmosphere. A quadrupole mass spectometer, supplemented by an enrichment system and a gas purification cell, will be included in the payload [46]. Since Jupiter is so much different from the terrestrial planets, determination of the composition of its atmosphere will be a major step in furthering our knowledge of the solar system.

While no missions have yet been planned which will carry mass spectrometers to the other outer planets, this will surely happen. There is so much to be learned.

A RENDEZVOUS MISSION TO A COMET

Comets are among the most interesting unexplored objects in the solar system. It is generally believed that they represent material left over when the solar system was created and may preserve a record of the physical and chemical processes which took place in the very early days. They have been "parked" for 4.6 billion years at vast distances from the sun, and out of reach of its heat. A random change in the positions of the stars unbalances the forces acting on a comet, and they feel a net force toward our sun and go into orbit about the sun.

The original bodies, called the nuclei, are believed to have average diameters in the range of 1 to 10 km and to have masses of from 10^{10} to 10^{18} grams, respectively. They have sometimes been described as dirty snowballs, consisting of ices, primarily H_2O and other volatile molecules made of light elements. Also present is rocky material, much of which is finely divided dust, in the micron size range.

As a comet approaches the sun the ices begin to sublime, carrying with them the dust. Because of the small size of the solid body, the gravitational pull is very low and gases and dust can readily escape, the escape velocity lying in the 1 to 5 m/s range. The

nuclei are too small to be seen directly, and observation is through the reflection or emission of light from the evaporating cloud (or atmosphere) of gas and dust.

The gas in the coma (the region around the nucleus) appears to consist of stable (or parent) molecules such as H_2O, HCN, CH_3CN, etc. Also seen at larger distances are radicals - CN, C_2, C_3, CH, and others. As the comet moves through its trajectory, it has a tail containing ions of the various neutral constituents seen in the coma. The fact that organic molecules are seen in the cometary atmosphere, as well as in interplanetary space is intriguing, leading some to suggest that the primitive earth obtained organic material by comet bombardment.

It is obvious that a mass spectrometer would be a very powerful tool for studying a cometary atmosphere, and indeed in any mission to a comet, mass spectrometers will be among the key instruments employed. To carry out the actual measurements is by no means simple. First of all, the atmosphere is extremely tenuous. For example, for Tempel-2, a comet under consideration for a rendezvous mission, the gas densities at 100 and 1000 km from the nucleus are estimated to be 10^7 and 10^5 molecules/cm^3, respectively. Since most of the gas is almost certainly water vapor, the interesting constituents have lower densities. A very sensitive mass spectrometer will obviously be required. The reader is reminded that 10^5 molecules/cm^3 corresponds to a pressure of 2.5×10^{-12} T at room temperature.

While a fly-by mission to a comet could produce some useful scientific results, including measurements from mass spectrometers, the time available would be limited. Accordingly, there is general agreement that a rendezvous mission would be highly desirable since it would give time to make comprehansive measurements, including studies of the nucleus. Such a mission would certainly be a challenge for mass spectroscopy.

In addition to the high sensitivity requirement, the instrument would have to be able to withstand bombardment by dust and possible sand or larger size solids; the closer one came to the comet, the greater would be the hazard. In order to study the interesting radicals which have been observed one would almost certainly want to employ an open ion source, a complication if dust protection is required. Since radicals are very likely fragments formed from parent molecules, many are likely to possess kinetic energy well above the energy of the parent molecules which are expected to reach speeds of some hundreds of meters/sec. at distances of 1000 km from the nucleus. Since the speeds of parent molecules are radially outward from the nuclei, whereas dissociation fragments will have omnidirectional velocity distributions, a properly designed ion source will have the possibility of distinguishing between parent and daughter particles.

Of special interest will be the analysis of gases adsorbed on, or embedded in, the dust particles. Also of great interest will be a study of the ions found around and in the tail of the comet. If a landing on the nucleus itself can be achieved, a sampling of the surface will be of great importance.

All in all, it can be seen that mass spectroscopy has a vital role to play in studying the nature of what many believe are the most pristine objects in the solar system.

CONCLUSIONS

No discussion of the employment of mass spectrometry in planetary studies would be complete without at least a mention of the many analyses of meteoritic and lunar samples which have been made. Hundreds, if not thousands, of samples have been examined and determinations made of the amounts of rare gases present and their isotopic constitution. 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.

At the present time matters are very much in a state of flux. A theory which appears reasonable in explaining the composition of one planet may be inconsistent with what we have learned from meteorites or from other planets. A discussion of successes and failures of the various theories is beyond the scope of the present article and the reader is referred to a number of excellent reviews [47-53]. While the interpretation of data may be in question, the fact that mass spectrometry has played a vital role in providing clues relating to the origin and evolution of the solar system is not. Because of its power and versatility, it will continue to be an essential instrument in space science studies.

REFERENCES

1. A. Dalgarno, W.B. Hanson, N.W. Spencer, and E.R. Schmerling, Radio Science 8, 263-266 (1973).
2. A.O. Nier, W.E. Potter, D.R. Hickman, and K. Mauersberger, Radio Science 8, 271-276 (1973).
3. D.T. Pelz, C.A. Reber, A.E. Hedin, and G.R. Carignan, Radio Science 8, 277-285 (1973).
4. N.W. Spencer, H.B. Niemann, and G.R. Carignan, Radio Science 8, 287-296 (1973).
5. L. Colin, Science 203. 743-745 (1979).
6. H.B. Niemann, R.E. Hartle, W.T. Kasprzak, N.W. Spencer, D.M. Hunten, and G.R. Carignan, Science 203, 770-772 (1979).
7. U. von Zahn, D. Krankowsky, K. Mauersberger, A.O. Nier, and D.M. Hunten, Science 203, 768-770 (1979).
8. J.H. Hoffman, R.R. Hodges, Jr., M.B. McElroy, T.M. Donahue, and M. Kolpin, Science 203, 800-802 (1979).
9. M. Ya. Marov, Ann. Rev. Astron. Astrophys. 16, 141-169 (1978).
10. R.Z. Sagdeev, V.I. Movoz, and T. Breus, in NASA Special Publication, SP-461 (1983).
11. A.O. Nier, W.B. Hanson, M.B. McElroy, A. Seiff, and N.W. Spencer, Icarus 16, 74-91 (1972).
12. D.M. Anderson, K. Biemann, L.E. Orgel, J. Oro, T. Owen, G.F. Shulman, P. Toulmin III, and H.C. Urey, Icarus 16, 111-138 (1972).
13. J. Mattauch and R. Herzog, Z. Phys. 89, 786-795 (1934).
14. Galileo Electro-Optics Corp., Sturbridge, MA 01518, Type 4219.
15. J.O. Ballenthin and A.O. Nier, Rev. Sci. Instr. 52, 1016-1024 (1981).

16. E.J. Schaefer and M.H. Nichols, J. Geophys. Res. 69, 4649-4660 (1964).

17. N.W. Spencer and C.A. Reber, Space Science 3, 1151-1155 (1962).

18. A.O. Nier, J.H. Hoffman, C.Y. Johnson, and J.C. Holmes, J. Geophys. Res. 69, 979-989 (1964),

19. K. Mauersberger, D. Muller, D. Offerman, and U. von Zahn, Space Research 7, 1150-1158 (1966).

20. G.P. Newton, W.T. Kasprzak, and D.T. Pelz, J. Geophys. Res. 79, 1929-1941 (1974).

21. A.O. Nier, W.E. Potter, D.C. Kayser, and R.G. Finstad, Geophys. Res. Lett. 1, 197-200 (1974).

22. J.L. Hayden, A.O. Nier, J.B. French, N.M. Reid, and R.J. Duckett, Int. J. Mass Spectr. and Ion Phys. 15, 37-47 (1974).

23. D.C. Kayser, L.H. Johnson, W.E. Potter, and A.O. Nier, Space Sci. Instr. 4, 339-350 (1979).

24. D.C. Kayser, E.L. Brieg, K.A. Power, W.B. Hanson, and A.O. Nier, J. Geophys. Res. 84, 4321-4327 (1979).

25. D.F. Strobel, J. Geophys. Res. 76, 2441-2452 (1971).

26. K.M. Mauersberger, M.J. Engebretson, W.E. Potter, D.C. Kayser, and A.O. Nier, Geophys. Res. Lett. 2, 337-340 (1975).

27. U. von Zahn, W. Kohnlein, K.H. Fricke, U. Laux, H. Trinks, and H. Volland, Geophys. Res. Lett. 4, 33-36 (1977).

28. A.E. Hedin, J.E. Salah, J.V. Evans, C.A. Reber, G.P. Newton, N.W. Spencer, D.C. Kayser, D. Alcayde, P. Bauer, L. Cogger, and J.P. McClure, J. Geophys. Res. 82, 2139-2147 (1977).

29. A.E. Hedin, C.A. Reber, G.P. Newton, N.W. Spencer, H.C. Brinton, H.G. Mayr, and W.E. Potter, J. Geophys. Res. 82, 2148-2156 (1977).

30. A.E. Hedin, J. Geophys. Res. 88, 10,170-10,188 (1983).

31. G.A. Soffen, J. Geophys. Res. 82, 3959-3970 (1977).

32. V.G. Istomin and K.V. Grechnev, Icarus 28, 155-158 (1976).

33. V.T. Moroz, Icarus 28, 159-163 (1976).

34. A.O. Nier and M.B. McElroy, J. Geophys. Res. 82, 4341-4349 (1977).

35. R.T. Brinkman, Science 174, 943 (1971).

36. M.B. McElroy, Y.L. Yung, and A.O. Nier, Science 194, 70-72 (1976).

37. J.L. Fox and A. Dalgarno, Planet, Space. Sci. 28, 41-46 (1980).

38. K. Biemann, P. Toulmin III, L.E. Orgel, A.O. Nier, D.M. Anderson, P.G. Simmonds, D. Flory, A.V. Diaz, D.R. Rushneck, J.E. Biller, and A.L. LaFleur, J. Geophys., Res. 82, 4641-4658 (1977).

39. T. Owen, K. Biemann, D.R. Rushneck, J.E. Biller, D.W. Howarth, and A.L. LaFleur, J. Geophys. Res. 82, 4635-4639 (1977).

40. H.B. Niemann, W.T. Kasprzak, A.E. Hedin, D.M. Hunten, and N.W. Spencer, J. Geo. Phys. Res. 85, 7817-7827 (1980).

41. U. von Zahn, D. Krankowsky, K. Mauersberger, A.O. Nier, and D.M. Hunten, Science 203, 768-770 (1979).

42. K. Mauersberger and U. von Zahn, Geophys. Res. Lett. 6, 671-674 (1979).

43. J.H. Hoffman, R.R. Hodges, and K.D. Duerksen, J. Vac. Sci. Technol. 16, 692-694 (1979).

44. J.H. Hoffman, R.R. Hodges, T.M. Donahue, and M.B. McElroy, J. Geophys. Res. 85, 7882-7890 (1980).

45. J.H. Hoffman, V.I. Oyama, and U. von Zahn, J. Geophys. Res. 85, 7871-7881 (1980).

46. H.B. Niemann, Goddard Space Flight Center, Private communication.

47. D.M. Hunten, Space Sci. Rev. 12, 539-599 (1971).

48. E. Anders and T. Owen, Science 198, 453-465 (1977).

49. T. Lee, Rev. Geophys. and Space Phys. 17, 1591-1611 (1979).

50. J.B. Pollack and D.C. Black, Science 205, 56-59 (1979).

51. T.M. Donahue, J.H. Hoffman, and R.R. Hodges, Jr., Geophys. Res. Lett. 8, 513-516 (1981).

52. M.B. McElroy and M.J. Prather, Nature 293, 535-539 (1981).

53. J.B. Pollack and D.C. Black, Icarus 51, 169-198 (1982).

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

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ABSTRACT

Contrary to public opinion, Secondary Ion Mass Spectrometry (SIMS) has been with us for over half a century under various guises, the most recent reincarnation being "FAB" (Fast Atom Bombardment). This Retrospective traces the SIMS lifeline from its roots in the 1930's, through basic studies in the 1950's and 1960's, to the present explosive development of inorganic and organic applications. Special attention will be given to the various desorption modes of organic ions from solid and liquid surfaces.

INTRODUCTION

Secondary Ion Mass Spectrometry is a scientific and technical field whose roots go back much further than is generally known. This retrospective will illuminate - from a personal, therefore subjective, point of view - how SIMS had a slow, hesitant start many decades ago, then went through several developmental stages, and finally blossomed out into a fertile specialty that so far has produced well over four thousand publications.

The first problem we face concerns NOMENCLATURE: what should we call this field? As suggested by the allegorical story of the blind men and shown in Fig. 1, each person feels a different part of the whole and labels it accordingly to his own limited view and preference. As a result, there now exists a confusingly large crop of acronyms many of which refer to the same system (see Fig. 2). Before 1969, we simply spoke of "Sputtered Secondary Particles" (positive and negative ions, and neutrals), but it was Benninghoven (BEN 1969) who started using acronyms and later coined "SIMS" (BEN 1970). Werner, in 1972, developed a complete SIMS family tree (WER 1972), but stated with regrets at the end of his article that his freshly-coined acronyms were too difficult to pronounce, and for this reason it would be best to stick to "SIMS" with appropriate modifiers. On the QUADRUPOLE front, there has been disagreement where to place the "Q" (KUS 1977, MAG 1978). Primary NEUTRALS appeared under three different guises, the latest invention being FAB - but more about this later. The uninitiated might not realize that ^{252}Cf PLASMA refers to FISSION FRAGMENTS which are equivalent to MeV HEAVY IONS produced in tandem accelerators. The tongue-in-cheek acronym to end all acronyms was recently offered by Burlingame (BUR 1982), but "PIANO SIMS", for all its musical overtones, does appear a bit far-fetched. So this author decided to have the last word and add his own two-cents' worth on the bottom line of Fig. 2 which should cover the entire waterfront. Nevertheless, for the sake of convenience, the term "SIMS" will be used throughout the remainder of this paper.

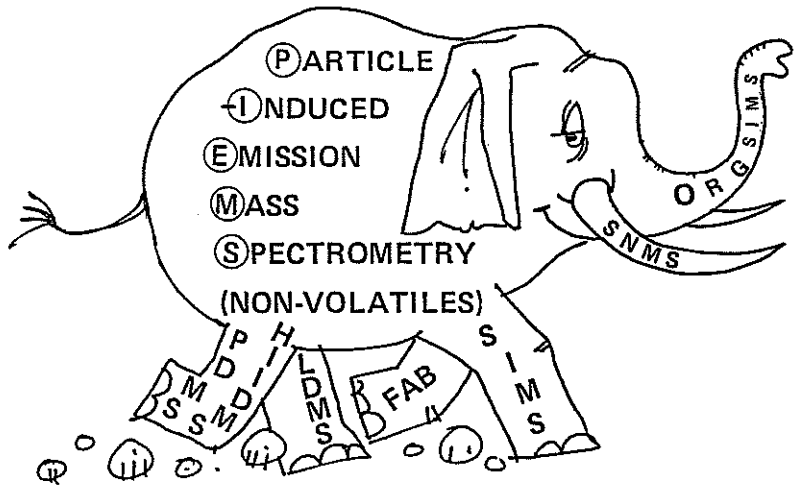


Fig. 1. Definition of the Subject Matter.

HISTORY

After these preliminaries, let us now get to the heart of the matter: how and when did SIMS see the light of day? If we were to accept the verdict of the otherwise comprehensive bibliographies by Yin (YIN 1980, 1981), it would seem to be our own work at RCA Laboratories, published after considerable delay in 1958. However, the roots of SIMS go back considerably further. The first mention of secondary ions apparently was made by Sir J. J. Thomson in 1910 who with uncanny insight offered the amazingly accurate assessment shown in Fig. 3 (THO 1910). After Thomson, nothing of import happened for the next 20 years, until there developed some activity in Dempster's Laboratory at the University of Chicago. So-called "reflected" ions observed by R. B. Sawyer (SAW 1930) were correctly reinterpreted by K. S. Woodcock (WOO 1931) and J. S. Thompson (THO 1931) as secondary negative ions. They then proceeded to use a 180° mass spectrometer (Fig. 4) to record negative ion spectra from the bombardment of NaF and CaF_2 targets by 500 eV ions from a Li source (Fig. 5). This work was apparently not known to F. L. Arnot and J. C. Milligan (ARN 1936) who postulated "a new process of ion formation" by double electron attachment. This is based on the presumed production of Hg^- by a Hg^+ beam falling on a Ni surface. Since the Hg^- ion is unstable, I interpret their data as the desorption of HgH^- or HgO^- ions from the Hg-covered Ni electrode bombarded by 200 eV Hg^+ ions. Two years later, R. H. Sloane and R. Press used a bakeable double mass spectrometer to prove that in a CLEAN vacuum system Hg^+ ion bombardment does not yield Hg^-, but will produce secondary negative ions of adsorbed light elements with large electron affinities (SLO 1938).

THE GREAT ACRONYM STEW
PARTIAL LISTING

	ACRONYM	DEFINITION	AUTHOR	YEAR	REFERENCE
keV PRIMARY IONS	SI PSI NSI	SECONDARY IONS POSITIVE NEGATIVE	BENNINGHOVEN	1969	BEN 1969
	SIMS	"STATIC" "DYNAMIC"	BENNINGHOVEN	1970	BEN 1970
	SSIMS DSIMS SIIMS SIMMS	STATIC DYNAMIC IMAGING MICROPROBE	WERNER	1972	WER 1972
	QSIMS	QUADRUPOLE	KUSAO	1977	KUS 1977
	SIQMS	QUADRUPOLE	MAGEE ET AL.	1978	MAG 1978
	LIQUID -SIMS	LIQUID (SAMPLE)	ABERTH ET AL.	1982	ABE 1982
	SNMS	NEUTRAL	OECHSNER ET AL.	1977	OEC 1977
keV PRIMARY NEUTRALS	SIMS/NPB NPB-SIMS	NEUTRAL PRIMARY BEAM	BORCHARDT, SCHERRER, ET AL.	1980 1983	BOR 1980 BOR 1983
	MBSA	MOLECULAR BEAM SOLID ANALYSIS	DEVIENNE, ROUSTAN	1982	DEV 1982
	FAB	FAST ATOM BOMBARDMENT	BARBER ET AL.	1981	BAR 1981A
	FABQMS	QUADRUPOLE	SURMAN, VICKERMAN	1981	SUR 1981
MeV PRIMARY IONS	252Cf-PDMS	CALIFORNIUM-252 PLASMA DESORPTION	MACFARLANE ET AL.	1974	TOR 1984
	HIIDMS	HEAVY-ION-INDUCED DESORPTION	DÜCK ET AL. HÅKANSSON, SUNDQUIST ET AL.	1980 1981	DÜC 1984 HÅK 1981
LASER	LDMS	LASER DESORPTION	HILLENKAMP ET AL. KISTEMAKER ET AL.	1976 1978	UNS 1976 POS 1978
COMPREHENSIVE	PIANO- SIMS	PRIMARY IONS/ ATOMS NEGOTIATE OBSERVATION (OF SPUTTERED)	BURLINGAME ET AL.	1982	BUR 1982
	PIEMS	PARTICLE- INDUCED EMISSION	HONIG	1984	

Fig. 2.

At this point, World War II intervened, and there is no further published SIMS work until 1949 when R. F. K. Herzog and F. P. Viehböck submitted a brief letter to the Editor (HER 1949) tersely entitled "Ion Source for Mass Spectrometry". A rough schematic diagram shows a 20 kV primary ion source used to bombard a target, and an electric field arrangement to draw out the secondary positive ions produced from some metals and

LXXXIII. *Rays of Positive Electricity.*
By Sir J. J. Thomson *.

I FIND that the investigation of the Positive Rays or Canalstrahlen is made much easier by using very large vessels for the discharge-tube in which the rays are produced. With large vessels the dark space around the cathode has plenty of room to expand before it reaches the walls of the tube; the pressure may therefore be reduced to very low values before this takes place, and in consequence the potential

. . . .

I had occasion in the course of the work to investigate the secondary Canalstrahlen produced when primary Canalstrahlen strike against a metal plate. I found that the secondary rays which were emitted in all directions were for the most part uncharged, but that a small fraction carried a positive charge.

I have much pleasure in thanking Mr. F. W. Aston, of Trinity College, Cambridge, and Mr. E. Everett, for the kind assistance they have given me with these experiments.

Fig. 3. Sir J. J. Thomson's Discovery of Secondary Ions in 1910.

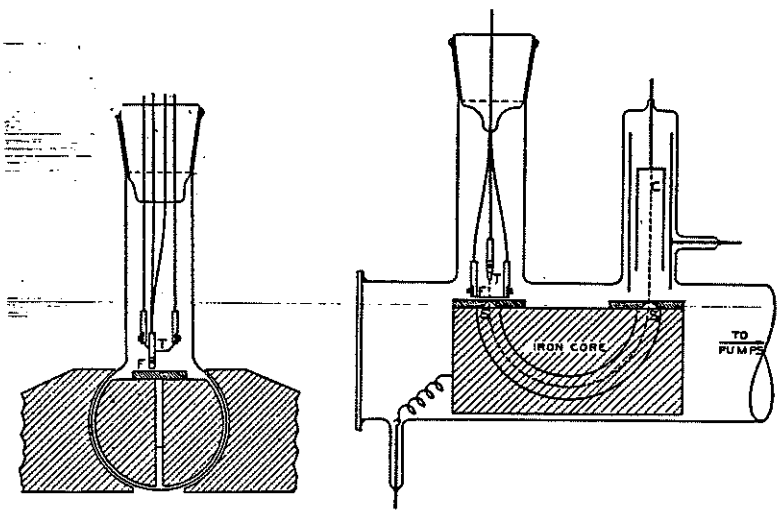


Fig. 4. Dempter's 180° Mass Spectrometer Used by K. S. Woodcock in 1931.

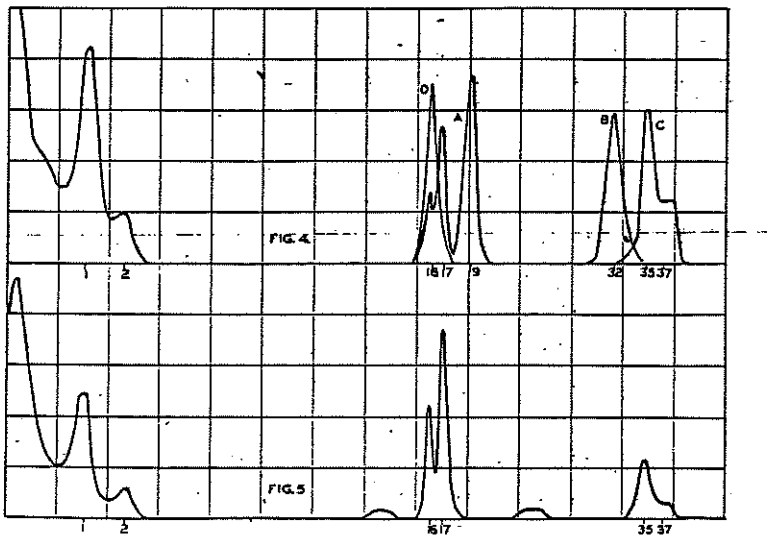


Fig. 5. Woodcock's Secondary Negative Ion Spectra (1931).

salts. The letter contains no further details or results. It is only through the kind assistance of Dr. Herzog that I recently gained access to a copy of Viehböck's

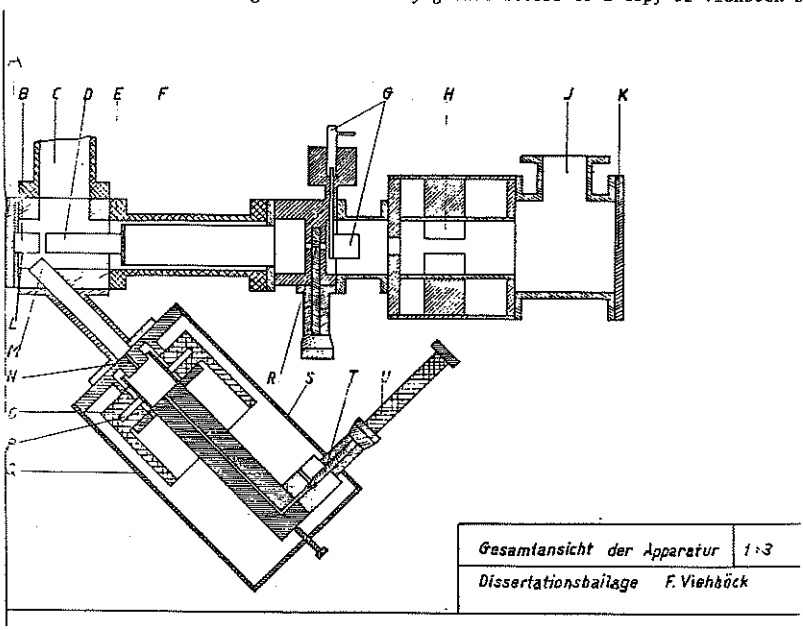


Fig. 6. Herzog and Vieböck's 1948 Apparatus: Positive Ion Source and Parabola Spectrograph.

doctoral dissertation (VIE 1948) on which their Letter is based. It turns out that Viehböck had constructed a discharge source to produce the primary ions used to bombard various targets, including Fe, Ni, Cu, Aℓ, $CaWO_4$, $Ba(OH)_2$, and H_2TeO_3(?). The resulting positive secondary ions were accelerated and then analyzed in a Thomson parabola apparatus (Fig. 6). The equipment is based on a design patented by Herzog in 1942 (HER 1942). Since rare gases were unavailable in Vienna in 1948, Viehböck stated regretfully that he had to use air to produce his primary ions, a fact that no doubt greatly enhanced his secondary ion yields.

In 1950, a project was started at RCA Laboratories to study the surface composition of oxide-coated cathodes by secondary ions emitted during primary ion bombardment. My early concept of a double mass spectrometer (Fig. 7) was presented in 1951 by my colleague R. H. Plumlee at the First International Conference on Mass Spectrometry at NBS, Washington, D.C. (PLU 1953). Figure 8 shows the instrument actually constructed (HON 1958), in which the primary ion selector was eliminated in order to boost the overall sensitivity since at that time electron multipliers were not yet generally available. The bulk of the early results was obtained in 1954/55, but publication of this work was delayed until 1958.

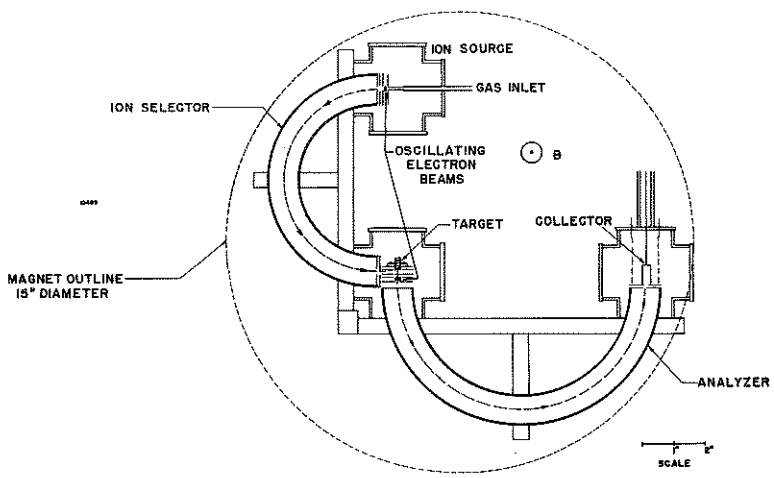


Fig. 7. Double Spectrometer Proposed by Honig in 1951.

RECENT DEVELOPMENTS

In the years to follow, SIMS started to gain momentum, slowly at first, then at an ever-increasing rate, as seen in Fig. 9 which presents the number of papers published

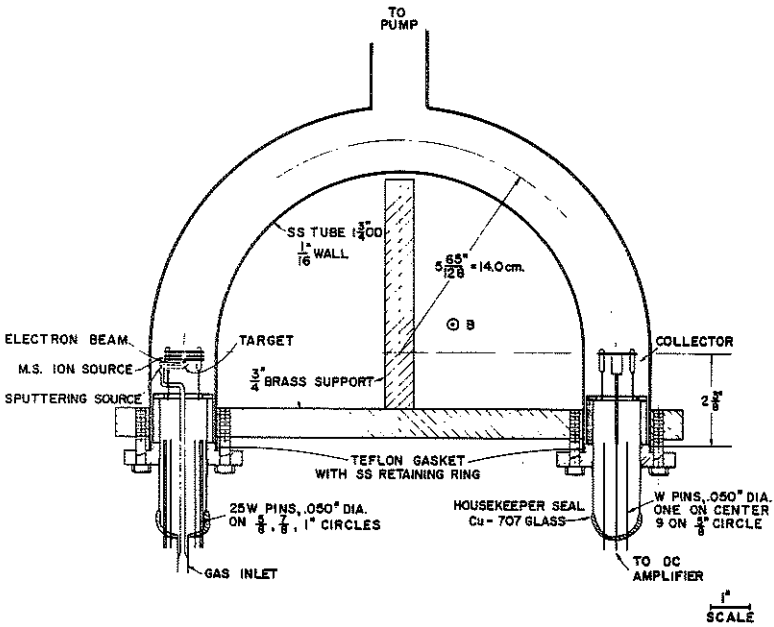


Fig. 8. Secondary Ion Mass Spectrometer Constructed at RCA Laboratories in 1954.

vs. time. While the starting point on the time scale is arbitrary, the steep rise since 1968 suggests that by 1990 the yearly crop of papers may exceed 1000! This plot makes it crystal-clear that the remainder of this review has to be highly selective, if we wish to cover the field in a reasonable space. However, every effort will be made to include most major developments. In particular, we shall focus our attention on the effects of sophisticated source design on lateral resolution, and on the extension of SIMS to ORGANIC problems.

The development of SIMS instruments with moderate lateral resolution is shown in Fig. 10. Early SIMS studies had used primary beams of mm dimensions. The reduction in ion beam size began in 1963 with an improved source design by Liebl (LIE 1963). Starting in the early nineteen seventies, SIMS studies branched out into two separate routes:

1) Low primary current density work ("STATIC" SIMS) using large beams. This is a concept developed by Benninghoven and his group specifically for surface analysis of ORGANIC samples. This topic will be discussed in detail in the final section of this paper, in conjunction with other related methods for the analysis of large organic molecules.

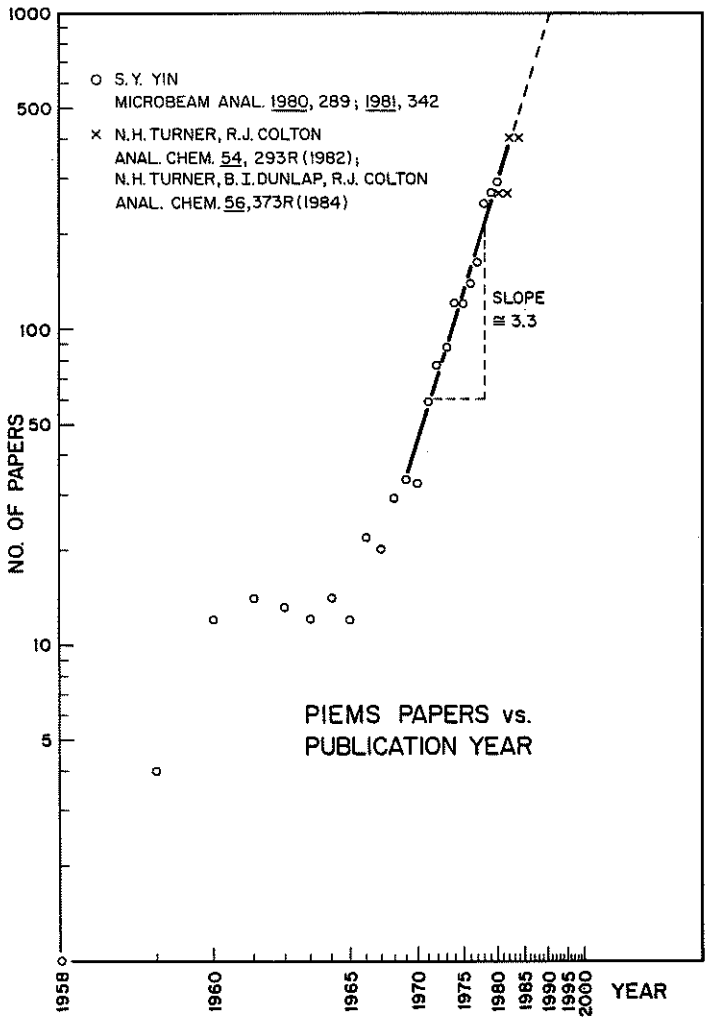


Fig. 9. The Exponential Rise of Annual SIMS Publications Since 1969.

2) High primary current density work ("DYNAMIC" SIMS) on INORGANIC samples, to obtain concentration profiles in depth and to identify trace impurities. Examples are Wittmaack's analyzer (WIT 1973), and the secondary ion quadrupole mass spectrometer (SIQMS) developed by Magee et al. (MAG 1978) specifically for profiles with high depth resolution (see Fig. 11). In these studies major emphasis was placed on achieving depth

SIMS DEVELOPMENT I

MODERATE LATERAL RESOLUTION (>10μm)

HERZOG/VIEHBÖCK	1948/49
VEKSLER	1956
HONIG	1958
LIEBL/HERZOG	1963

"DYNAMIC SIMS"	"STATIC SIMS"
INORGANIC DEPTH PROFILES, TRACES	SURFACE DESORPTION: BENNINGHOVEN 1970
WITTMAACK 1973	"ORGANIC SIMS":
MAGEE ET AL. 1978	BENNINGHOVEN ET AL. 1976

Fig. 10.

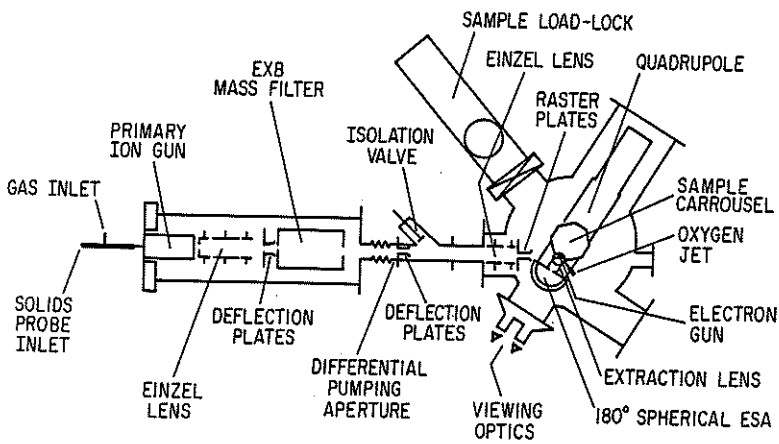


Fig. 11. Magee's Quadrupole Instrument of 1978.

profiles over a wide concentration range, down to the parts-per-million level or even lower at moderate lateral resolution. Further development of this branch occurred due to improved source designs which produced high lateral resolution.

Figure 12 shows how high lateral resolution instrumentation developed along two parallel paths during the past two decades: ion MICROSCOPES on one hand, and ion MICROPROBES on the other (LIE 1975). In the ion MICROSCOPE, as shown in Fig. 13a, the sample is irradiated with a BROAD beam of primary ions.
High lateral resolution, on the order of a μm, is achieved by forming on the screen a magnified image of the object with a NARROW beam of secondary particles which have passed through appropriate optics and a filter for mass analysis. The ion MICROPROBE (Fig. 13b), on the other hand, uses a primary beam, focused down to μm dimensions, that can be rastered over the sample. A selected portion of the secondaries is analyzed in a suitable mass filter.

SIMS DEVELOPMENT II

HIGH LATERAL RESOLUTION (0.1-10μm)

ION MICROSCOPE	
CASTAING/SLODZIAN	1962
ROUBEROL ET AL.	1969
"CAMECA IMS 300"	
ROUBEROL ET AL.	1980
"CAMECA IMS 3F"	

ION MICROPROBE	
LIEBL ARL "IMMA"	1967
"UMPA"	1971
"COALA"	1972
WITH LIQUID METAL ION SOURCE:	
KROHN, RINGO	1975
RÜDENAUER ET AL.	1982
BAYLY, WAUGH, & ANDERSON	1983

Fig. 12.

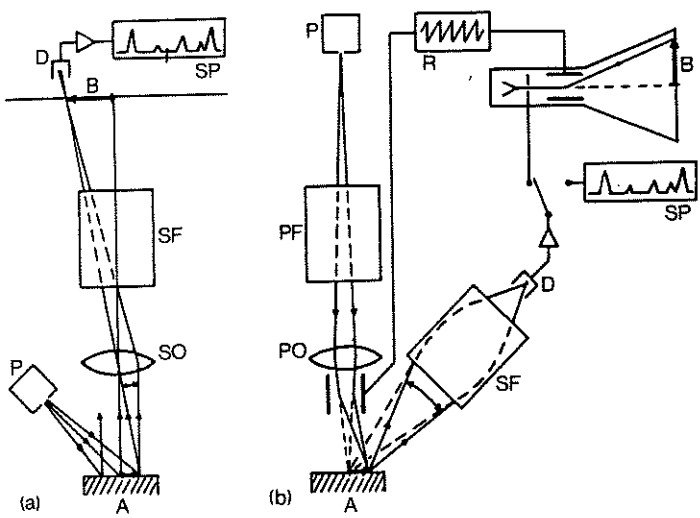


Fig. 13. Schematic Diagrams of: (a) the Ion Microscope
(b) the Ion Microprobe [After Liebl (LIE 1974)].

The prototype of the ion microscope was developed over 20 years ago by Castaing and Slodzian (CAS 1962) and served as the basis for two generations of sophisticated commercial instrumentation. The "CAMECA IMS 300" (Fig. 14), developed by a French team in 1969 (ROU 1969), offered many interesting features, including a prism-mirror-prism combination for mass- and energy-analysis, and a multiple detection and recording system. It has been applied by many groups to a wide variety of practical problems, e.g. semiconductor studies by Werner and his coworkers (HOF 1973). The second-generation "CAMECA 3f" shown in Fig. 15 incorporates many improvements, including a triple-focusing mass spectrometer capable of high mass resolution, housed in an ultrahigh vacuum system (ROU 1980).

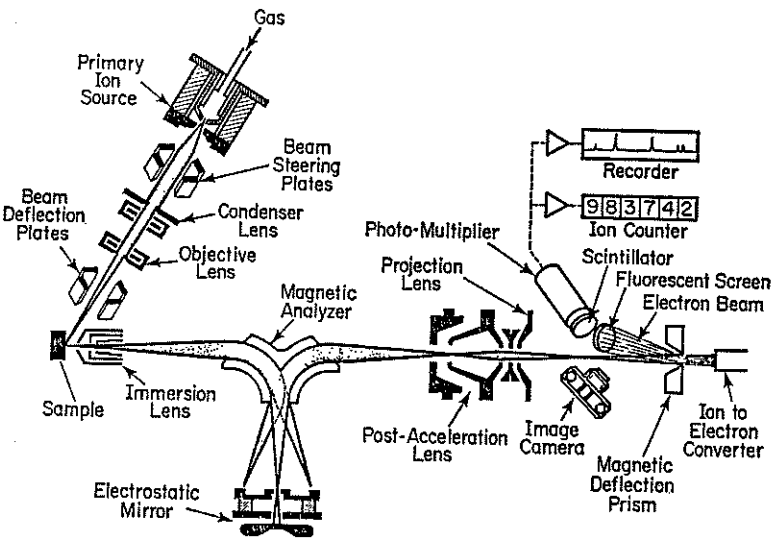
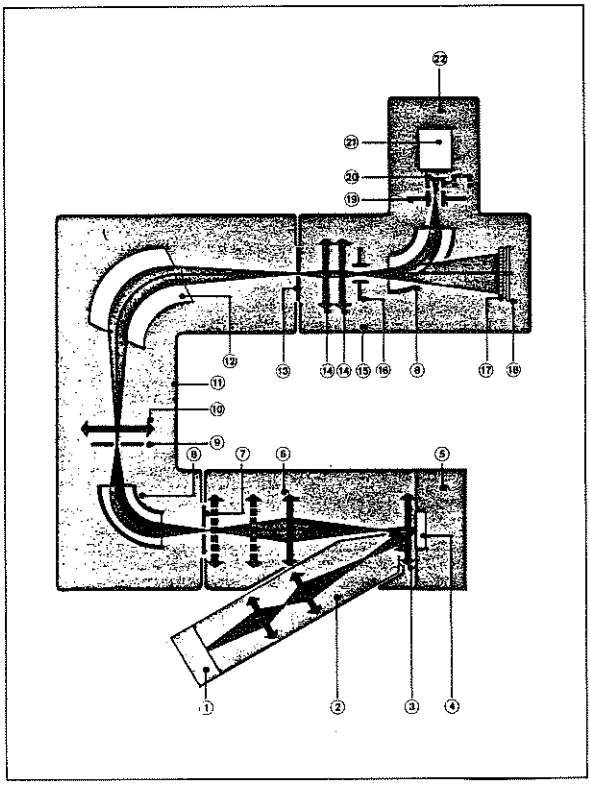


Fig. 14. Schematic Diagram of the "CAMECA IMS 300" Ion Microscope (1969).

As an example of an ion microprobe, Fig. 16 presents a schematic diagram of "IMMA" developed by Liebl in 1967 and produced commercially by ARL (LIE 1967). It includes a duoplasmatron ion source; a primary ion mass filter and electrostatic focusing and rastering system; a double-focusing secondary mass spectrometer; and a multiple ion detection system. This design achieved a lateral resolution of about one μm.

Substantial further improvements in lateral resolution have been made recently by incorporating into a microprobe the liquid metal source developed by Krohn and Ringo some years ago (KRO 1975) which is capable of producing a primary ion beam less than 0.1 μm in diameter. The potential of this source has been explored in some detail by Rüdenauer and collaborators (RÜD 1982) who quote spot sizes as small as 0.04 μm. A recent commercial instrument, the "VG Scientific MIG 100" ion microprobe, is based on



① Ion gun
② Primary column
③ Immersion lens
④ Specimen
⑤ Specimen chamber
⑥ Transfer optics
⑦ Entrance slit
⑧ Electrostatic analyzer
⑨ Energy slit
⑩ Image transfer lens
⑪ Spectrometer
⑫ Electromagnet
⑬ Final slit
⑭ Projection lenses
⑮ Projection, display and detection system
⑯ Deflector
⑰ Channel-plate
⑱ Fluorescent screen
⑲ Deflector
⑳ Remote controled Faraday cup
㉑ Electron multiplier
㉒ Detection system

Fig. 15. Schematic Diagram of the "CAMECA 3f" Ion Microscope (1980).

the liquid gallium source, and its designers, Bayly et al., claim a beam size of ca. 0.1 μm (BAY 1983). From an actual secondary ion line scan of a test pattern (Fig. 17), a resolution of ca. 0.3 μm can be inferred.

What are the practical problems that this highly developed instrumentation has been applied to? Initially they were, almost exclusively, inorganic in nature and mainly of

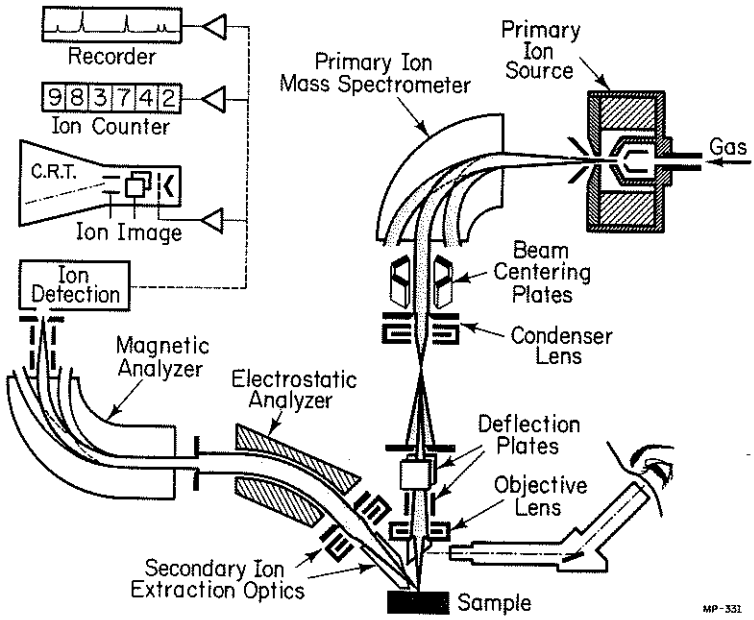


Fig. 16. Schematic Diagram of Liebl's "IMMA" Ion Microprobe.

interest to the electronics industry. Two of the key areas have been depth profiling and analysis for trace impurities. A knowledge of concentration profiles, as a function of depth, of major components and dopants is of prime importance in semiconductor research. It is not surprising that many papers have been published by many groups in many countries. To name just a few: Werner and collaborators in Eindhoven; Wittmaack in Germany; Huber and colleagues in France; Evans and coworkers, and Magee in USA. This literature has been thoroughly reviewed by Zinner in two recent papers (ZIN 1980, 1983). No effort has been spared to make depth profiles accurate through specialized instrumentation, e.g. raster-gating (MAG 1978), and to make the method more quantitative. The problems of quantitation have been fully reviewed by Wittmaack (WIT 1980), and by Morrison and collaborators (MOR 1982), who emphasized the use of ion implantation for in-situ ion microprobe analysis (LET 1980). While they make reference to prior implantation work by Gries (GRI 1979A, 1979B), it is interesting to note that this method had been used previously for many years, e.g. by Gittins et al. (GIT 1972), and by Croset and Dieumegard (CRO 1976).

Much attention has been devoted over the years to increasing and stabilizing secondary ion yields in order to make SIMS more sensitive and quantitative. The importance of oxidizing the surface with an O_2 jet had been recognized many years ago by Slodzian and Hennequin (SLO 1966), but it was Andersen in 1969 who popularized the idea of using O_2^+ primary ions for the same purpose (AND 1969). It is interesting to note that the

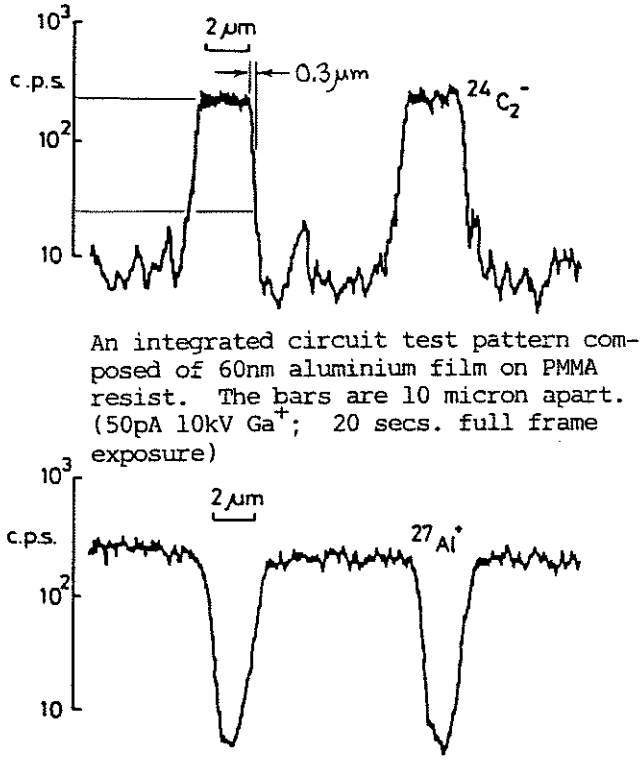


Fig. 17. High-Resolution Line Scan Obtained on the "VG Scientific MIG 100" Ion Microprobe by Bayly et al. (1983).

same concept had been published by Benninghoven two years earlier (BEN 1967). In subsequent papers, Andersen and Hinthorne (AND 1972, 1973) described secondary ion emission in terms of their "Local Thermal Equilibrium" (LTE) model which is based on the Saha-Eggert equation. While the basic assumption of thermal equilibrium is difficult to justify, the model does, with the help of two adjustable parameters (a fictitious temperature T and an electron density N_e), permit to interpret sputtered ion intensities of major and minor constituents in terms of their concentrations in the solid.

In this context, it should be mentioned, if only briefly, that the theoretical aspects of secondary ion emission have been studied over many years by many workers, among them Sroubek (SRO 197), Wittmaack (WIT 1977), Blaise and Nourtrier (1979), and Williams (1979, 1982). Another important related area that can be only touched on is the emission of ion CLUSTERS which were already observed in early studies (HON 1958, 1962). Their impact on the theory of ion emission has been considered by Winograd (WIN 1982) and by Colton and coworkers (COL 1983, TUR 1984).

Returning to the problem of quantitation, we should mention the different approach taken by Coburn and Kay (COB 1971, 1974) and Oechsner and coworkers (OEC 1972, 1979).

They post-ionized sputtered secondary NEUTRALS in a discharge to obtain quantitative analyses of solids. While secondary ION yields vary over many orders of magnitude for different elements, the ionization cross sections of NEUTRALS are well defined and can be determined. In spite of this substantial advantage, secondary NEUTRAL mass spectrometry so far has not found wide acceptance, mainly because it cannot be applied to small areas. However, an exciting new method has been developed recently for the post-ionization of sputtered neutrals which is based on Multiphoton Ionization by a laser beam. The approach, first proposed by Hurst and coworkers (HUR 1979), uses RESONANT radiation and is still in the testing stage (DON 1982, PAR 1983). Similar experiments are being carried out at this time by Kimock, Winograd, and coworkers at Penn State (KIM 1983A, 1983B). A parallel aproach has been adopted by Becker and Gillen (BEC 1984) who used NONRESONANT radiation which appears to be preferable whenever survey analyses are to be made.

ORGANIC PROBLEMS

So far, we have reviewed the large volume of work dealing with INORGANIC problems. Interest in ORGANIC systems is much more recent, although there exist a few early exploratory experiments, e.g. a study of ethyl monolayers adsorbed on germanium (HON 1962), and a study of polymers (DIL 1968). It was largely Benninghoven's "STATIC" SIMS approach (BEN 1970) which first made possible the analysis of organic systems by ion bombardment without destroying the desorbed molecules in the process. Benninghoven has pointed out the importance of limiting the total dose of primary ions to 10^{12} - 10^{13} cm^{-2}, to insure that most of the secondary ions are emitted from areas not previously damaged. This dose corresponds to an aggregate bombarded area amounting to 1-10% of the total area. Typical bombardment conditions are: primary current densities of 10^{-9}A cm^{-2} or less for about 1000 seconds. To increase the sensitivity of the method, it is necessary to work with large sample areas. Initially, static SIMS was applied to monomolecular layers adsorbed on metals (BEN 1970), and only several years later to the desorption and analysis of organic molecules (BEN 1976).

In the meantime, interest had increased greatly in the identification of large involatile molecules which lead to the development of several alternative approaches. In the last section of this retrospective, we shall examine more closely (see Fig. 18) various methods which are capable of desorbing these molecules, most of them intact. In each case, the primary agent supplies energy which is transformed to a level that matches the binding energies, allowing a fraction of the molecules to be desorbed as intact ions, usually as $(M + 1)^+$ and $(M - 1)^-$. It is surprising that for different desorption methods the mass spectra obtained are found to be reasonably similar.

The first method to be discussed is laser desorption. The use of laser sources in mass spectrometry dates back to 1963 when the first exploratory experiments made at RCA Laboratories with a ruby laser produced positive ions from metals, semiconductors, and insulators (HON 1963A, 1963B). A few years later, Vastola, Knox and collaborators at Penn State started a program of laser-induced vaporization of solids which also included inorganic compounds (VAS 1968). However, it was only in the mid-seventies that NANOSECOND pulse lasers were coupled to sophisticated time-of-flight mass spectrometers by

DESORPTION OF LARGE ORGANIC MOLECULES

HISTORIC PROGRESSION

1. LASER (LDMS)
   - VASTOLA ET AL. 1968
   - HILLENKAMP, UNSÖLD ET AL. 1976
   - KISTEMAKER, POSTHUMUS ET AL. 1978
2. FIELD (FDMS)
   - BECKEY 1969
3. ELECTROHYDRODYNAMIC (EHMS)
   - EVANS, SIMONS ET AL. 1974
4. ^{252}Cf PLASMA (PDMS)
   - MACFARLANE, TORGERSON ET AL. 1974
5. "STATIC" SIMS
   - BENNINGHOVEN ET AL. 1976
   - COOKS ET AL. 1977
6. HEAVY ION-INDUCED (HIID)
   - DÜCK ET AL. 1980
   - HÅKANSSON, SUNDQUIST ET AL. 1981
7. FAST ATOM BOMBARDMENT (FAB)
   - BARBER ET AL. 1981

Fig. 18.

Hillenkamp and coworkers in Germany (UNS 1976) to study in detail the desorption of large organic molecules. A different approach was taken by Kistemaker and collaborators in Holland (POS 1978) who used a conventional magnetic spectrometer capable of recording simultaneously a limited spectral range with a channel-plate array. Since then, LDMS has been widely applied to many problems, especially to microparticulates. The latest commercial version, "LAMMA 1000", was developed by Leybold-Heraeus and utilizes the T-O-F "Reflectron" principle (MAM 1973) capable of improved mass resolution (Fig. 19). The field of LDMS was reviewed in detail by Conzemius and Capellen (CON 1980), and there has recently appeared a full bibliography covering the period 1963-1982 (CON 1983).

The next two methods listed in Fig. 18 are FIELD DESORPTION (FDMS) developed by Beckey (BEC 1969), and ELECTROHYDRODYNAMIC DESORPTION, mainly employed by Simons, Evans, and coworkers (SIM 1974). Since strictly speaking they do not fit into the framework of SECONDARY particle mass spectrometry, they are only mentioned here for the sake of completeness.

Mass spectrometry of large involatile organic molecules was given a considerable boost by the development of the ^{252}Cf PLASMA DESORPTION method by Macfarlane and coworkers (TOR 1974, MAC 1976). This method is based on a chance observation made when these authors studied recoil ions from β-decay and found additional peaks representing adsorbed molecules. These peaks were subsequently greatly enhanced through the use of a ^{252}Cf source which spontaneously produces two fission fragments with energies close to 100 MeV each. The method was termed PLASMA desorption because the fission fragments presumably lose energy in the solid through the production of microplasmas. While only a few laboratories are equipped to employ this specialized technique, it has made significant contributions to the identification of large involatile molecules.

A technique similar to plasma desorption, but more flexible in several aspects is based on the bombardment by heavy ions with MeV/amu energies produced in a tandem accelerator. The HEAVY ION INDUCED DESORPTION method was developed independently by

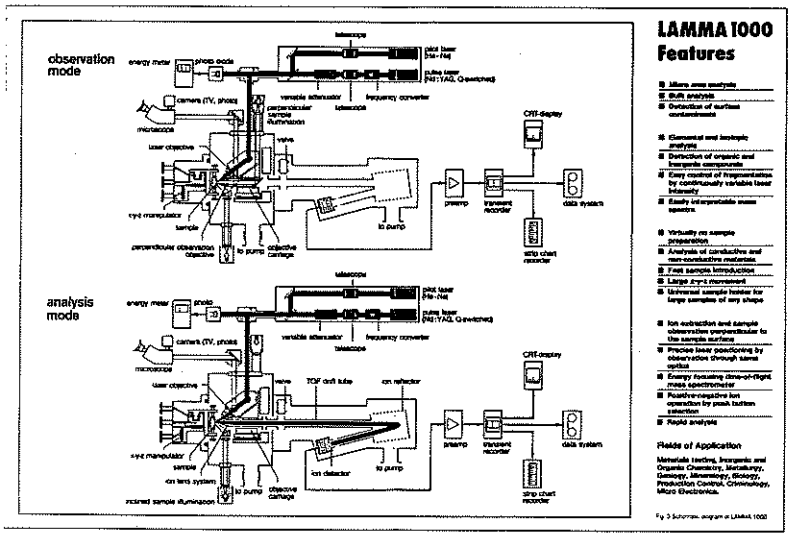


Fig. 19. Schematic Diagram of "LAMMA 1000" Laser Desorption Time-Of-Flight Spectrometer.

Dück et al. in Germany (DÜC 1980) and Sundquist and his Group in Uppsala (HÅK 1981). The spectra obained by HIID are similar to PD spectra, but afford further insight into the desorption process because energy, charge state, angle of incidence, and mass of the primary ions are adjustable parameters. Desorption yields have been measured as a function of these variables, allowing some tentative conclusions to be drawn concerning the role of electronic energy loss and the desorption mechanism (HÅK 1982, VOI 1983, MAC 1983).

The last two desorption methods to be discussed are STATIC SIMS and FAB, the non-identical twins. The historical evolution of static SIMS has already been outlined above, and its capabilities and limitations mentioned. Since 1976, a large volume of work has been published by Benninghoven and collaborators, as well as by many other groups, including Colton et al., Cooks et al., Hercules et al., and Kambara et al. Further details concerning these studies will be found in recent reviews by Benninghoven (BEN 1983), Colton et al. (TUR 1982, 1984), and Burlingame et al. (BUR 1982, 1984).

- The story of FAST ATOM BOMBARDMENT (FAB) is a fascinating one. The two initial publications by Barber (BAR 1981A, 1981B) emphasize the fact that the primary particles used were neutrals rather than ions, in order to avoid the charging-up of organic samples which usually are insulators. However, this approach is not novel since it was employed in prior work by Lehrle, Dillon et al. (LEH 1962, DIL 1968), Devienne, Roustan et al. (reviewed in DEV 1982), and Borchardt, Scherrer et al. (BOR 1980) to investigate inorganic and organic insulators. It is noteworthy that the NOVEL feature of Barber's method comes to light only in a later publication (BAR 1982): the use of a LIQUID matrix, such as glycerol, in which the organic sample is dissolved. This system allows

the solute to circulate freely, assuring a fresh supply of sample molecules to be exposed to the primary particles for many hours. The long sample life in the FAB source is clearly one of the major advantages over the older static SIMS approach. It has made the new method popular with many laboratories, and has sparked the design of several small neutral particle sources. The large volume of recent FAB studies has been reviewed by Fenselau (FEN 1983), Colton and colleagues (TUR 1982, 1984), and Burlingame et al. (1982, 1984).

The various methods to desorb large involatile organic molecules from solid or liquid substrates, as outlined above, produce spectra that are remarkably similar in nature. For example, direct comparisons have been carried out for various organic molecules between laser desorption and ^{252}Cf plasma desorption (SCH 1979, 1980), and between ^{252}Cf plasma desorption and SIMS (ENS 1981, KAM 1982). Figure 20 demonstrates the similarity of positive as well as negative secondary ion spectra for the last-named two systems (ENS 1981). These results are indeed surprising in view of the fact that

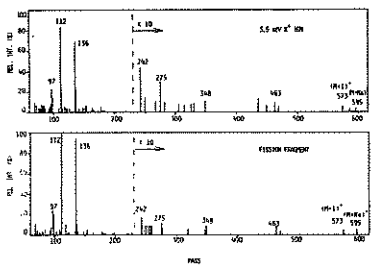


Figure 1. Adenylyl-(3′→5′)-cytidine positive ion spectra: upper, 3.5-keV K^+ ion bombardment; lower, ^{252}Cf fission fragment bombardment.

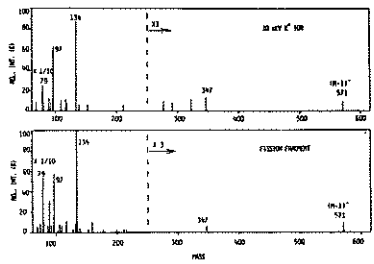


Figure 2. Adenylyl-(3′→5′)-cytidine negative ion spectra: upper, 10-keV K^+ ion bombardment; lower, ^{252}Cf fission fragment bombardment.

[FROM H. ENS, K. G. STANDING, B. T. CHAIT, AND F. H. FIELD (ENS 1981)]

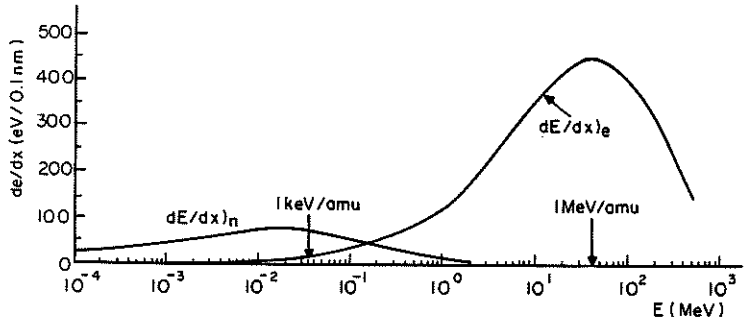
Fig. 20. Comparison of Two Desorption Methods: "Static" SIMS vs. ^{252}Cf Plasma Desorption.

the modes of primary energy input differ widely for photons, low-energy (keV/amu) particles, and high-energy (MeV/amu) ions. It can be shown from LSS theory that in the keV/amu region (SIMS and FAB) primary energy is lost through NUCLEAR interactions, while in the MeV/amu region (^{252}Cf PD and HIID) ELECTRONIC interactions play a major role. This becomes apparent from the energy loss curves shown in Fig. 21 which were computed by P. K. Haff for the specific case of $^{35}C\ell$ in $^{27}A\ell$ (HAF 1981).

The fact that large thermally unstable organic molecules can be desorbed intact leaves us with two questions that still need to be answered more fully:

1) How can primary energy quanta ranging from keV to MeV break multiple molecular adsorption bonds that lie in the eV range, without wrecking the molecule in the process?

2) Why are the mass spectra obtained by laser irradiation, keV/amu particles, and MeV/amu ions so similar, in spite of wide differences in the first step of primary energy conversion?



NUCLEAR AND ELECTRONIC STOPPING POWERS FOR $^{35}Cl \rightarrow {}^{27}Al$
(AFTER P.K.HAFF, 1981)

Fig. 21.

The case of keV/amu primary particles has been investigated by Benninghoven (BEN 1982), Garrison (GAR 1982), and Magee (MAG 1983). Garrison has performed classical dynamics calculations for relatively simple systems (e.g., C_6H_6/Ni) to show that desorption of the molecular ions, along with some fragments and clusters, can be expected. Benninghoven and Magee showed qualitatively that at a certain distance, a few nm from the point of primary impact, the initial energy carried by the primary particle has been delocalized through collision cascades to the eV level, suitable for the breaking of adsorption bonds.

The production of molecular ions by MeV/amu primary particles has been treated in detail by Macfarlane (MAC 1982) who portrays the sequence of events in terms of an intense ionization track about 10 nm wide, consisting of separated positive ion-electron pairs which later recombine. The released energy is transferred via vibrations to the sample surface where it induces desorption of molecular ions. Garrison has addressed the same problem again via a classical dynamics model (GAR 1983). On the other hand, Krueger (KRU 1983) postulates that, for all three methods discussed, fast energy dissipation at the surface leads to a non-equilibrium phase transition of surface material which produces ions instanteously. At this time it it seems that there are as many models as there are theoreticians studying the problem.

CONCLUSION

The evolution of Secondary Ion Mass Spectrometry, or "Particle-Induced Emission Mass Spectrometry", has been and continues to be an exciting one, featuring many interesting developments, as well as occasional disagreements and polemics. This introductory, superficial survey could do little more than scratch the surface (pun intended!) of a vast, rapidly growing field. It will have served its purpose if it provided the reader with an up-to-date overview, and at the same time reduced the potential number of reinvented wheels.

ACKNOWLEDGEMENT

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BIBLIOGRAPHY

ABE 1982 W. Aberth, K. M. Straub, and A. L. Burlingame "Secondary Ion Mass Spectrometry with Cesium Ion Primary Beam and Liquid Target Matrix for Analysis of Bioorganic Compounds" Anal. Chem. 54, 2029-2034 (1982)

AND 1969 C. A. Andersen "Progress in Analytic Methods for the Ion Microprobe Mass Analyzer" Int. J. Mass Spectrom. Ion Phys. 2, 61-74 (1969)

AND 1972 C. A. Andersen and J. R. Hinthorne "Ion Microprobe Mass Analyzer" Science 175, 853-860 (1972)

AND 1973 C. A. Andersen and J. R. Hinthorne "Thermodynamic Approach to the Quantitative Interpretation of Sputtered Ion Mass Spectra" Anal. Chem. 45, 1421-1438 (1973)

ARN 1936 F. L. Arnot and J. C. Milligan "A New Process of Negative Ion Formation" Proc. Roy. Soc. A 156, 538-560 (1936)

BAR 1981A M. Barber, R. S. Bordoli, R. D. Sedgwick, and A. N. Tyler "Fast Atom Bombardment of Solids (F. A. B.): A New Ion Source for Mass Spectrometry" J.C.S. Chem. Comm. 1981, 325-327

BAR 1981B M. Barber, R. S. Bordoli, R. D. Sedgwick, and A. N. Tyler "Fast Atom Bombardment of Solids as an Ion Source in Mass Spectrometry" Nature 293, 270-275 (1981)

BAR 1982 M. Barber, R. S. Bordoli, G. J. Elliott, R. D. Sedgwick, and A. N. Tyler "Fast Atom Bombardment Mass Spectrometry" Anal. Chem. 54, 645A-657A (1982)

BAY 1983 A. R. Bayly, A. R. Waugh, and K. Anderson "High Resolution Scanning Secondary Ion Mass Spectrometry (SIMS) Using Liquid Metal Field-Ionization Sources" Scanning Electron Microscopy 1983, 23-29

BEC 1969 H. D. Beckey "Field Desorption Mass Spectrometry: A Technique for the Study of Thermally Unstable Substances of Low Volatility" Int. J. Mass Spectrom. Ion Phys. 2, 500-503 (1969)

BEC 1984 C. H. Becker and K. T. Gillen "Surface Analysis by Nonresonant Multiphoton Ionization of Desorbed or Sputtered Species" Anal. Chem. (to be published)

BEN 1967 A. Benninghoven "Die positive Sekundärionenemission von sauerstoffbedeckten Metallen" Z. Naturforsch. 22a, 841-843 (1967)

BEN 1969 A. Benninghoven "Zum Mechanismus der Ionenbildung und Ionenemission bei der Festkörperzerstäubung" Z. Physik 220, 159-180 (1969)

BEN 1970 A. Benninghoven "Die Analyse monomolekularer Festkörperoberflächenschichten mit Hilfe der Sekundärionenemission" Z. Physik 230, 403-417 (1970)

BEN 1976 A. Benninghoven, D. Jaspers, and W. Sichtermann "Secondary-Ion Emission of Amino Acids" Appl. Phys. 11, 35-39 (1976)

BEN 1982 A. Benninghoven
"Secondary Ion Mass Spectrometry of Organic Compounds"
in: "Secondary Ion Mass Spectrometry SIMS III", A. Benninghoven, J. Giber, J. László, M. Riedel, and H. W. Werner, Eds., (Springer-Verlag, New York, 1982), pp. 438-442

BEN 1983 A. Benninghoven
"Secondary Ion Mass Spectrometry of Organic Compounds"
in: "Ion Formation From Organic Solids", A. Benninghoven, Ed., (Springer-Verlag, New York, 1983), pp. 64-87

BLA 1979 G. Blaise and A. Nourtier
"Experimental and Theoretical Approaches to the Ionization Process in Secondary-Ion Emission" Surf. Sci. 90, 495-547 (1979)

BOR 1980 G. Borchardt, H. Scherrer, S. Weber, and S. Scherrer
"Local In-Depth Analysis of Ceramic Materials by Neutral Beam Secondary Ion Mass Spectrometry" Int. J. Mass Spectrom. Ion Phys. 34, 361-373 (1980)

BOR 1983 G. Borchardt, H. J. Franek, H. Scherrer, S.Scherrer, and S. Weber
"Neutral Primary Beam SIMS Analysis of Surface Layers on Glass" Int. J. Mass Spectrom. Ion Phys. 46, 507-510 (1983)

BUR 1982 A. L. Burlingame, A. Dell, and D. H. Russell
"Mass Spectrometry" Anal. Chem. 54, 363R-409R (1982)

BUR 1984 A. L. Burlingame, J. O. Whitney, and D. H. Russell
"Mass Spectrometry" Anal. Chem. 56, 417R-467R (1984)

CAS 1962 R. Castaing and G. Slodzian
"Microanalyse par émission ionique secondaire" J. Microscopie 1, 395-410 (1962)

COB 1971 J. W. Coburn and E. Kay
"Plasma Diagnostics of an rf-Sputtering Glow Discharge" Appl. Phys. Letters 18, 435-438 (1971)

COB 1974 J. W. Coburn, E. Taglauer, and E. Kay
"Glow-Discharge Mass Spectrometry - Technique for Determining Elemental Composition Profiles in Solids" J. Appl. Phys. 45, 1779-1786 (1974)

COL 1983 R. J. Colton
"Secondary Ion Mass Spectrometry: High-Mass Molecular and Cluster Ions" Nucl. Instr. Meth. 218, 276 (1983)

CON 1983 R. J. Conzemius and J. M. Capellen
"A Review of the Applications to Solids of the Laser Ion Source in Mass Spectrometry" Int. J. Mass Spectrom. Ion Phys. 34, 197-271 (1980)

CON 1983 R. J. Conzemius, D. S. Simons, Z. Shankai, and G. D. Byrd
"Laser Mass Spectrometry of Solids: A Bibliography 1963-1982" Proc., 18th Ann. Conf. Microbeam Anal. Soc. 1983, 301-332

CRO 1976 M. Croset and D. Dieumegard
"Quantitative Secondary Ion Mass Spectrometry Analysis of Oxygen Isotopes and Other Light Elements in Silicon Oxide Films" Corrosion Science 16, 703-715 (1976)

DEV 1982 F. M. Devienne and J.-C. Roustan
"'Fast Atom Bombardment'--A Rediscovered Method for Mass Spectrometry" Org. Mass Spectrom. 17, 173-176 (1982)

DIL 1968 A. F. Dillon, R. S. Lehrle, J. C. Robb, and D. W. Thomas "Positive Ion Emission from Polymers under Ion Impact" in: "Advances in Mass Spectrometry" Vol. 4, E. E. Kendrick, Ed., (London: Institute of Petroleum, 1968), pp. 477-490

DON 1982 D. L. Donohue, J. P. Young, and D. H. Smith "Determination of Rare-Earth Isotope Ratios by Resonance Ionization Mass Spectrometry" Int. J. Mass Spectrom. Ion Phys. 43, 293-307 (1982)

DÜC 1980 P. Dück, W. Treu, W. Galster, H. Fröhlich, and H. Voit "Heavy Ion Induced Desorption of Organic Compounds" Nucl. Instr. Methods 168, 601 (1980)

ENS 1981 W. Ens, K. G. Standing, B. T. Chait, and F. H. Field "Comparison of Mass Spectra Obtained with Low-Energy Ion and High-Energy Californium-252 Fission Fragment Bombardment" Anal. Chem. 53, 1241-1244 (1981)

FEN 1983 C. Fenselau "Fast Atom Bombardment (Review)" in: "Ion Formation from Organic Solids", A. Benninghoven, Ed. (Springer-Verlag, New York, 1983), pp. 90-100

GAR 1982 B. J. Garrison "Organic Molecule Ejection from Surfaces due to Heavy Particle Bombardment" J. Am. Chem. Soc. 104, 6211-6217 (1982)

GAR 1983 B. J. Garrison "A Classical Dynamics Model of Plasma Desorption Mass Spectrometry Experiments" J. Am. Chem. Soc. 105, 373-378 (1983)

GIT 1972 R. P. Gittins, D. V. Morgan, and G. Dearnaley "The Application of the Ion Microprobe Analyser to the Measurement of the Distribution of Boron Ions Implanted into Silicon Crystals" J. Phys. D: Appl. Phys. 5, 1654-1663 (1972)

GRI 1979A W. H. Gries "Quantitative Ion Implantation: Theoretical Aspects" Int. J. Mass Spectrom. Ion Phys. 30, 97-112 (1979)

GRI 1979B W. H. Gries "Quantitative Ion Implantation: The Practice" Int. J. Mass Spectrom. Ion Phys. 30, 113-125 (1979)

HAF 1981 P. K. Haff "Erosion of Surfaces by Fast Heavy Ions" CIT Report BAP-22 (1981) To be published in: "Heavy Ion Science", Vol. III, D. A. Bromley, Ed. (Plenum Press, New York, 1984)

HÅK 1981 P. Håkansson, A. Johansson, I. Kamensky, B. Sundqvist, J. Fohlman, and P. Peterson "Fast Heavy-Ion Induced Desorption of Biomolecules" IEE Trans. Nucl. Sci. NS-28, 1776-1778 (1981)

HÅK 1982 P. Håkansson, I. Kamensky, and B. Sundqvist "Fast Heavy-Ion Induced Desorption of Biomolecules" Nucl. Instr. Meth. 198, 43-51 (1982)

HER 1942 R. F. K. Herzog "Massenspektrometer" German Patent DRP H172192 IX a/42h (1942)

HER 1949 R. F. K. Herzog and F. P. Vieböck "Ion Source for Mass Spectrography" Phys. Rev. 76, 855L-856L (1949)

HOF 1973 W. K. Hofker, H. W. Werner, D. P. Oosthoek, and H. A. M. deGrefte
"Influence of Annealing on the Concentration Profiles of Boron Implantations in Silicon" Appl. Phys. 2, 265-278 (1973)

HON 1958 R. E. Honig
"Sputtering of Surfaces by Positive Ion Beams of Low Energy" J. Appl. Phys. 29, 549-555 (1958)

HON 1962 R. E. Honig
"Mass Spectrometric Studies of Solid Surfaces"
in: "Advances in Mass Spectrometry", Vol. 2, R. M. Elliott, Ed. (Pergamon Press, New York, 1962), 25-37

HON 1963A R. E. Honig and J. R. Woolston
"Laser-Induced Emission of Electrons, Ions, and Neutral Atoms from Solid Surfaces" Appl. Phys. Letters 2, 138-139 (1963)

HON 1963B R. E. Honig
"Laser-Induced Emission of Electrons and Positive Ions from Metals and Semiconductors" Appl. Phys. Letters 3, 8-11 (1963)

HUR 1979 G. S. Hurst, M. G. Payne, S. D. Kramer, and J. P. Young
"Resonance Ionization Spectroscopy and One-Atom Detection" Rev. Mod. Phys. 51, 767-777 (1979)

KAM 1982 I. Kamensky, P. Håkansson, B. Sundqvist, C. J. McNeal, and R. MacFarlane
"Comparison of Biomolecule Desorption Yields for Low and High Energy Primary Ions" Nucl. Instr. Meth. 198, 65-68 (1982)

KIM 1983A F. M. Kimock, J. P. Baxter, and N. Winograd
"Ion and Neutral Yields from Ion Bombarded Metal Surfaces during Chemisorption using Low Dose SIMS and Multiphoton Resonance Ionization" Surf. Sci. 124, L41-L48 (1983)

KIM 1983B F. M. Kimock, J. P. Baxter, and N. Winograd
"Detection of Sputtered Neutrals by Multi-Photon Resonance Ionization" Nucl. Instr. Meth. 218, 287-292 (1983)

KRO 1975 V. E. Krohn and G. R. Ringo
"Ion Source of High Brightness using Liquid Metal" Appl. Phys. Letters 27, 479-481 (1975)

KRU 1983 F. R. Krueger
"Thermodynamics of Ion Formation by Fast Dissipation of Energy at Solid Surfaces" Z. Naturforsch. 38a, 385-394 (1983)

KUS 1977 K. Kusao, Y. Yoshioka,, and F. Konishi
"Development and Applications of Quadrupole Type Secondary Ion Mass Spectrometer (QSIMS)" Nat. Tech. Rep. 23, 14 (1977)

LEH 1962 R. S. Lehrle, J. C. Robb, and D. W. Thomas
"A Modified Time-of-Flight Mass Spectrometer for Studying Ion-Molecule or Neutral Particle-Molecule Interactions" J. Sci. Instr. 39, 458-463 (1962)

LET 1980 D. P. Leta and G. H. Morrison
"Ion Implantation for In-Situ Quantitative Ion Microprobe Analysis" Anal. Chem 52, 277-280 (1980)

LIE 1963 H. J. Liebl and R. F. K. Herzog
"Sputtering Ion Source for Solids" J. Appl. Phys. 34, 2893-2896 (1963)

LIE 1967 H. J. Liebl
"Ion Microprobe Mass Analyzer" J. Appl. Phys. 38, 5277-5283 (1967)

LIE 1975 H. J. Liebl
"Ion Microprobe Analysers: History and Outlook" Anal. Chem. 46, 23A-30A (1975)

LIE 1980 H. J. Liebl
"SIMS Instrumentation and Imaging Techniques" Scanning 3, 79-89 (1980)

MAC 1976 R. D. Macfarlane and D. F. Torgerson
"Californium-252 Plasma Desorption Mass Spectroscopy" Science 191, 920-925 (1976)

MAC 1982 R. D. Macfarlane
"Particle-Induced Desorption Mass Spectrometry of Large Involatile Biomolecules: Surface Chemistry in the High-Energy-Short-Time Domain" Acc. Chem. Res. 15, 268-275 (1982)

MAC 1983 R. D. Macfarlane
"High Energy Heavy-Ion Induced Desorption (Review)"
in: "Ion Formation from Organic Solids", A. Benninghoven, Ed. (Springer-Verlag, Berlin, 1983), pp. 32-46

MAG 1978 C. W. Magee, W. L. Harrington, and R. E. Honig
"Secondary Ion Quadrupole Mass Spectrometer for Depth Profiling - Design and Performance Evaluation" Rev. Sci. Instr. 49, 477-485 (1978)

MAG 1983 C. W. Magee
"Sputtering of Organic Molecules" Int. J. Mass Spectrom. Ion Phys. 49, 211-221 (1983)

MAM 1973 B. A. Mamyrim, V. I. Karataev, D. V. Shmikk, and V. A. Zagulin
"The Mass-Reflectron, a New Nonmagnetic Time-of-Flight Mass Spectrometer with High Resolution" Sov. Phys.-JETP 37, 45-48 (1973)

MOR 1982 G. H. Morrison
"Quantifications of SIMS"
in: "Secondary Ion Mass Spectrometry, SIMS III, A. Benninghoven, J. Giber, J. László, M. Riedel, J. W. Werner, Eds., (Springer-Verlag, Berlin, 1982), pp. 244-256

OEC 1972 H. Oechsner and W. Gerhard
"A Method for Surface Analysis by Sputtered Neutrals" Phys. Letters 40A, 211-212 (1972)

OEC 1977 H. Oechsner and E. Stumpe
"Sputtered Neutral Mass Spectrometry (SNMS) as a Tool for Chemical Surface Analysis and Depth Profiling" Appl. Phys. 14, 43 (1977)

OEC 1979 H. Oechsner, W. Rühe and E. Stumpe
"Comparative SNMS and SIMS Studies of Oxidized Ce and Gd" Surf. Sci. 85, 289-301 (1979)

PAR 1983 J. E. Parks, H. W. Schmitt, G. S. Hurst, and W. M. Fairbank, Jr.
"Sputter-Initiated Resonance Ionization Spectroscopy" Thin Solid Films 108, 69-78 (1983)

PLU 1953 R. H. Plumlee
"Mass Spectrometric Studies in Solids"
in: "Mass Spectroscopy in Physics Research", National Bureau of Standards Circular 522 (Washington, D.C., 1953), pp. 232

POS 1978 M. A. Posthumus, P. G. Kistemaker, H. L. C. Meuzelaar, and M. C. Ten Noever de Brauw
"Laser Desorption-Mass Spectrometry of Polar Nonvolatile Bio-Organic Molecules" Anal. Chem. 50, 985-991 (1978)

ROU 1969 J. M. Rouberol, J. Guernet, P. Deschamps, J.-P. Dagnot, and J.-M. Guyon de la Berge
"Microanalyseur par émission ionique secondaire"
in: "Proc. 5th Int. Conf. on X-Ray Optics and Microanalysis (Springer-Verlag, Heidelberg, 1969) pp. 311-318

ROU 1969 J. M. Rouberol, M. Lepareur, B. Autier, and J. M. Gourgout
"A New Secondary Ion Emission Microanalyzer"
in: "X-Ray Optics and Microanalysis", D. R. Beaman, R. E. Ogilvie, D. B. Wittry, Eds. (Pendell Pub. Co., Midland, Mich., 1980)

RÜD 1982 F. G. Rüdenauer, P. Pollinger, H. Studnicka, H. Gnaser, W. Steiger, and M. J. Higatsberger
"First Results on a Scanning Ion Microprobe Equipped with an EHD-Type Indium Primary Ion Source"
in: "Secondary Ion Mass Spectrometry SIMS III, A. Benninghoven, J. Giber, J. László, M. Riedel, and H. W. Werner, Eds. (Springer-Verlag, New York, 1982), pp. 43-48

SAW 1930 R. B. Sawyer
"The Reflection of Lithium Ions from Metal Surfaces" Phys. Rev. 35, 1090 (1930)

SCH 1979 B. Schueler and F. R. Krueger
"Spectra of Quaternary Ammonium Salts Taken by Fission-Fragment and Laser-Induced Desorption" Org. Mass Spectrom. 14, 439-441 (1979)

SCH 1980 B. Schueler and F. R. Krueger
"Comparative Study of Pulsed Laser and Fission Fragment Induced Desorption with Nucleotic Compounds" Org. Mass Spectrom. 15, 295-301 (1980)

SIM 1974 D. S. Simons, B. N. Colby, and C. A. Evans, Jr.
"Electrohydrodynamic Ionization Mass Spectrometry - The Ionization of Liquid Glycerol and Non-Volatile Organic Solutes" Int. J. Mass Spectrom. Ion Phys. 15, 291-302 (1974)

SLO 1938 R. H. Sloane
"The Formation of Negative Ions by Positive-Ion Impact on Surfaces" Proc. Roy. Soc. A 168, 284-301 (1938)

SLO 1966 G. Slodzian and J.-F. Hennequin
"Sur l'émission ionique secondaire des métaux en présence d'oxygène" C. R. Acad. Sc. Paris 263, 1246-1249 (1966)

SRO 1974 Z. Sroubek
"The Theoretical and Experimenal Study of the Ionization Processes during the Low Energy Sputtering" Surf. Sci. 44, 47 (1974)

SUR 1981 D. J. Surman and J. C. Vickerman
"Fast Atom Bombardment Quadrupole Mass Spectrometry" J.C.S. Chem. Comm. 1981, 324-325

THO 1910 J. J. Thomson
"LXXXIII. Rays of Positive Electricity" Phil. Mag. 20, 752-767 (1910)

THO 1931 J. S. Thompson
"A New Method of Producing Negative Ions" Phys. Rev. 38, 1389L (1931)

TOR 1974 D. F. Torgerson, R. P. Skowronski, and R. D. Macfarlane
Biochem. Biophys. Res. Comm. 60, 616 (1974)

TUR 1982 N. H. Turner and R. J. Colton
"Surface Analysis: X-Ray Photoelectron Spectroscopy, Auger Electron Spectroscopy, and Secondary Ion Mass Spectrometry" Anal. Chem. 54, 293R-322R (1982)

TUR 1984 N. H. Turner, B. I. Dunlap, and R. J. Colton
"Surface Analysis: X-Ray Photoelectron Spectroscopy, Auger Electron Spectroscopy and Secondary Ion Mass Spectrometry" Anal. Chem. 56, 373R-416R (1984)

UNS 1976 E. Unsöld, F. Hillenkamp, and R. Nitsche
"Laser Microprobe Mass Analysis of Biological Tissues" Analusis 4, 115-119 (1976)

VAS 1968 F. J. Vastola and A. J. Pirone
"Ionization of Organic Solids by Laser Irradiation"
in: Adv. Mass Spectrom. 4, E. Kendrick, Ed. (Inst. Petrol., London, 1968) pp. 107-111

VEK 1956 V. I. Veksler and M. B. Ben'iaminovich
"The Production of Secondary Ions from Tantalum and Nickel Bombarded by Positive Cesium Atoms" Sov. Phys.-Tech. Phys. 1, 1626-33 (1957)

VIE 1948 F. Viehböck
"Über eine neue Ionenquelle" Doctoral Dissertation (Unpublished), University of Vienna (1948)

VOI 1983 H. Voit, H. Fröhlich, P. Dück, B. Nees, E. Nieschler, W. Bischof, and W. Tiereth
"Heavy Ion Induced Desorption of Biomolecules: Dependence on the Heavy Ion Parameters" IEEE Trans. Nucl. Sci. NS-30, 1759-1761 (1983)

WER 1972 H. W. Werner
"Instrumental Aspects of Secondary Ion Mass Spectrometry and Secondary Ion Imaging Mass Spectrometry" Vacuum 22, 613-617 (1972)

WIL 1979 P. Williams
"The Sputtering Process and Sputtered Ion Emission" Surf. Sci. 90, 588-634 (1979)

WIL 1982 P. Williams
"On Mechanisms of Sputtered Ion Emission" Appl. Surf. Sci. 13, 241-259 (1982)

WIN 1982 N. Winograd
"Characterization of Solids and Surfaces Using Ion Beams and Mass Spectrometry" Prog. Solid St. Chem. 13, 285-375 (1982)

WIT 1973 K. Wittmaack, J. Maul, and F. Schulz
"A Low Background Secondary Ion Mass Spectrometer with Quadrupole Analyser" Int. J. Mass Spectrom. Ion Phys. 11, 23-35 (1973)

WIT 1977 K. Wittmaack
"Secondary Ion Production Due to Ion-Surface Bombardment"
in: "Inelastic Ion-Surface Collisions", N. H. Tolk, J. C. Tully, W. Heiland, C. W. White, Eds. (Academic Press, New York, 1977), p. 153+

WIT 1980 K. Wittmaack
"Aspects of Quantitative Secondary Ion Mass Spectrometry"
Nucl. Instr. Meth. 168, 343-356 (1980)

WOO 1931 K. S. Woodcock
"The Emission of Negative Ions Under the Bombardment of Positive Ions" Phys. Rev. 38, 1696-1703 (1931)

YIN 1980 S.-Y. Yin
"Eighteen Years of Secondary Ion Mass Spectrometry: A Bibliography of SIMS, 1958-1975" Proc., 15th Ann. Conf. Microbeam Anal. Soc. 1980, pp. 289-311

YIN 1981 S.-Y. Yin
"Recent Developments in Secondary Ion Mass Spectrometry: A Bibliography of SIMS, 1976-1980" Proc., 16th Ann. Conf. Microbeam Anal. Soc. 1981, pp. 342-378

ZIN 1980 E. Zinner
"Depth Profiling by Secondary Ion Mass Spectrometry" Scanning 3, 57-78 (1980)

ZIN 1983 E. Zinner
"Sputter Depth Profiling of Microelectronic Structures"
J. Electrochem. Soc. 130, 199C-222C (1983)

MASS SPECTROSCOPY - WAYS AND MEANS - A HISTORICAL PROSPECTUS

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The development of mass spectroscopy and its instruments did not take place by a simple linear series of events. Rather, it involved a complex interweaving of a number of strands starting with experiments by men whose names are now obscure. I propose here to review briefly the development of mass spectroscopy and tell you something of the work of men on whose shoulders we stand. It was not always as we have it now!

If we are to recognize an individual as the real "father of mass spectroscopy" it has to be physicist John Joseph Thomson, better known as J. J. whose picture is given in Fig. 1 as he looked about the time he was doing his classic work on positive rays. Thomson was quick to realize far reaching implications of his work but it was many years before chemists fully realized the wisdom of his words.

> "•••••••••• I HAVE DESCRIBED AT SOME LENGTH THE APPLICATION OF POSITIVE RAYS TO CHEMICAL ANALYSIS; ONE OF THE MAIN REASONS FOR WRITING THIS BOOK WAS THE HOPE THAT IT MIGHT INDUCE OTHERS, AND ESPECIALLY CHEMISTS, TO TRY THIS METHOD OF ANALYSIS. I FEEL SURE THAT THERE ARE MANY PROBLEMS IN CHEMISTRY WHICH COULD BE SOLVED WITH FAR GREATER EASE BY THIS THAN ANY OTHER METHOD. THE METHOD IS SURPRISINGLY SENSITIVE -- MORE SO EVEN THAN THAT OF SPECTRUM ANALYSIS, REQUIRES AN INFINITESIMAL AMOUNT OF MATERIAL, AND DOES NOT REQUIRE THIS TO BE SPECIALLY PURIFIED; THE TECHNIQUE IS NOT DIFFICULT IF APPLIANCES FOR PRODUCING HIGH VACUA ARE AVAILABLE. ••••••••"
>
> CAMBRIDGE, 4 OCTOBER 1913 J. J. THOMSON
>
> TAKEN FROM THE PREFACE TO
> "RAYS OF POSITIVE ELECTRICITY AND THEIR APPLICATION TO CHEMICAL ANALYSIS"

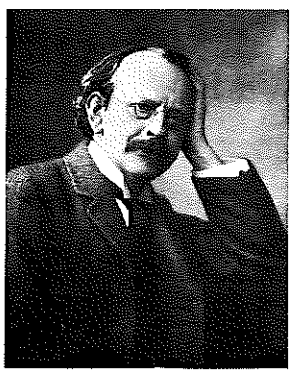


Fig. 1. J. J. Thomson.

There were some fundamental chemical implications in his work however because it started the unravelling of mysteries concerning the nature of atoms in a way which led to many of those things we assume today concerning the structure and diversity of atoms. Keep in mind that our notions about atoms and molecules did not exist in Thomson's time. Indeed, it was just a little bit before this time that scientists recognized the existence of one of the building blocks of atoms, namely electrons. Thomson also had shoulders on which to stand because of the flurry of activity surrounding the mystery of what went on in discharge tubes. In 1852, Grove recognized that gases provided a powerful resistance to the passage of an electric current until the pressure was reduced sufficiently to produce a "lambent light". Further pressure reduction caused the light to disappear and the resistance to

increase again. The phenomena was first mentioned by J. Walsh in 1773, confirmed by W. Morgan in 1785 and again by H. Davy in 1822. The mechanism for conduction was not understood and Grove thought the stratification observed in the discharge was due to mechanical pulses taking place in the rarified gas. J. P. Gassiot (1859) supported this view when he observed a series of deposits on a glass bulb after repeated discharges. At about the same time (1859, 1862) M. Plücker showed that a magnet affected the discharge beam and J. Tyndall (1860) said "The action of a magnet on a splendid stream of green light caused the light to be bent hither and thither as the position of the poles of the magnet were changed. On further approach of the magnet the light was torn asunder and the passage of current interrupted". In 1858 Plücker described the green fluorescence of the inner surfaces of glass discharge tubes and ascribed it to current passing from the cathode to the walls of the tube. W. Hittorf in 1869 showed that in a bent discharge tube the fluorescence occurred opposite the cathode and furthermore would cast a shadow of an object placed in the way of the rays. Eugen Goldstein, also actively pursuing research with discharges, named these rays cathode rays and explained the shadows as a result of the rays being projected from the cathode in a direction perpendicular to its surface. In 1886 Goldstein experimented with discharge tubes containing perforated cathodes hoping to see their shadowy images but observed faint streamers emerging behind the holes in the cathode. These he called "kanalstrahlen" or canal rays. About this time activity concerned with discharge tubes increased tremendously. H. Hertz (1892) found that cathode rays would penetrate metal foils. J. Perrin (1895) demonstrated that cathode rays consisted of negatively charged carriers by bending the rays with a magnetic field so they would fall on a faraday cup which collected a very large negative charge recorded by an electrometer. The same year W. Roentgen discovered the penetrating secondary rays known as x-rays produced when cathode rays struck a solid surface. In 1897 J. J. Thomson determined the mass-to-charge ratio of the "corpuscles" (Varley, 1871) in cathode rays by sending a collimated stream of rays through crossed magnetic and electric fields and decided that the mass of the electron was small compared to that of the hydrogen atom. Wilhelm Wien (1897-1902) showed that whereas cathode rays were greatly deflected by a modest magnetic field it took a very strong magnetic field to deflect canal rays at all. However, the deflection was opposite that of canal rays so Wien concluded that canal rays were positively charged. The way in which the story about both cathode rays and canal rays developed in the first decade of this century is fascinating but will not be considered here. Suffice it to say however, that it was during this time that many observations were made that led to our present view of atoms and molecules. Stoney gave us the word "electron" which originally referred to the charge on positively or negatively charged particles but which was eventually applied to the particles in cathode rays taken from the Greek ηλεκτρον for amber, known to be electrified when rubbed with a sheep skin (Thales ~600 B.C.). The carriers of positive electricity became known as "ions" (from the Greek ιον, traveller).

During the first decade of this century Thomson turned his attention from cathode rays to "anode rays" as he called Goldstein's "kanalstrahlen". In experiments with a discharge bulb with a cathode containing a fine tube he passed positive rays through combined magnetic and electric fields as shown in Fig. 2. The result of this was parabolic streaks visible on a fluorescence screen consisting of natural zinc silicate (willemite). Later a photographic plate was substituted for the willemite in order to obtain a permanent record of what was being observed. A copy of one of his photoplates is shown in Fig. 3. By varying the strength of fields and their polarity Thomson was able to change the positions of the parabolic streaks. He was also able to observe streaks due to negative ions. On the basis of a mathematical treatment of what was expected and a knowledge of the field strengths he was able to identify the mass-to-charge ratio of particles causing the streaks. Note the somewhat obscured evidence that neon did not consist of atoms with m/z 20.2 as suggested by the known atomic weight but rather atoms of weight 20 and perhaps 22! Actually there is much more information in these parabolic patterns than the m/z ratio for constituents in the discharge tube. Note the molecular ions for CO and CO_2. Consider also the fact that the length of the streaks are related to the excess kinetic energy of the ions. In other experiments Thomson was even able to show that various metastable transitions and charge exchanges took place as ions traversed the various spaces in the apparatus. He was also concerned about the neutral particles existing in discharge tubes. Thomson commented on the richness of chemical information in positive ray spectra.

"IF A SPECTROSCOPIST OBSERVES A LINE UNKNOWN TO HIM IN THE SPECTRUM OF A DISCHARGE TUBE, THE MOST HE CAN INFER IS THAT THERE IS SOME UNKNOWN SUBSTANCE IN THE TUBE, AND EVEN THIS MIGHT BE DOUBTFUL, AS THE NEW LINE MIGHT BE DUE TO SOME ALTERATIONS IN THE CONDITIONS OF THE DISCHARGE. BUT IF WE OBSERVE A NEW PARABOLA IN THE POSITIVE RAY SPECTRUM ALL WE HAVE TO DO IS MEASURE THE PARABOLA AND AT ONCE THIS TELLS US WHAT IS THE ATOMIC WEIGHT OF THE PARTICLES WHICH PRODUCED IT".

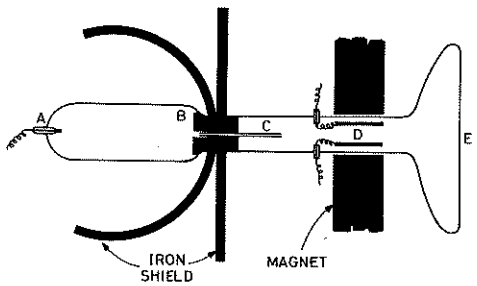


Fig. 2. J. J. Thomson Positive Ray Apparatus.

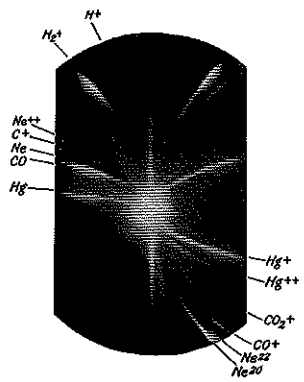


Fig. 3. Photoplate from J. J. Thomson experiment with Neon.

In very large measure Thomson's successes with his positive ray research was dependent upon getting a good vacuum in his apparatus and being able to outpump the rate of outgassing from the walls and components of the apparatus. Early evacuation of discharge tubes were by means of Sprengel or Töpler pumps. Work with these involved tedious manual labor and vacuums attainable were at best poor by our standards (10^{-2} to 10^{-3} Torr). The advent of the rotary mercury pump invented by Gaede in 1905 alleviated this situation by making vacuums as low as 10^{-5} to 10^{-6} Torr attainable. Subsequent development of scraping vane mechanical pumps, and diffusion and condensation pumps settled the question for subsequent mass spectroscopists of how to obtain good vacua.

With the publication of his book in 1913 came the end of Thomson's great contributions to mass spectroscopy. The subject was continued admirably by William Francis Aston who took the place of G. W. C. Kaye as Thomson's assistant at the Cavendish Laboratory at Cambridge University. In the years just prior to World War I, Aston began his work with positive rays in England and Arthur Jeffery Dempster did the same in the United States. Aston utilized a discharge bulb as a source of ions whereas Dempster obtained positive ions from salts on heated filaments and by electron bombardment of vapors emitted from these filaments. Aston's Mass Spectrograph involved both velocity and direction focusing while

Dempster used mainly direction focusing. Aston's apparatus was unique in that it was used mainly by himself whereas Dempster's apparatus is the basis for many modern deflection instruments.

Figure 4 illustrates diagramatically the ion optics of Aston's Mass Spectrograph (a term he coined) consisting of both an electric field and magnetic field. Figure 5 is a photograph of Aston's first mass spectrograph. [Aston built 3 mass spectrographs.] Note the discharge bulb B, the magnet M, and the Gaede Rotary mercury pump G. Electric sources were batteries and control of current and voltages was by means of variable resistors and voltage dividers. Despite what appears to be by our standards a rather crude piece of equipment, Aston obtained the first conclusive results indicating the existence of isotopes of the stable elements, a fact already established for radioactive elements. Indeed, in 1910 Soddy had already coined the word "isotope" from the Greek "ισοτοπος" meaning in the same place (in the periodic table), to explain the existence of radioactive elements with the same chemical properties but different atomic weights.

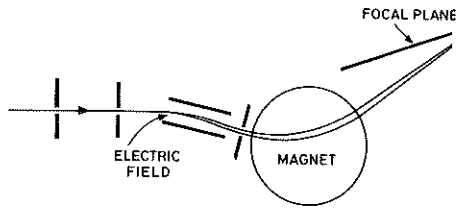
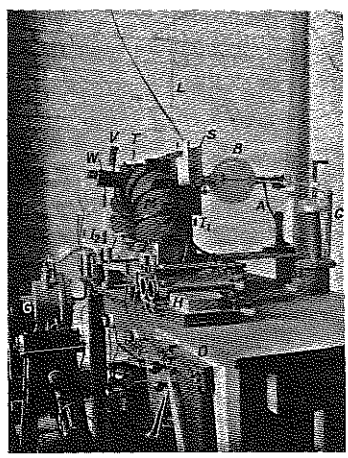


Fig. 4. Ion optics of Aston's mass spectrograph.



The Original Mass Spectrograph set up in the Cavendish Laboratory in 1919; now in the Science Museum, South Kensington.

Fig. 5. The original mass spectrograph set up in the Cavendish Laboratory in 1919.

Aston's results were recorded photographically and Fig. 6 is an example of some of his earliest results for Ne, Cl, Ar, and Kr. These results proved the existence of ^{20}Ne and ^{22}Ne, and thereby settled the question raised by Thomson's results for neon. [Thomson suspected two forms for atoms of neon but because of his awareness of ion/molecule

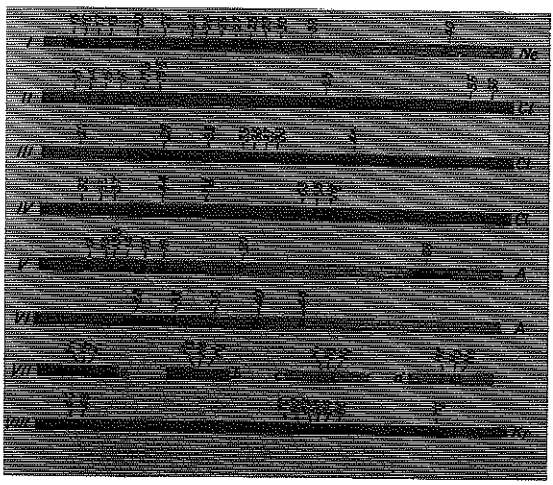


Fig. 6. Typical mass spectra obtained with the first mass spectrograph, 1920.

interactions considered also that the parabola at mass 22 could be due to a hydride, NeH_2.] Aston also settled the problem of the atomic weight of chlorine, the value 35.46 being due to the weighted average of its isotopes based on the abundances of ^{35}Cl and ^{37}Cl. Note also the heterogenous character of Kr. Aston also showed that molecular species could be used as sources of ions in a discharge bulb. He went on to study the isotopic constitution of most of the elements. During the course of this work he diffused neon through clay pipe stems to separate the neon isotopes partially, developed the art of making fine slits to collimate ion beams, perfected the use of electric discharges as sources of ions of the more volatile elements, perfected the use of photographic plates for recording spectra [we still use Ilford plates today], used transmission of light through lines as a means of determining isotopic abundances, became aware of departures from the whole number rule for nuclide masses, invented the methods of bracketing and use of doublets for mass determinations, and did extensive work to map "mass defects" of the nuclides. He also invented new vacuum seals and extended the use of high vacuum technology when the practice was in its infancy. Aston was well aware of the foibles we experience doing mass spectroscopy. In speaking of his apparatus he said:

> "IT BEHAVES AT TIMES IN THE MOST CAPRICIOUS AND UNACCOUNTABLE MANNER ••••• ••• WHEN BY GOOD FORTUNE ALL IS WELL THE ARRANGEMENT IS CAPABLE OF GOOD PERFORMANCES. THUS, AFTER A FAVORABLE SETTING OF THE APPARATUS, SIX ELEMENTS WERE SUCCESSFULLY ANALYZED IN AS MANY WORKING DAYS. ON THE OTHER HAND, AFTER DISMANTLING BECAME IMPERATIVE AND IT HAD TO BE CLEANED AND REBUILT, EXACTLY AS BEFORE AS FAR AS ONE COULD TELL, NO RESULTS OF ANY VALUE WERE OBTAINED DURING WEEKS OF WORK."
>
> DECEMBER 1941 FRANCIS WILLIAM ASTON
>
> TAKEN FROM: "MASS SPECTRA AND ISOTOPES", Second Edition

At the same time Aston was beginning and extending his work in England, A. J. Dempster was similarly at work in the Ryerson Laboratory at the University of Chicago. In 1918 he

published results due to "A New Method of Positive Ray Analysis" in which he observed $^{23}Na^{+}$ and $^{39}K^{+}$ ions when aluminum phosphate was heated on a thin platinum strip. These ions were probably due to impurities in the $AlPO_4$ and their presence was augmented by bombardment by electrons from a hot metal filament. Such ions had very little kinetic energy so Dempster accelerated them by means of a simple electric field (see Fig. 7), separated them according to their momentum in a 180° homogeneous magnetic field and detected them with a quadrant electrometer. Dempster followed up this work with an improved electron bombardment ion source (Fig. 8) and used the then new Wilson tilting electrometer which eliminated problems due to gravity on the electrometer leaf as a means of measuring currents.

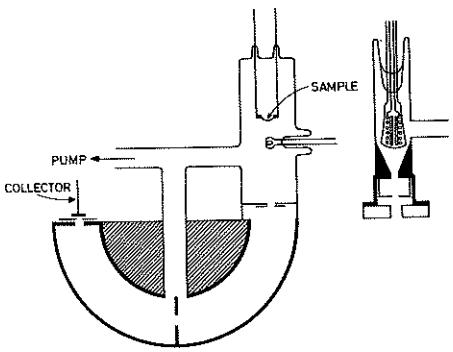


Fig. 7. Dempster's first apparatus.

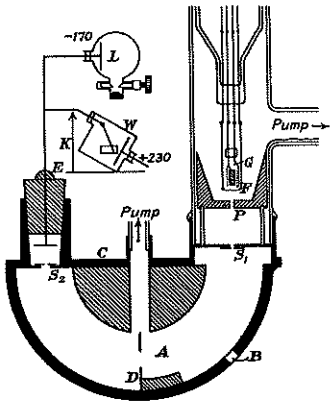


Figure 8. Dempster's modified apparatus.

In 1920 Dempster published the abundances of ^{24}Mg, ^{25}Mg, ^{26}Mg and ^{39}K and ^{40}K based on measurements with the tilting electrometer. An interesting example of how good his abundance measurements were is indicated by using them with whole number masses of the isotopes to calculate a "mass spectrometric atomic weight". His calculated value of 24.38 for Mg agreed quite well with the chemical value of 24.36 in use at the time. If the present nuclidic masses were used, the atomic weight for Mg would be 24.318, in excellent agreement with the value 24.305 accepted in 1975. Thus began the ultimate demise of chemically-determined atomic weights at about the time when determining them chemically was being developed to a fine art. Dempster along with Aston and others continued to investigate the isotopic composition of the elements until in 1935 the last of the elements Pt and Ir were successfully measured by Dempster using ions created in a high voltage, high frequency spark. Not too long after, Aston during a talk in Britain made the claim that mass spectroscopy had served its purpose and would die away as a field for research.

Consider the properties of a moving particle. It will have kinetic energy, momentum, and velocity. These properties are the basis for components of mass spectroscopes. Thus we have:

COMPONENTS OF A MASS SPECTROSCOPE

ENERGY SELECTORS	
Radial Electric Field	$\frac{mv^2}{2} = \frac{REz}{2}$
Parallel Plate Accleration	$\frac{mv^2}{2} = zE$
MOMENTUM SELECTOR	
Homogeneous Magnetic Field	$mv = RHz$
VELOCITY SELECTORS	
Cross Electric-Magnetic Fields	$v = \frac{E}{H}$
Time-of-Flight	
Cyclotron	
Mass Synchrometers	
RF Fields	
Linear Accelerator	
Others	

The case involving kinetic energy and momentum selectors was used by Dempster to establish the relationship $\frac{m}{z} = \frac{H^2R^2}{2E}$ where m = mass, H = magnetic field strength, E = electric field strength, R = radius of curvature in a field and z = the charge on an ion. Velocity selection is achieved in many different ways. The crossed electric/magnetic field device was used by J. J. Thomson to determine the mass-to-charge ratio of the electron in 1897 and is the basis for the so-called Wien filter. Combining any two or more of these "selectors" results in an analytical expression defining the path of ions in a mass spectroscope.

One of the first mass spectrographs to utilize a velocity selector was that of K. Bainbridge in 1931 (then of the Franklin Institute - later Harvard University) who used a crossed field velocity selector in combination with a 180° magnetic field (Fig. 9) to determine the masses of ions formed in a discharge bulb. A schematic diagram of Bainbridge's mass spectrograph is shown in Fig. 10. Using the doublet method he established one of the earliest precision values for the masses of hydrogen and deuterium.

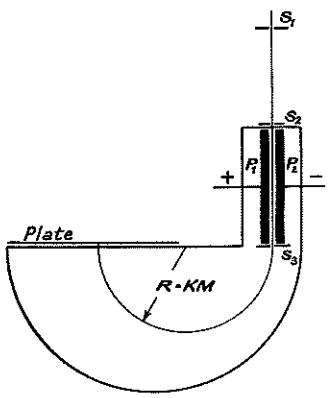


Fig. 9. Diagram of velocity selector.

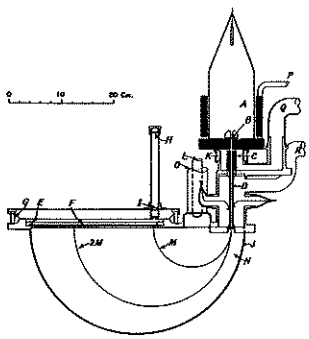


Fig. 10. Diagram of Bainbridge's apparatus.

Another early use of velocity selection was due to W. R. Smythe and J. Mattauch (1932) (then at California Institute of Technology). They set up an instrument with no magnetic fields (Fig. 11, note side and top views). Rather the ion beam was made to traverse a series of parallel plate condensers to which an alternating voltage was applied. These condensers act as a set of "electrical gates" which open and close regularly. Only those ions with the proper velocity pass when all the gates are open --- others are shunted to the side. Ions are formed at 5000-8000 volts in a discharge tube. After the ion beam passes through all the gates, the beam containing only certain velocities is deflected through 90° by an electrostatic field (Energy Selection) thereby bringing to focus on the final slit ions of a particular m/z ratio. The apparatus was tested with air but many artifacts due to the positioning of the condensers and the frequency of the a.c. voltage were observed. It was used successfully for some ^{18}O measurements.

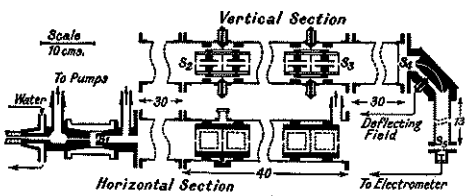


Fig. 11. Diagram of the Smythe-Mattauch Mass Spectrometer.

In 1946 W. E. Stephens proposed another scheme for velocity selection, namely the time it takes for a pulse of ions to fly down a long tube. If they would all start with the same energy, ion bunches due to different masses have different velocities. These could then be collected sequentially using a fast amplifier, the output of which would be a mass spectrum. Two years later A. E. Cameron and D. F. Eggers constructed such an apparatus which they called an ion "Velocitron" and achieved a mass resolution of ~25, good enough for work with only light ions but capable of recording many mass spectra per second by using an oscilloscope to observe peaks due to different values for m/z. The apparatus was tested with Freon-12 (CF_2Cl_2) and all possible ion fragments were observed. A prototype of a modern time-of-flight (Fig. 12) mass spectrometer was developed by W. C. Wiley and I. H. McLaren in 1955. Their design was produced as a commercial instrument which was marketed by the Bendix Corporation. The Bendix TOF instrument was capable of scanning a mass range from 1 ~ 600 and 10000 or more spectra per second. The TOF instrument is a unique mass spectrometer because it is capable of monitoring variations in reaction rates and monitoring reaction profiles of as little as ~100 μs duration. The principle has been exploited very well in several recent instruments involving particle and laser bombardment of solids.

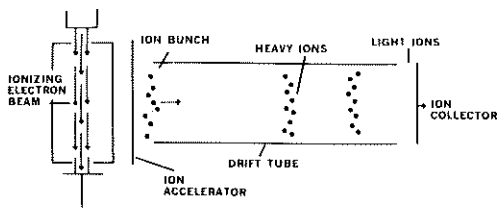


Fig. 12. Diagram of time-of-flight mass spectrometer.

In 1948 J. Hipple, H. Somer, and H. Thomas described another velocity selector based on the cyclotron principle (Fig. 13). They called their device an omegatron. Such an

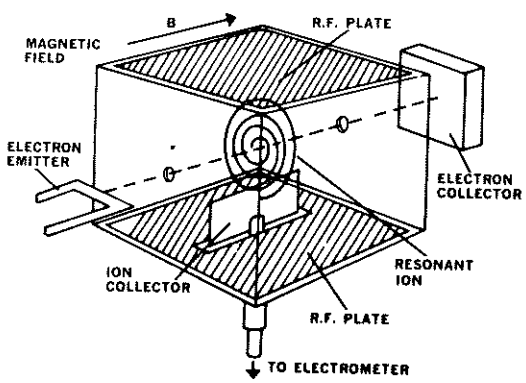


Fig. 13. Diagram of omegatron.

instrument was developed further by the General Electric Co. and sold commercially. Its greatest virtue was for light ions and for a while was used as a leak detector. Modern day cyclotron resonance instruments are based on this principle. In the classical omegatron the expanding spiral of resonant ions emerges through a final slit and is measured by an electron multiplier or electrometer. In cyclotron resonance instruments ion detection is based on the absorption of resonant radiofrequency energy, which gives rise to the expanding spiral motions, i.e. the work required to accelerate the ions. Lincoln Smith further refined the cyclotron-type spectrometer in his mass synchrometer which started out as a super velocity selector but was subsequently developed into the most precise method for measuring some nuclidic masses because of the correlation between mass and the precisely known pulsing frequency used to accelerate the ions.

Two other velocity selector instruments are worth mentioning. The first is that due to W. H. Bennett (National Bureau of Standards) whose instrument (Fig. 14) consisted of a parallel plate energy selector coupled with a series of electrical grids to which radio frequency (RF) voltages were applied. Thus all ions leaving the ion source had the same energy. As they passed through the series of grids, only those arriving at a grid when the RF voltage went to zero passed through. Ions with a particular velocity were matched to a pulsing frequency. Thus mass scans were achieved by varying the frequency. Bennett developed his RF mass spectrometer and achieved moderate mass resolution. The device was relatively compact but had limited application so it had its place for a while and then disappeared for a while. However some recent proposals for improvements have appeared and so we might see its revival.

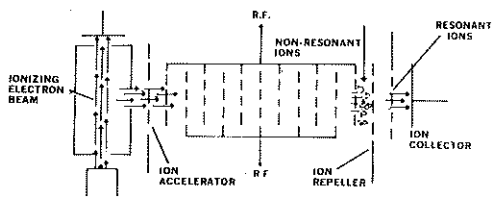


Fig. 14. Diagram of Bennett mass spectrometer.

The other velocity selector involves incremental increases in energy based upon the principle of the linear accelerator. Such an instrument was actually developed commercially by the Beckman Instrument Co. A diagrammatic view of the arrangement is given in Fig. 15. Like the Bennett tube, this device appeared on the scene, had its day and then faded away.

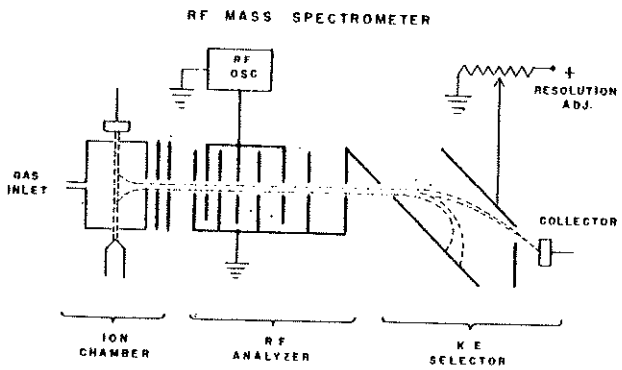


Fig. 15. Diagram of linear accelerator mass spectrometer.

HIGH POWERED MASS SPECTROGRAPHS AND SPECTROMETERS.

The whole number rule which Aston established with his first mass spectrograph was never meant to be mathematically exact. Any deviation from the rule was only measurable at first with any kind of accuracy for H but it soon became apparent that ^{6}Li and ^{7}Li had masses (relative to ^{16}O) which slightly exceeded whole numbers. The first attempt to measure these deviations with an accuracy greater than 1/1000 was made by Costa in 1925 with a mass spectrograph set up in Paris. He was able to make comparisons with an accuracy of 1/3000 using the method of bracketing and proved that masses of He, C, ^{6}Li, N, and ^{7}Li did indeed deviate positively from whole numbers. During the same year Aston set up his second mass spectrograph at the Cavendish Laboratory with which he was able to make measurements accurate to about 1/10000. With this instrument Aston was able to confirm Costa's results and also to establish that the masses of some elements were less than the expected whole number. Thus started a flurry of research in several laboratories to establish nuclidic masses as accurately as possible. To obviate problems caused by energy spread of the ions, other double focusing instruments were designed and built.

In 1929 Bartky and Dempster developed the theory for a double focusing mass spectrograph involving a 90° electrostatic analyzer and a 180° magnetic analyzer. An instrument was described in 1935 (Fig. 16) along with results for the isotopic compositions of Pd, Ir, Pt and Au using a spark source. The instrument utilized photographic detection and Dempster studied deviations from the whole number rule, now called the packing fraction, for selected nuclides from Al to Th and U showing both positive and negative deviations from the whole number rule. Indeed, it was the fact that heavy elements like Th and U deviate positively that makes them candidates for fissioning with the release of tremendous amounts of energy. A later version of an instrument based on the Bartky-Dempster optics is shown in Fig. 17. This was used by J. Gorman, J. Hipple and J. E. Jones at the National Bureau of Standards for some early spark source analyses of stainless steels.

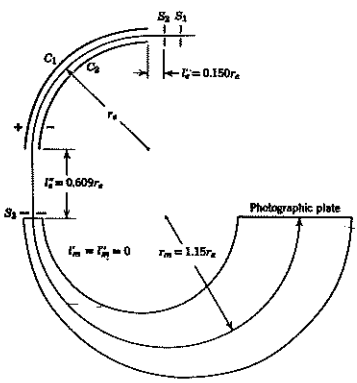


Fig. 16. Bartky-Dempster ion optics.

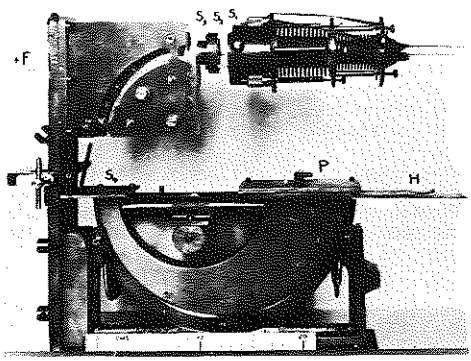


Fig. 17. Inner components of Dempster-Bartky mass spectrograph used at the National Bureau of Standards.

In 1936 K. Bainbridge and E. Jordan described another double focusing mass spectrograph (Fig. 18) capable of establishing nuclidic mass accurate to five and six significant figures. The following year Aston described his third mass spectrograph which was similar to that of Bainbridge and Jordan as far as accuracy was concerned.

These instruments had a true focus at only one point on a photographic plate detector which caused some problems when nuclides of widely different masses were compared. This situation was alleviated by J. Mattauch and R. Herzog in 1934 with the publication of the theory which provided an ion optic system (Fig. 19) which gave perfect first order focusing over the entire length of a photoplate. An instrument based on this theory was described in 1936 and results were published during the next couple of years. The instrument gave remarkably sharp lines and many multiplets were measured. An example is shown in Fig. 20.

All of the nuclidic mass measurements prior to the early 1950's were made by measuring

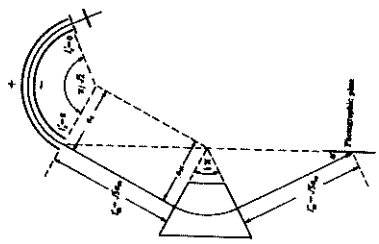


Fig. 18. Ion optics of Bainbridge-Jordan mass spectrometer.

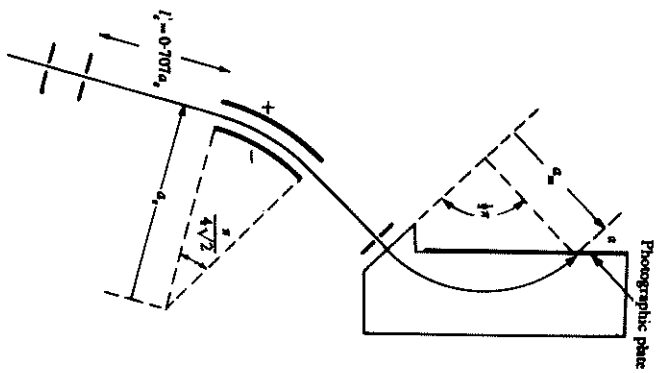


Fig. 19. Mattauch-Herzog ion optics.

the distances between lines on photographic plates. Nier proposed to do the same electrometrically in order to inject into the work a different approach, one which would also not be susceptible to the same systematic errors. In 1951 Nier and Roberts reported the measurement of several light elements using a double focusing mass spectrometer (Fig. 21). The abberations associated with the ion optics of this instrument employing a 90° electric sector (R_e = 7.5 inches) and 60° magnetic sector (R_m = 6 inches) were worked out by Edgar Johnson and Nier in 1953 who showed that it had first order velocity focusing and second order angular focusing at the focal point. The arrangement has henceforth been known as "Nier-Johnson" optics and is extensively used in high resolution mass spectrometers devoted to studies in Organic Chemistry. In 1956 K. Quisenberry, T. Scolman, and Nier published two classic papers in which they report atomic masses of stable nuclides from ^{1}H to ^{30}Si. In the first paper are reported reference atomic masses for ^{1}H, D, ^{12}C and ^{32}S based on a series of 25 doublets and in the second paper masses of all the stable isotopes between ^{10}B and ^{30}Si. A larger double focusing mass spectrometer of Nier-Johnson ion optics was constructed (R_e = 20 inches; R_m = 16 inches) for this work and the doublets were measured by the peak matching technique of Lincoln Smith and C. Damm (Fig. 22). Mass measurements with this new instrument were generally accurate to a micromass or less. This technique is widely used now in high resolution organic mass spectrometry to discern the elemental composition of ion fragments. In this country Lincoln Smith further

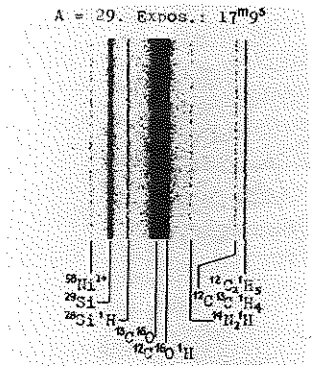


Fig. 20. Multiplet at m/z = 29 recording with Mattauch-Herzog mass spectrograph.

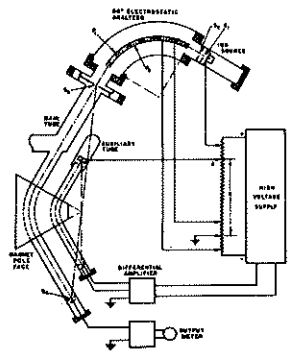


Fig. 21. Diagram of Nier-Roberts mass spectrometer.

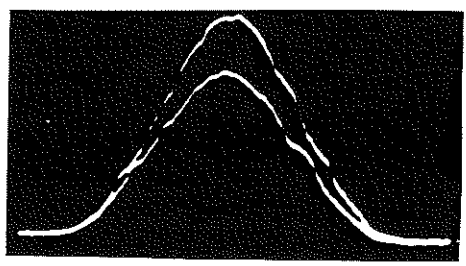


Fig. 22. Peak matching using an oscilloscope.

refined his mass synchrometer to produce perhaps the most precise mass measurements ever made. His untimely death on December 9, 1972 cut off further extensions of his work. In Japan, Ogata and Matsuda (1955) constructed a large double focusing mass spectrometer with a resolution $\Delta M/M$ of 1/500,000.

Ion sources have played an important role in how mass spectrometry developed. The ion source which found extensive use in chemical work is the "electron bombardment" or "electron impact" source. This was first used by Dempster in 1918 with improvements made by him in subsequent years. In 1925 H. D. Smyth dissociated H_2 by varying the electron energy. W. Bleakney (1930, 1932) was the first to collimate the electron beam with a magnetic field and the first to calibrate the true electron energy in an ion source by comparing appearance energies of ions with that of Ar^+ (15.76 eV). Further improvements in electron bombardment ion sources was based on work by John Tate's students W. Bleakney, W. W. Lozier and P. T. Smith. Another of these students, Alfred O. C. Nier used the Smith and Bleakney ideas in his early work with mass spectrometers and ultimately developed what we now call "Nier-type" ion sources. This kind of ion source was used in Nier's 1940, sector instrument and a variation of the source was used in his 1947 dual-ion-beam collecting instrument. The 1940 paper by Nier in Rev. Sci. Instrum. is a landmark paper for chemists interested in tracing the fate of atoms in chemical reactions. This instrument, capable of very high sensitivity, and good resolution for C, N, O and S set off a flurry of activity in many fields. Much of what we know today about the metabolism of carbohydrates, fats and proteins owes its beginning to this instrument. All kinds of organic reaction sequences were also worked out because this easy-to-use mass spectrometer was available with which the fate of C, N, O and H could be traced in organic reactions.

Nier spent the years during World War II associated with the Manhattan Project and was involved in developing instruments capable of handling the very corrosive UF_6 in order to monitor progress in separating ^{235}U and ^{238}U by gaseous diffusion. He also was instrumental in developing a special He sensitive instrument (Fig. 23) which was used to find leaks

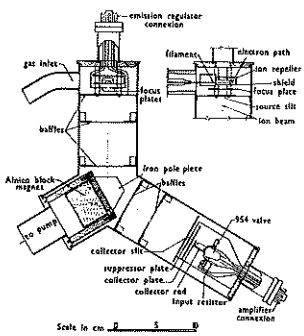


Fig. 23. 60° sector helium leak detector.

in vacuum and gas handling apparatus. The idea was commercialized very early by the General Electric Co. in much the same form (R_m = 5 cm) as shown in the figure and later by the Consolidated Engineering Co. (also known as Consolidated Electrodynamics Corp.; Bell and Howell; Dupont Instruments) with a tiny mass tube that they called the Diatron (Fig. 24). Another, double ended 60° deflection instrument capable of simultaneous collection of positive and negative ions produced in a single electron beam was developed by Flesch and Svec in 1968. It was ideally adapted to studies of the energetics of ion-pair production and had some unique analytical capabilities.

First order aberrations are present in magnetic single deflection instruments. However when the ion path is cycloidal, perfect double focusing is achievable. This was proposed by W. Bleakney and J. Hipple in 1938 who found that a prolate cycloid ion path produced in a combined electric and magnetic field apparatus gave the best results (Fig. 25) after a number of experimental versions were built. In 1956 C. F. Robinson and L. G. Hall described a small instrument with a resolving power of ~150 and the instrument was commercially available from Consolidated Electrodynamics Corporation (Fig. 26). Mass peaks in cycloidal instruments have trapezoidal shapes, flat tops and there is little or no

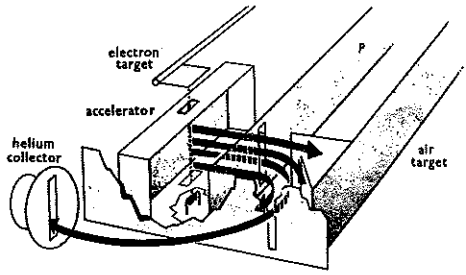


Fig. 24. Diatron helium leak detector.

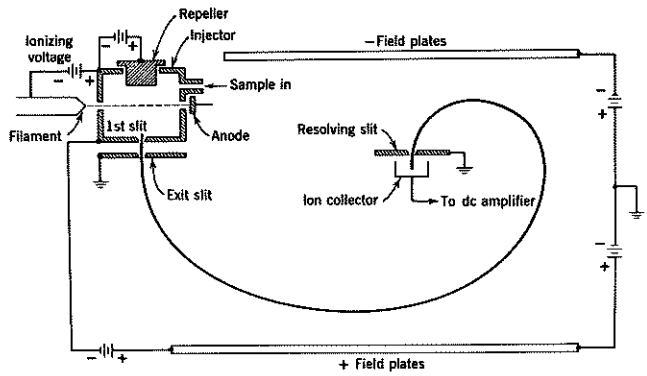


Fig. 25. Cycloidal ion path.

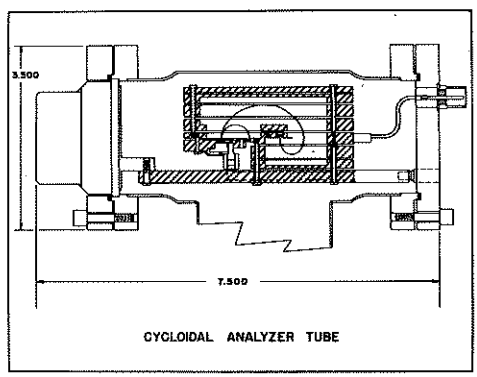


Fig. 26. Cycloidal mass spectrometer.

tailing. Consequently such instruments inherently have high abundance sensitivity.

In 1954 N. B. Hannay described a spark source mass spectrograph, SSMS, based on the ion optic system of Mattauch and Herzog. As a source of ions Hannay used a high frequency, high voltage spark between two electrodes in the form of rods 0.030" to 0.040" diameter and Ilford Q-2 plates for ion detection. The apparatus was pumped with three different diffusion pumps and ion currents were monitored by partially intercepting the beam just before it entered the magnetic field. The instrument was highly sensitive for impurities in conducting samples. Early results indicated facile detection of impurities at the 0.1 ppma level with exposures of only ~5 minutes. An accompanying paper by A. Ahearn and Hannay in Anal. Chem. put the SSMS solidly in place as the second general analytical tool applicable to solids. (The first was Bunsen and Kirchoff's development of the optical spectrograph ~100 years earlier.) Soon after Hannay's announcement, John Waldron pushed the development of a commercial instrument (MS-7) at Metropolitan-Vickers, later Associated Electrical Industries. When the MS-7 was announced, there was a concerted effort by many people concerned with the analysis of solids to procure one. The first MS-7 in this country was in the David Sarnoff Research Laboratories of R.C.A. in Princeton and was used by Rick Honig and his associates for the analysis of many solid state problems. We obtained a SSMS in 1963 from the Nuclide Corp. and proceeded to develop electrical detection for the instrument. Subsequently, our developments to control the spark, the ion illumination angle and the absolute sensitivity of the instrument took place, making it possible to do precise analytical work on solids with the SSMS that far surpasses early prospects. However, today the use of high powered lasers to ionize solids promises to make the SSMS obsolete.

Perhaps the most significant but not so recent development in mass spectrometry as far as chemical applications is concerned is that of W. Paul. In 1958 Paul, H. Reinhard and U. von-Zahn described the Quadrupole mass filter in Zeitschrift für Physik at just the right time (Fig. 27). Early attempts to couple a gas chromatograph with a TOF mass spectrometer were

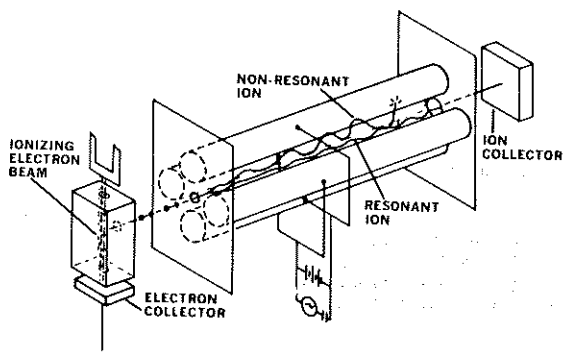


Fig. 27. Diagram of quadrupole mass spectrometer.

already underway but the characteristic of the quadrupole filter was ideal for the GC/MS combination. Paul described three modes of quadrupole operation. 1) As a filter for single ions. 2) As a scanning device capable of producing a mass spectrum. 3) As a selective ion rejection device. The first two modes have been well used in the development of GC/MS and tandem instruments. The third mode has great promise which makes possible the rejection of intense ion beams from mixtures thereby making it possible to enhance the sensitivity of a second quadrupole or other mass spectrometer for measuring trace quantities in mixtures. This usage is just now being implemented in some laboratories.

Mass spectroscopy until recent times has dealt only with gaseous charged particles and direct mass spectra and characterization of neutral particles has remained obscure. An early attack on the problem began in 1960 with the work of D. Beck, A. Niehaus and O. Osbergaus at Bonn and Freiburg, later with C. Melton at Oak Ridge and culminated with the work of M. Tsuchiya, F. Preston, J. Reeher, G. Flesch and H. Svec at the Ames Laboratory (see Fig. 28) operated by Iowa State University. Thus mass spectroscopy is now applicable

to all of the problems originally cited by J. J. Thompson (Fig. 29).

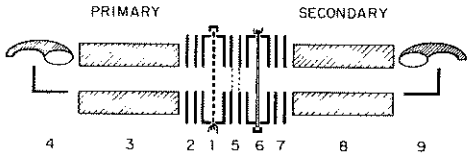


Fig. 28. Diagram of double-ended neutral fragment mass spectrometer.

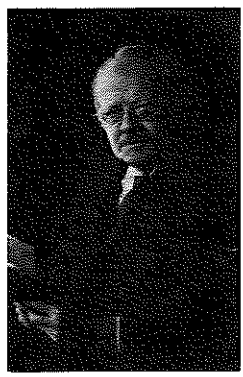


Fig. 29. J. J. Thomson - late years.

ACKNOWLEDGEMENT

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BIBLIOGRAPHY

W. R. Grove, Philos. Trans. Roy. Soc. London, 142 (1852) 87; Ibid., 148 (1858) 1.

J. Walsh, Philos. Trans. Roy. Soc. London, 63 (1773) 461.

W. Morgan, Philos. Trans. Roy. Soc. London, 75 (1785) 272.

H. Davy, Philos. Trans. Roy. Soc. London, 112 (1822) 64.

J. P. Gassiot, Philos. Trans. Roy. Soc. London, 149 (1859) 137.

M. Plücker, Philos. Mag. IV, 16 (1858), 119, 408 [translation from Poggendorff. Ann., 103 (1858) 88]; Poggendorff. Ann., 107 (1859) 77; 116 (1862) 27.

J. Tyndall, Discourses Roy. Inst. London, Friday, Jan. 20, 1860.

E. Goldstein, Berl. Monats. (1876) 234; Berl. Ber., 39 (1886) 1130; Sitzungberichte Königlich Preussichen Akad. Wissenshaft, Berl., 38 (1886) 691-99.

H. Hertz, Wied. Ann., 45 (1892) 28.

J. Perrin, C. R. Acad. Sci., 121 (1895) 1130.

W. C. Roentgen, Physico-Medical Soc. Würzberg (1895).

C. F. Varley, Proc. Roy. Soc., London 19 (1871) 236.

J. J. Thomson, Philos. Mag. V, 44 (1897) 293; Proc. Camb. Philos. Soc., 9 (1897) 243.

W. Wien, Verh. Phys. Gesell., (1898) 7; Wied. Ann., 65 (1898) 440; Ann. Phys. Leipzig, 8 (1902) 224.

W. Gaede, Phys. Z., 6 (1905) 758.

J. J. Thomson, "Rays of Positive Electricity and the Application to Chemical Analyses, Longmans Green & Co., London 1913.

F. W. Aston, "Isotopes", 2nd Edition, Edward Arnold & Co., London 1924; Philos. Mag. VI, 38 (1919) 707.

A. J. Dempster, Phys. Rev., 11 (1918) 316.

F. Soddy, Chem. Soc. Ann. Rep. (1910) 285.

A. J. Dempster, Science, 52 (1920) 559.

K. T. Bainbridge, J. Franklin Inst., 212 (1931) 317.

W. R. Smythe, J. Mattauch, Phys. Rev., 40 (1932) 429.

W. E. Stephens, Phys. Rev., 69 (1946) 691.

A. E. Cameron, D. F. Eggers, Jr., Rev. Sci. Instrum., 19 (1948) 605.

W. C. Wiley, I. H. McLaren, Rev. Sci. Instrum., 26 (1955) 324.

J. A. Hipple, H. Sommer, H. A. Thomas, Phys. Rev., 76 (1949) 1877.

W. H. Bennett, J. Appl. Phys., 21 (1950) 143.

P. L. Hartman, L. P. Smith, Rev. Sci. Instrum., 10 (1939) 223.

J. L. Costa, Ann. Phys., 4 (1925) 425.

W. Bartky, A. J. Dempster, Phys. Rev., 33 (1929) 1019.

J. S. Gorman, J. A. Hipple, J. E. Jones, Anal. Chem., 23 (1951) 438.

K. T. Bainbridge, E. B. Jordan, Phys. Rev., 50 (1936) 282.

J. Mattauch, R. F. K. Herzog, Z. Phys., 89 (1934) 786.

A. O. C. Nier, T. R. Roberts, Phys. Rev., 81 (1951) 507.

E. G. Johnson, A. O. C. Nier, Phys. Rev., 91 (1953) 10.

K. S. Quisenberry, T. T. Scolman, A. O. C. Nier, Phys. Rev., 102 (1956) 1071; 1076.

L. G. Smith, C. C. Damm, Rev. Sci. Instrum., 27 (1956) 638.

H. D. Smyth, Phys. Rev., 25 (1925) 452.

W. Bleakney, Phys. Rev., 40 (1932) 496; Ibid., 35 (1930) 139.

J. T. Tate, P. T. Smith, Phys. Rev., 40 (1934) 773.

J. T. Tate, W. W. Lozier, Phys. Rev., 39 (1932) 254.

A. O. C. Nier, Rev. Sci. Instrum., 11 (1940) 212.

A. O. C. Nier, Rev. Sci. Instrum., 18 (1947) 398.

W. Bleakney, J. Hipple, Phys. Rev., 53 (1938) 521.

N. B. Hannay, Rev. Sci. Instrum., 25 (1954) 644.

W. Paul, H. P. Reinhard, U. vonZahn, Z. Phys., 152 (1958) 143.

D. Beck, O. Osberghaus, Z. Phys. 160 (1960) 406.

D. Beck, A. Niehaus, J. Chem. Phys., 37 (1962) 2705.

A. Niehaus, Z. Naturforsch., A22 (1967) 690.

C. E. Melton, J. Sci. Instrum., 43 (1966) 927.

G. D. Flesch, H. J. Svec, Int. J. Mass Spectrom. Ion Phys., 1 (1968) 41.

F. Preston, M. Tsuchiya, H. J. Svec, Int. J. Mass Spectrom. Ion Phys., 3 (1967) 323.

J. Reeher, G. D. Flesch, H. J. Svec, Int. J. Mass Spectrom. Ion Phys., 19 (1976) 351.

REMINISCENCES OF THE EARLY DAYS OF MASS SPECTROMETRY IN THE PETROLEUM INDUSTRY

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Abstract

This retrospective lecture traces the development of commercial mass spectrometers for use in the petroleum industry, starting with the formation of Consolidated Engineering Corporation (CEC) in 1937 and installation of their first instruments in 1942 and 1943. During the middle and late forties, just keeping the machines running placed major demands on the time, energy, and ingenuity of mass spectrometrists. The 1950s saw progressive exploration of the chemical basis of mass spectra, culminating in the Eighth Annual Meeting of ASTM Committee E-14 on Mass Spectrometry in 1960. This meeting marked a turning point in the development of the field -- its transformation from what was originally almost a cult to a widely accepted and recognized branch of physical organic chemistry.

Introduction

Most of us learned early in our careers to look chiefly to the academic world for important new scientific developments, and this was indeed the source of the instruments that we know as mass spectrometers (1). Among those responsible for major early developments, we all recognize the names of Goldstein, Wien, Thomson, Aston, Dempster, and, somewhat later, Nier, Mattauch, and Herzog. But for many years, these machines were found only in the laboratories and shops of academic physicists and, even to those chemists who might have been aware of their existence, they remained little more than laboratory curiosities. Not until the '30s were the first mass spectra of organic molecules recorded. The subsequent developments and discoveries that laid the groundwork for mass spectrometry as a tool for study of the structures and gas-phase ionic reaction mechanisms of organic compounds took place chiefly in the laboratories of the petroleum industry. Some years were to pass before academic chemists generally recognized the significance of mass spectrometry to their discipline and started to move into the field in substantial numbers.

I think mass spectrometrists today are generally aware of the bare fact of where it started, but with the passage of time the events comprising that early history have started to fade into obscurity. Thus when Graham Cooks was putting this program of retrospective lectures together, he asked me to address the question, "How did it all happen?" To try to answer that question and to clarify some of the connecting

links to modern organic mass spectrometry, I have assembled a collection of reminiscences of the early days of mass spectrometry in the petroleum industry. I have relied chiefly on materials scattered through my files and on my memory, which may not always be as trustworthy as I would like. Moreover, I did not come on the scene till 1946, some four years after installation of the first commercial analytical mass spectrometer, so some of the events I will be sketching are assembled from my recollections of what I heard from others a good many years ago. I have made some modest attempts to check these recollections, and several colleagues have been most generous in sharing with me their files -- both hard copy and their memories. I am especially indebted to Harold Wiley, who played a major role as a key member of the CEC organization from something close to time zero until his retirement early in 1970 from his then position as a vice-president of Bell and Howell, heading their CEC/Analytical Instruments Division. Norm Foster of Texas Woman's University and Rod Page of ARCO have been of great help in giving me access to pertinent materials from their files. Frank Melpolder of ARCO recounted for me the events leading up to and following acquisition of the first CEC analytical mass spectrometer by Atlantic Refining Company in Philadelphia. Charles Johannsen, a long-time member of the CEC organization, is the source of the photograph reproduced as Figure 2 of this report. Any errors in this presentation are of course solely my responsibility. I will welcome all corrections and additions.

I hired in to Standard Oil Company (Indiana) and started to work in mass spectrometry in November 1946. Figure 1 shows the red brick building in the middle of the Whiting Refinery that then housed our Research Department and the plant

Figure 1. Research Department and Plant Hospital, Whiting Refinery, Standard Oil Company (Indiana). Photograph taken in 1960, just prior to demolition.

hospital as well. The mass-spectrometer laboratory was on the first floor, looking out on the adjacent railroad siding visible in the figure. It was the only laboratory in the building equipped with air conditioning, for the benefit of the mass spectrometer, of course, not for the comfort of those of us who worked there. Years later I came to realize that my timing was auspicious indeed. Among the people who entered the field during the two-year period from 1946 to 1948 were John Beynon, Jim Morrison, and Fred Lossing. One could hardly hope for more distinguished company.

Prior to 1945, my knowledge and even awareness of mass spectrometry was limited to a half-page discussion in an introductory physics textbook. I spent the better part of that year on an army assignment as technical liaison officer on a Manhattan District project for which Standard Oil Company (Indiana) was the contractor (2). The project mission was separation of the boron isotopes, and the laboratory was equipped with a big black box that I was advised was a mass spectrometer that performed the necessary isotopic analyses. I first met Charles Judson, whom many of you know well, on that job, where he was a member of the project team. I was aware that a bank of calutrons -- sometimes referred to as a mass spectrometer factory -- was in operation at Oak Ridge, Tennessee, for separation of uranium isotopes, and I remember hearing a description of a calutron at Harwell, where one could observe the light emission of intense beams of ions traversing the analyzer.

What was the state of mass spectrometry, especially in relation to organic chemistry, when I entered the field, late 1946?

Beginnings: The CEC Model No. 21-101 Analytical Mass Spectrometer

One instrument dominated the commercial market, the CEC Model 21-101; its background is crucial to this story (3,4). A decade earlier, in 1935, the United Geophysical Company was organized by Herbert Hoover, Jr., to engage in petroleum exploration under contract to oil producing companies. About that time, the Texas Company won a long court battle over the ownership of the basic patents covering seismic prospecting. Texaco then set up a licensing arrangement whereby all licensees were required to put their patents into a shared pool. In part as a stratagem to get around the need to cross-license, Hoover's firm, like others in the business, set up a separate company, Consolidated Engineering Corporation (CEC), to design electronic instruments needed by United in its geophysical operations. The new company was incorporated in 1937, with Hoover as president and Harold Washburn as vice-president in charge of research. At the time of CEC's incorporation and the separation of its activities from United, provision was made for the new company to have ownership of all geophysical equipment and to lease this equipment exclusively to United for its use. This constituted the company's principal business until 1941. In that year CEC made its first sales of a new line of vibration instruments; by the end of 1942

it had a production plant in full operation, and the volume of sales had developed sufficiently to enable it to sell all its geophysical equipment to United and to operate thereafter solely as an instrument design and manufacturing organization. A 1945 CEC prospectus assigned less than 15% of their total sales to United.

As part of a search for new methods of oil prospecting, the CEC team learned of an abortive attempt at California Institute of Technology to develop a mass spectrometer that could perhaps be useful for analyzing refinery streams. Following discussions with Robert A. Millikan there, CEC borrowed that instrument, which had been torn down by this time, and hired Dwight Taylor, who had worked with it at Cal Tech, to explore its potential for soil gas analysis, but with an eye also on the original Cal Tech objective of analyzing refinery streams. This instrument didn't work well but it looked possible, and a research and development program was launched to develop an instrument that would work well. Interest in soil gas analysis waned, but the program was successful in producing an instrument that would analyze refinery gases and low-boiling liquids (5). The photograph labeled Figure 2, probably taken in 1940, shows a pre-prototype or breadboard version of the new machine, based on Dempster geometry -- single focusing, 180° analyzer. The resulting commercial instrument, designated the CEC Model 21-101 analytical mass spectrometer, is shown in Figure 3. As it happened, Westinghouse went after the

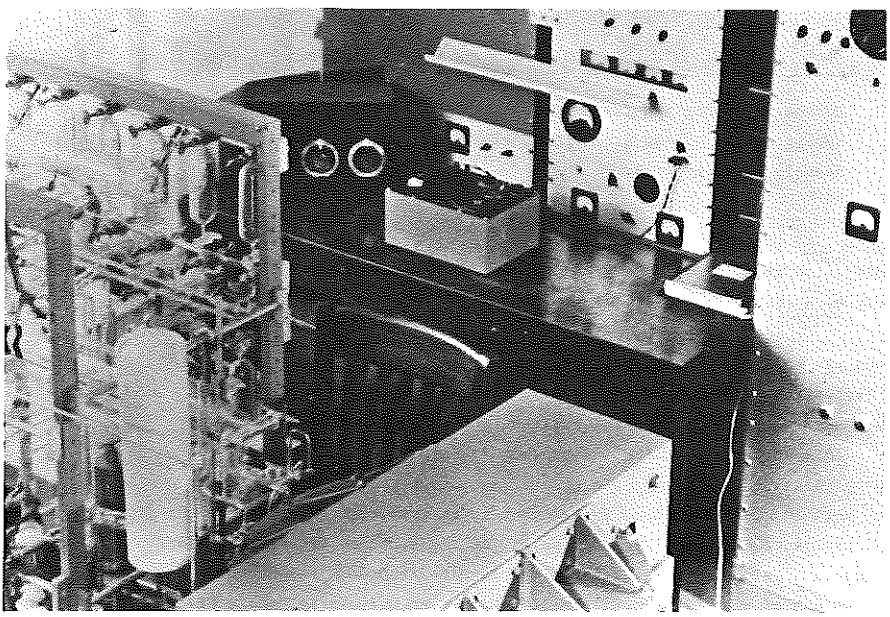

Figure 2. Pre-prototype of analytical mass spectrometer, Consolidated Engineering Corporation, probably 1940. Photo courtesy of C. J. Johannsen.

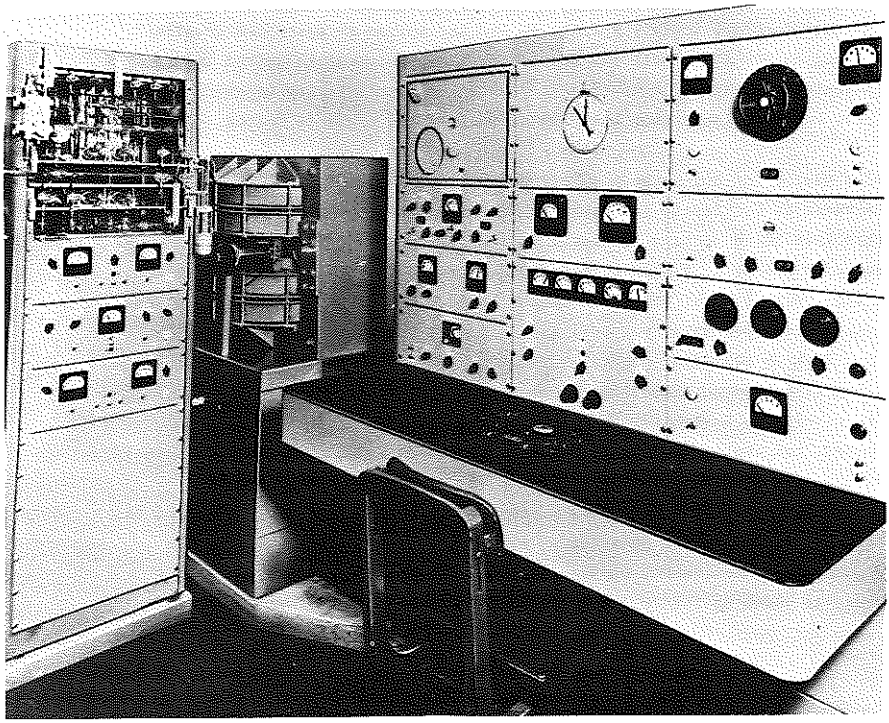

Figure 3. Consolidated Engineering Corporation Model 21-101 analytical mass spectrometer. Photo from CEC Model 21-101 Operating and Maintenance Manual, courtesy of R. P. Page.

same application about the same time; John Hipple and Dave Stevenson are the names associated with that effort in my memory.

Wiley, who was intimately involved in the development of the 21-101, thinks the crucial factor that gave CEC an edge over Westinghouse was probably their oscillographic recorder, which was inherited from their seismic prospecting business. This unit employed four galvanometers in parallel, with relative responses of 1:3:10:30, giving a far greater dynamic range and much more rapid recording than other devices then in existence. Without this recorder, the project might not have succeeded until perhaps years later. A second factor that Wiley recalls made a huge difference was CEC's rubber-base stopcock grease, which they picked right out of a handbook, while Westinghouse and university people kept struggling to find a grease that did not absorb the light hydrocarbon gases.

With the Texaco case as precedent, CEC incorporated a provision in their original purchase contracts requiring purchasers to give them information on instrument improvements, including royalty-free licenses on patents. This provision covered, for example, a patent granted to John Strange and Henry Grubb of Standard Oil Company (Indiana), entitled, "Apparatus for Pressure Measurement" (6). The device described there has for many years now been widely known and used under the name of capacitance micromanometer. Curiously, the patent was based on a prophetic disclosure; Strange and Grubb never built a working model. Many of the devices and instrument modifications thus originated by users were incorporated into the design of later models of the CEC instruments.

The first firm order for a 21-101 was from Atlantic Refining Company in Philadelphia; O. L. Roberts, Director of Physical Research, was the key person responsible for Atlantic's decision to gamble on the first of these new machines. Their instrument, installed in 1942, had been built by the research people who had designed it. J. C. Pemberton, of CEC's Engineering Department, did the initial hook-up; Harold Wiley, of the Research Department, then came out to start up the machine and conduct the necessary training. This first installation went remarkably smoothly. Atlantic assembled the top-notch team of Bill Young, Ralph Brown, and Frank Melpolder for the task of converting the promise into reality, and they contributed immensely over the ensuing years to the development of analytical mass spectrometry. All subsequent instruments were built by CEC's Manufacturing Department and, in Wiley's words, "... this almost put us out of business. Their first attempt, the Standard Oil Co. of Indiana instrument, was a disaster. The next four or five were only slightly better. I was the guy who had to make them all work and it was an almost impossible task ... I received a lot of help and cooperation from our customers, and this was absolutely vital to our success." The Standard Oil machine, installed in 1943, had not been system-tested before shipment and contained many mistakes. The whole glass inlet system had to be rebuilt on site; a glassblower was brought out from the University of Chicago to do this. Specifications for transformers had to be rewritten and they all had to be replaced. I recall hearing descriptions of this long-drawn-out installation period, during which Wiley was at times so discouraged that he talked about throwing in the towel, commenting, "There's got to be an easier way to make a living." Some of these sentiments must have gotten into his reports to the home office; a letter coming back to him in response to one of his reports during this period closes with the statement, "I hope that you have licked the stopcock problem and have not found it necessary to join the Army." It was during this period that E. B. Tucker, then Group Leader in charge of Analytical in our laboratory, came up with his classic characterization of a mass spectrometer as a "machine that almost doesn't quite work."

The original price of a 21-101 was $19,500 plus installation and training on a per diem basis. Later it was changed to $21,500 all-inclusive. To appreciate the

significance of this price, which seemed then far higher than it does today even apart from inflation, it needs to be viewed in the context of wartime demands on the oil industry. Wiley emphasizes as a major factor in CEC's success "the tremendous need for aviation gasoline and the new control requirements it created. Otherwise," he opines, "we would never have been able to sell such an expensive and complicated instrument for refinery control analysis."

Analytical Mass Spectrometry: Trials and Tribulations

Thus, instrument No. 2, the first to come off what CEC liked to refer to as their production line, was the machine that I worked with during my first year and a half as a mass spectrometrist. The other chemists in our group who were concerned with this instrument were Henry Grubb, Grace Marsh, and L. J. Schmauch. E. B. Tucker was our group leader and the man who went out on a limb in recommending to management the expenditure of a then unheard-of sum for a piece of laboratory equipment, although years later, at the time of his retirement, he thanked Grubb for teaching him to think in terms of kilobucks.

At the time I broke in, recording a spectrum required sitting at the console with one's eyes glued to the ionizing-current meter and a hand on the filament-current potentiometer, which had to be adjusted manually to try to keep the ionizing current as nearly constant as possible during the 15 minutes or so required for a run. Grubb had a year earlier built and reported to CEC a negative-feedback automatic-control circuit to perform this function (7), but the device was being revised and rebuilt at the time I arrived. The original filament current supply consisted of storage batteries -- two batteries in a wooden box, one in use and one on charge at all times. In 1950 Grubb and I reported that long-term stability of the filament current could be increased substantially by replacing the lead-acid batteries with a nickel-cadmium battery and associated circuitry to provide automatic control of the charging rate (8). To protect personnel, high voltage was automatically shut off when the battery box was opened. But other spectrometer parts also at high voltage were more exposed. Thus in our laboratory we had a club restricted to those persons who had been bitten by the high voltage and all of us who worked around the instrument qualified for membership sooner or later.

The temperature-control chassis, which, of course, was at high voltage, was located behind a door in the wooden base of the magnet. Our operating and maintenance manual contained a warning that a gremlin living in that chassis was especially prone to short the high voltage when we were showing our equipment to visitors. To try to avoid such incidents, the manual advised leaving a dime on top of the chassis for the gremlin whenever we expected visitors. Moreover, the manual went on, if the temperature controller starts going up in smoke, don't just make a bee-line for the nearest exit; come back and turn off the high voltage first.

Despite all the difficulties that we lived with, we felt we had good reason to marvel at how well the machine performed most of the time. This was especially so in view of some of the built-in limitations that were beyond the capabilities of our friends at CEC to control. In particular, much of the R&D effort that culminated in the 21-101 instrument took place during wartime, when materials and parts were hard to get and quality control was often nonexistent.

For example, we were well aware that the magnetic field in our instrument was lacking a good deal in homogeneity, and the explanation for this was that the iron used to make the magnet came over the fence of a navy shipyard in the dead of night. CEC people, like many others in those days, scrounged wherever they could and nobody asked too many questions.

Another example, though less spectacular, comes to mind. A persistent source of headaches for many years was gas sensitivity, indicated by severe spectral instability that in our laboratory seemed to be brought on particularly by oxygen-containing compounds. I recall an attack of this malady in 1949, on a day when I was off sick. We had moved into our new Research Laboratories a mile from the refinery a year earlier and at that time I shared responsibility for the operation of our second mass spectrometer, a CEC Model 21-102, with Ed Gustely, who had hired in recently and was still in the process of learning his way around the instrument. He recognized that something was wrong and phoned Grace Marsh, who had remained in Tech Service with the original instrument, to ask for help. To Ed's description of the symptoms, Grace responded promptly and decisively, "Oh, you've got gas sensitivity. Before you leave the lab tonight, start butene flowing through the instrument. In the morning, check the performance again. If the symptoms are gone, it was temporary gas sensitivity. If they're still there, it's permanent gas sensitivity." Her advice was excellent; in fact, it constituted the sum total of our understanding of gas sensitivity at that time. Not until some years later did Jack Sharkey and Gus Friedel of the Bureau of Mines and Charles Robinson of CEC pinpoint the origin of gas sensitivity in compositional and structure changes in the tungsten filament, involving a mix of tungsten carbides and oxides as well as carbon deposits (9). Wiley tells me that the original supply of high-purity tungsten used to make filaments exhibited no gas sensitivity; but when a shortage of tungsten developed, a new source of supply had to be found, and no supply was again found that did not give gas sensitivity.

We used this machine entirely for quantitative analysis of gaseous mixtures -- i.e., light hydrocarbons and fixed gases -- and selected fractions from low-temperature fractional distillations of hydrocarbon streams. My major discovery during my first year in the mass-spectrometry laboratory was that the analysis of C_5 cuts from such low-temperature distillation, which we had been doing routinely for some time, was impossible. The close similarity of the spectra of the isomeric pentenes allowed too little leverage to distinguish among them in mixtures. A slight variation in

the calculating procedure -- which might be introduced, for example, simply by giving the job to another clerk -- resulted in a grossly different analysis. A satisfactory solution to this problem -- focused, however, on the butenes rather than the pentenes -- employing a combination of mass-spectral and infrared data was reported in 1950 by Jack O'Neal, of Shell Oil (10).

Our survival through and emergence from those difficult early years must be attributed in large part to the camaraderie and close cooperation that developed among working mass spectrometrists and between users and manufacturers of the instruments -- certainly CEC and, I suspect, Westinghouse and General Electric as well during the few years that these two firms also built and marketed analytical mass spectrometers. For years essentially nobody entering the field had any prior training specifically in mass spectrometry. We came from many areas of chemistry, physics, and engineering, and we all were engaged in a joint bootstrap operation. In addition, Wiley points out, because of the wartime demands alluded to above, oil companies were cooperating in the use of the new analytical instruments. In order to survive, we -- companies and individuals alike -- learned to seek and extend help unhesitatingly, sharing experience and spare parts as circumstances dictated.

Over the decade from 1944 to 1954, CEC, functioning as a clearinghouse for helpful information, issued 108 MS Group Reports to users of their instruments. A breakdown by subject matter, shown in Table I, reveals a heavy emphasis on seemingly mundane but very pressing concerns; and a breakdown by source, shown in Table II, reflects the heavy concentration of mass-spectrometer users in laboratories of the oil companies and other organizations with closely allied interests.

TABLE I

CEC MS Group Reports - Breakdown by Subject Matter

Instrumental devices and techniques	35
Calculating methods	11
Computing equipment	5
Spectra and spectral correlations	6
Effects of temperature, initial energy, isotopic composition; bimolecular contributions; etc.	8
Analytical applications, quantitative	34
Analytical applications, qualitative	2
Isotopic labeling, appearance and ionization potentials	7
Total	108

TABLE II

CEC MS Group Reports - Breakdown by Source

Oil Companies	79
Chemical companies with substantial petrochemical interests	4
Companies engaged in design and construction of refining units	3
CEC	9
Government laboratories (7 from Bureau of Mines)	9
Universities	4
Total	108

Following two informal sessions with a few users in 1944, CEC initiated in 1945 a series of annual users' meetings, which were paralleled by similar GE-sponsored meetings in 1949-51. In 1952, the two groups scheduled their meetings as part of the Pittsburgh Conference, which met in Pittsburgh in those days, with separate users' clinics conducted by the two manufacturers. The groundwork was laid that year for a single mass-spectrometry organization, Committee E-14 of the American Society for Testing Materials (ASTM), with the objective defined as "promotion of knowledge and advancement of the art of mass spectrometry." Its principal activity was the organization of an Annual Conference on Mass Spectrometry, continuing under new auspices the meetings previously arranged by the manufacturers. A further change in auspices took place with the formation of an independent professional organization, the American Society for Mass Spectrometry, in 1968. So the several-hour meeting in Pasadena in 1944 of about ten mass-spectrometer users or prospective users who had come to Los Angeles to attend a conference sponsored by the wartime Rubber Reserve was the start of an unbroken series of annual meetings leading directly to the Conference that has brought us all here this week.

At the same time that these annual meetings were getting started, first steps were being taken to make available both reference calibrating compounds and reference spectra. The records of the Pure Compound Bank in my laboratory show the earliest entries, in 1943, consisting of Phillips Research Grade hydrocarbons. In January 1944 the National Bureau of Standards (NBS) first announced a group of 15 hydrocarbons of known high purity available for calibrating analytical instruments in the laboratories of the petroleum, rubber, chemical, and allied industries. In July of that same year, a cooperative undertaking was initiated between NBS and the American Petroleum Institute (API) Committee on Hydrocarbons for

Spectrometer Calibration, and the program subsequently prepared and made available a great many API-NBS Standard Samples of Hydrocarbons. Other API programs established at various academic institutions produced standard samples of oxygen-, sulfur-, and nitrogen-containing compounds. In addition, the distribution of reference spectra under joint API-NBS auspices started in 1947. The library of mass spectra that resulted has continued to issue additions since then, although the physical location of the project is no longer the NBS. Even today, this collection is probably the most trustworthy set of reference mass spectra being marketed.

Mechanistic Studies: Organic Ions in the Gas Phase

In preparing this presentation, I have viewed it as consisting of three interrelated parts, two of which I have now covered -- the beginnings, centering around CEC; and my first few years working in mass spectrometry. The third will focus on our studies at Whiting of the chemistry underlying mass spectra. I feel somewhat hesitant to talk so much about personal experiences. But, of course, my associates and I at Whiting were not operating in a vacuum. We were part of a network of people in many laboratories trying to keep our machines operating, to increase their reliability, and to expand their capabilities to satisfy the ever-growing demands placed on us. Thus, our counterparts in other laboratories, with their varying specific interests and priorities, were contributing in their own ways to building the art and science of mass spectrometry. It is in this sense that I offer these reminiscences as more or less illustrative of the way in which research programs in mass spectrometry developed, largely in the petroleum industry at first, but with interest and participation gradually expanding to the entire gamut of laboratories represented at this conference.

Our program of exploratory studies of the chemistry underlying mass spectra was started some 30 years ago. For a time in 1951-52, I received a steady stream of alkylbenzene samples from certain exploratory studies in organic chemistry in our Research Department. Many of the mass spectra we obtained from those samples seemed so clean that I felt almost certain the samples had to be essentially single compounds of high purity. However, the spectra did not match anything in our then very limited library of reference spectra, and finding a good match was the only way we had at that time to identify an unknown. Poring over those spectra, I had the feeling that the samples and the spectrometer together were doing their level best to give me the information I was seeking, but I was simply too dense to be able to translate those spectra into chemistry. Kinney and Cook's correlation study on the mass spectra of alkylbenzenes and alkylthiophenes (11) appeared about that time and helped greatly, but the data reported there extended only part-way through species with five alkyl carbons, and I found myself stranded there. The resulting frustration prompted me to start rounding up samples of all the alkylbenzenes of known structure I could locate and trying to correlate their mass spectra with molecular structures.

The timing was fortuitous. By that time, John Hipple and his associates at Westinghouse had clearly defined the origins of the diffuse signals that we know as metastable peaks (12). Alois Langer, also at Westinghouse, had collected all the then known examples of seemingly anomalous fragment ions in a paper entitled, "Rearrangement Peaks Observed in Some Mass Spectra" (13). Dave Stevenson, briefly at Westinghouse and afterward at Shell Development Company, had performed his early labeling experiments (14) and had published several papers on the measurement of ionization and appearance potentials and their interpretation in terms of ion structures, decomposition processes, and thermochemistry (15), building on the pioneering studies in the '30s by J. T. Tate and his associates at Minnesota (16) and Walker Bleakney and his associates at Princeton (17). Frank Field, then at the University of Texas, had published his first few studies utilizing critical-potential data (18). In 1952, he moved to Humble Oil and Refining Company, where Joe Franklin and Earl Lumpkin had initiated a program also in this area (19), and the Field and Franklin collaboration soon took off in high gear (20). Merrill Wallenstein's Ph. D. thesis at the University of Utah in 1951 and Henry Rosenstock's in 1952 assembled most of what was then known or suspected about the processes underlying mass spectra of organic compounds and constructed the quasi-equilibrium theory. Their findings, reported in two 1952 publications coauthored by Wallenstein, Rosenstock, and their professors, Austin Wahrhaftig and Henry Eyring (21), placed mass spectrometry firmly within the discipline of chemistry, although a gestation period of some years was required before chemists generally stopped viewing mass spectrometry as black magic.

My paper reporting the correlations I found for alkylbenzenes was published in 1955 (22), and the mechanistic questions they raised provided much of the driving force for a series of more probing studies over the next several years. A number of happy circumstances came together to help get the program off the ground.

First, Harold Hart, of Michigan State University, was a summer professor at our laboratories in Whiting in 1954. He was interested in using deuterium labeling as a mechanistic probe in his studies and inquired as to what help I could furnish in determining isotopic enrichment and perhaps also in locating tagged atoms in labeled molecules. My response was that I could make no promises but I'd be glad to try. This was the source of the first labeled alkylbenzenes that came my way.

Second, the correlations I had found convinced me of the validity of a general conclusion at which some other workers had already arrived, that the molecular events underlying mass spectra are networks of competing and consecutive chemical reactions. Moreover, I was struck by close parallels in several cases between the reactions that seemed to be occurring in my instrument and reactions known to occur in conventional chemical systems. Over a period of a few months, I made frequent visits to the office of a section leader in organic chemistry to point out these parallels, to suggest that such relationships might well prove of considerable

interest to organic chemists, and to tell him that I needed the help of a good organic chemist to pursue these leads. The upshot was the assignment of Paul Rylander, a gifted physical-organic chemist, to work with me on the project.

Third, from the very start, Henry Grubb, to whom I reported during much of this period, and E. B. Tucker, to whom Grubb reported, gave me all the encouragement and support that anyone could have wished, and they continued to do so through the ensuing years.

As our initial studies progressed, we decided early on that organic chemists were the audience we wanted most to reach, and we recognized that drastic measures would be needed to do so. With this audience in mind, we chose as a series title "Organic Ions in the Gas Phase"; we took a chance in referring to "electron impact" in the abstracts but did not use it in a title until paper number 3; neither the titles nor the abstracts of the first few papers used the term "mass spectra" or "mass spectrometry"; and we targeted the first three papers for publication in the Journal of the American Chemical Society rather than, say, the Journal of Chemical Physics or Physical Review, where much of the mass-spectral literature up to that time had appeared. The specific titles of these first three papers, published in 1956 and 1957, are: "I. The Cationated Cyclopropane Ring" (23); "II. The Tropylium Ion" (24); and "III. $C_6H_5^+$ Ions from Benzene Derivatives by Electron Impact" (25). We succeeded in reaching organic chemists and many others as well; in particular, these and subsequent papers attracted much interest from radiation chemists, which we had not anticipated. Moreover, we have been gratified at the staying power of the three initial topics. Each has figured in numerous papers by other authors since then and even now, more than a quarter-century later, new reports bearing on one or another of them continue to appear in the journals.

Once the project got moving and we began to publish, I started receiving requests from academic people for assistance with mass spectrometry in their research, chiefly in studies using stable isotopic tracers. The samples that came to me by this route triggered many of the specific studies in my laboratory over the years, and some of these initially informal arrangements developed into full-fledged collaboration.

The objective of all of this effort was and continues to be a systematic chemistry of gaseous organic ions. Because so very little was known at the time I started, my choice of specific problems to address or of specific compounds to work with was wide open. Under the circumstances, I was able to take the easy and economical route of formulating problems for investigation to take advantage of available compounds, whatever their source. This approach amounts to attacking a huge jigsaw puzzle by making many independent starts wherever one can spot a few pieces to fit

together and hoping that connecting links will turn up once enough small portions have been assembled. In fact, between work in our laboratory and elsewhere, this is precisely the way the field has developed.

I have mentioned that we observed many parallels between reactions in the mass spectrometer and those known to occur in more familiar organic-chemical systems. Early in the game, Grubb and I started to try to get this message across to organic chemists at Whiting. We argued that the organic chemist hoping to discover new chemistry might find it well worthwhile to invest some time and effort poring over mass spectra in a search for reactions that seem to take place in the mass spectrometer and that are not known to occur in the beaker or flask but would be of potential interest if they could be made to occur there. For a long time our message got nowhere. Organic chemists would reply that our proposal sounded fine, and where would we suggest they start? Unfortunately, neither of us was enough of an organic chemist to be able to respond adequately. Not until the early '60s did our campaign begin to bear fruit. Ellis Fields finally got our message. He started to come down frequently to my laboratory, where we paged through files of mass spectra and selected a few more or less at random, on which I proceeded to speculate about the underlying reactions. Whenever a reaction I suggested appeared potentially interesting and at least half-way feasible, Ellis jotted down a note to himself. He took these ideas back to his own laboratory and tried them out, usually simply passing the compound in question through a hot tube. The products collected at the far end of the tube came back to me for analysis. In a remarkable number of cases, we found strong evidence for precisely the reactions we were seeking. Our collaboration has given us added insights into the chemistry occurring both in the mass spectrometer and in more conventional molecular environments, which we have viewed as the two sides of a coin (26).

Among the newcomers to the ranks of mass spectrometrists through the decade starting in 1950 were several organic chemists who made extraordinary contributions not only to advancing our field but to interpreting it to other organic chemists. Fred McLafferty entered the scene soon after joining Dow Chemical in 1950; Klaus Biemann likewise after moving to M.I.T. in 1955; Carl Djerassi, at Stanford University, acquired his first mass spectrometer in 1960. By 1960, the period in which organic mass spectrometry was dominated by people in the petroleum industry was coming to an end. Practitioners of our art were by then widely dispersed among academic institutions, government laboratories, and a variety of industry laboratories; and in the years that have passed since then, both the number and variety of organizations in which mass spectrometrists labor has continued to grow.

In other respects as well, 1960 saw a kind of coming of age of our discipline. The accumulated results of the early studies of the chemistry underlying mass spectra seemed to attain a critical mass at about that time. I remember having the distinct impression that the 1960 Annual Conference on Mass Spectrometry, for the first time,

was marked by a widespread awareness of the large amount of structural information inherent in, and potentially extractable from, mass spectra of organic compounds. Thus the stage was set for the continuing explosion of new applications, new instrumental techniques, and new chemical insights that has characterized the field with scarcely a break right up to today.

Closing Thoughts

Looking back, I feel I have been fortunate indeed to be at the right place at the right time to be able to play some part in this extraordinary experience.

Let me mention two incidental items in closing. I have in my files a clipping from the Houston Chronicle sent me 20 years ago by Gus Carlson, of Shell Oil. The article reported the gift of a mass spectrometer by Shell to Rice University. The reporter, feeling an obligation to inform his readers of what this instrument is, explained that it is "used to determine the index of retraction." On the other hand, I believe it was Ben Freiser who pointed out at the Third Asilomar Conference on Mass Spectrometry last fall that EM-ES, the familiar name by which we all refer to our instruments and our discipline, is the Hebrew word for TRUTH.

Postscript: I regret that time/space limitations forced me to omit a number of important and fascinating aspects of this story, perhaps most notably the introduction of first analogue and then digital computers for mass-spectral calculations and the development of procedures for compound type analysis.

References

1. For brief historical reviews, see (a) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, NJ, 1965, Chapter 2; (b) M. C. Hamming and N. G. Foster, "Interpretation of Mass Spectra of Organic Compounds," Academic Press, New York, NY, 1972, Chapter 1; (c) S. P. Markey and G. W. A. Milne, American Society for Mass Spectrometry, 25th Annual Conference on Mass Spectrometry and Allied Topics, Washington, DC, 1977; (d) H. A. Laitinen and G. W. Ewing, Eds., "A History of Analytical Chemistry," Div. Anal. Chem., Am. Chem. Soc., Maple Press Co., York, PA, 1977, pp. 216-229; (e) J. H. Beynon and R. P. Morgan, Int. J. Mass Spectrom. Ion Phys. 27, 1 (1978).

2. A. L. Conn and J. E. Wolf, Ind. Eng. Chem. 80, 1231 (1958).

3. (a) F. A. White, "American Industrial Research Laboratories," Public Affairs Press, Washington, DC, 1961, pp. 144-152; (b) F. W. Karasek, Research/Development 22, No. 5, 51 (1971); (c) F. W. Karasek, Research/Development 23, No. 6, 26 (1972).

4. H. F. Wiley, private communications, 1983-84.

5. (a) H. Hoover and H. W. Washburn, Amer. Inst. Mining Metallurgical Engrs. Tech. Publ. No. 1205 (1940); (b) H. Hoover and H. W. Washburn, Calif. Oil World and Petroleum Industry, Second Issue, 21 (Nov. 1941); (c) H. W. Washburn, H. F. Wiley, and S. M. Rock, Ind. Eng. Chem., Anal. Ed. 15, 541 (1943); (d) Anon., Natl. Petroleum News, Tech. Sec. 35, R-258 (1943); (e) O. L. Roberts, Petroleum Refiner 22, 107 (1943); (f) J. G. Schaafsma, Oil Gas. J. 42, 57 (Apr. 6, 1944); (g) J. G. Schaafsma, Natl. Petroleum News, Tech. Sec. 36, R-196 (1944); (h) H. W. Washburn, H. F. Wiley, S. M. Rock, and C. E. Berry, Ind. Eng. Chem., Anal. Ed. 17, 74 (1945); (i) A. K. Brewer and V. H. Dibeler, J. Research Natl. Bureau Standards 35, 125 (1945); (j) W. S. Young, Natl. Petroleum News, Tech. Sec. 38, R-212 (1946).

6. J. H. Strange and H. M. Grubb, U.S. Patent No. 2,567,253, applied for May 9, 1945, granted September 11, 1951.

7. H. M. Grubb, CEC Mass Spectrometer Group Report No. 25 (1945).

8. H. M. Grubb and S. Meyerson, CEC Mass Spectrometer Group Report No. 76 (1950).

9. (a) C. F. Robinson and A. G. Sharkey, Rev. Sci. Instrum. 29, 250 (1958); (b) A. G. Sharkey, C. F. Robinson, and R. A. Friedel, Adv. Mass Spectrom. 1, 193 (1959).

10. M. J. O'Neal, Anal. Chem. 22, 991 (1950).

11. I. W. Kinney and G. L. Cook, Anal. Chem. 24, 1991 (1952).

12. (a) J. A. Hipple and E. U. Condon, Phys. Rev. 68, 54 (1945); (b) J. A. Hipple, R. E. Fox, and E. U. Condon, Phys. Rev. 69, 347 (1946); (c) J. A. Hipple, Phys. Rev. 71, 594 (1947).

13. A. Langer, J. Phys. Colloid Chem. 54, 618 (1950).

14. (a) D. P. Stevenson, Phys. Rev. 73, 537 (1948); (b) D. P. Stevenson and C. D. Wagner, J. Am. Chem. Soc. 72, 5612 (1950); (c) D. P. Stevenson, J. Chem. Phys. 19, 11, 17 (1951).

15. (a) D. P. Stevenson, J. Chem. Phys. 10, 291 (1942); (b) D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc. 64, 2766, 2769 (1942); (c) J. A. Hipple and D. P. Stevenson, Phys. Rev. 63, 121 (1943); (d) D. P. Stevenson, J. Am. Chem. Soc. 65, 209 (1943); (e) D. P. Stevenson, J. Chem. Phys. 18, 1347 (1950)); (f) D. P. Stevenson, Discussions Faraday Soc., No. 10, 35 (1951).

16. (a) J. T. Tate, P. T. Smith, and A. L. Vaughan, Phys. Rev. 48, 525 (1935); (b) P. Kusch, A. Hustrulid, and J. T. Tate, Phys. Rev. 52, 843 (1937).

17. J. Delfosse and W. Bleakney, Phys. Rev. 56, 256 (1939).

18. (a) F. H. Field, J. Chem. Phys. 19, 793 (1951); (b) F. H. Field, J. Chem. Phys. 20, 1734 (1952).

19. (a) J. L. Franklin and H. E. Lumpkin, J. Chem. Phys. 19, 1073 (1951); (b) J. L. Franklin and H. E. Lumpkin, J. Am. Chem. Soc. 74, 1023 (1952); (c) J. L. Franklin and H. E. Lumpkin, J. Chem. Phys. 20, 745 (1952).

20. (a) J. L. Franklin and F. H. Field, J. Chem. Phys. 21, 550 (1953); (b) J. L. Franklin and F. H. Field, J. Chem. Phys. 21, 2082 (1953); (c) J. L. Franklin and F. H. Field, J. Am. Chem. Soc. 76, 1994 (1954); (d) F. H. Field and J. L. Franklin, J. Chem. Phys. 22, 1895 (1954).

21. (a) M. Wallenstein, A. L. Wahrhaftig, H. Rosenstock, and H. Eyring, in "Symposium on Radiobiology: The Basic Aspects of Radiation Effects on Living Systems, Oberlin College, 1950," ed. by J. J. Nickson, Wiley, New York, NY, 1952, p. 70; (b) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, Proc. Natl. Acad. Sci. U.S. 38, 667 (1952).

22. S. Meyerson, Appl. Spectrosc. 9, 120 (1955).

23. P. N. Rylander and S. Meyerson, J. Am. Chem. Soc. 78, 5799 (1956).

24. P. N. Rylander, S. Meyerson, and H. M. Grubb, J. Am. Chem. Soc. 79, 842 (1957).

25. S. Meyerson and P. N. Rylander, J. Am. Chem. Soc. 79, 1058 (1957).

26. For reviews, see (a) E. K. Fields and S. Meyerson, Adv. Phys. Org. Chem. 6, 1 (1968); (b) E. K. Fields and S. Meyerson, Acc. Chem. Research 2, 273 (1969); (c) E. K. Fields and S. Meyerson, Chem. Tech., 104, 241 (1974); (d) E. K. Fields and S. Meyerson, Adv. Free-Radical Chem. 5, 101 (1975).

THE INTRODUCTION OF COMPUTERS TO MASS SPECTROMETRY FOR DATA ACQUISITION AND PROCESSING

A Retrospective

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A "retrospective" differs from a comprehensive review as it tells a "story" that recalls the sequence of events as they really happened and it does so from the vantage point of those involved in the developments, rather than sterile hindsight. For this reason, the following is a personal account of the earlier development of the use of computers in mass spectrometry. The astute reader will notice that this field, because of a number of unique quirks in history, brought advanced computer technology to the analytical organic chemistry laboratory earlier than would otherwise have been the case.

Within the limits of space it is not possible to account for each and every contribution to date but it is hoped that this paper will serve the intended purpose, the tracing of the currents that shaped the symbiosis of modern mass spectrometry and computers.

Today (1984) it is self understood that a mass spectrometer to be used for organic, environmental, biochemical or clinical samples comes with a data system based on a small but powerful computer for data acquisition and processing. This data system is most frequently used to acquire the raw data from a mass spectrometer interfaced to a gas chromatograph and converts them to a calibrated mass spectrum in numerical form, which is then available for various evaluation purposes, often with the aim to "automatically" identify some or all of the components eluting from the gas chromatograph. In many cases, quantitation of the compounds is an additional task.

While it is true that the operation of a modern GCMS system would be impossible without a built-in computer simply because of the fast MS scan rates demanded by a capillary gas chromatograph and the vast number of spectra produced during a single experiment, the first

use of computers in mass spectrometry predates the development of practical GCMS systems. It was the computational demands of high resolution mass spectrometry that prompted us to turn in that direction almost 25 years ago.

Many practitioners of mass spectrometry today may not remember the state of computer operations in the early 1960's. Computers available to chemists (those who were determined to overcome certain barriers) were very large machines used to solve complex mathematical problems rather than laboratory equipment for data acquisition. The "IBM card" was the most widely used mode of input and reams of paper the common output. As far as peripherals were concerned, digitization rates were slow (a few kHz at best) and video terminals rare or non-existent.

The mass spectrometry scene was dominated by the CEC 21-103C chiefly in the USA, the MS-2 of Metropolitan Vickers (then AEI and now Kratos) in the UK and the CH-4 of Atlas Werke (later Varian-MAT and now Finnigan-MAT) in central Europe and, for some reason, Australia. Unit-resolution mass spectra were recorded with oscillographs or auto-ranging pen-and-ink recorders in 5-20 min. per scan and electro-mechanical mass markers aided the chemist in the "counting" of spectra.

Around 1960, AEI brought out the first commercial high resolution mass spectrometer, the MS-9 (patterned after a prototype, the MS-8 built for J.H. Beynon, then at ICI, who had a strong hand in its design). This instrument was of the Nier-Johnson geometry and designed to generate unit resolution mass spectra, allow the selective recording of resolved multiplets at the same nominal mass and the determination of the exact mass of selected peaks by the "peak matching" method. These were the logical steps one would take in the identification of an unknown organic compound, a field which mass spectrometry was just entering at that time.

The MS-9 was soon followed by CEC's 21-110, a Mattauch-Herzog type, double focussing mass spectrometer designed to serve a dual purpose: equipped with a spark-source and a photoplate in the focal plane it could be used for quantitative inorganic analysis; with a heated reservoir inlet system, an electron impact ion source and an electron multiplier at the far end of the focal plane, it could record low and high resolution mass spectra of organic compounds, like the MS-9, except that the concept of "peak matching" had not yet

reached California.

We acquired one of the first CEC 21-110 mass spectrometers for our work on the determination of the structure of new natural products, at that time chiefly indole alkaloids, amino acids and related compounds. High resolution mass spectrometry seemed to be indispensable for that purpose since it allowed the determination of the elemental composition of the molecule without the hitherto used method of combustion of the often scarce material. In addition, and almost more importantly, the elemental composition of important fragment ions would clearly aid in arriving at the correct structure of the compound. Two factors led us to use the photoplate for recording of the high resolution mass spectra: the instrument had no peak matching capability and we did not know which fragment ions were multiplets and which ones would be important. Thus we had to record the entire spectrum at high resolution and in a permanent form. Today this can be done using a fast A/D converter and a minicomputer with large memory and disk storage. None of these existed at that time. The photoplate was an ideal data storage device but it only postponed the moment of reckoning because eventually line positions have to be measured to better than one micrometer, converted to mass with at least three decimal places and then all possible elemental compositions calculated for each ion.

The task was further complicated by the fact that one did not know which ion will be of importance in the interpretation and, in fact, which lines are due to the compound of interest and which ones are from the calibration compound (perfluorokerosene). Thus there was no choice but to measure all lines and sort them out later. But what a task! Even a graduate student (at that time Dominic Desiderio) could not be expected to lose his eyesight from centering line after line under the crosshair of the microscope of the Gaertner Comparator, wear out his fingers writing down endless rows of seven digit numbers and then making all the computations on an electromechanical calculation machine (no pocket calculators either in 1961!).

The answer for the calculation chore clearly was MIT's at that time rather unique, powerful and accessible computation center which had an IBM 7094. But that system accepted data only on IBM cards and it did not take us long to decide to build what one could call an "off line" interface for a mass spectrometer to the computer which consisted of photoplate,

motor-driven densitometer, position and density recorder, automatic card punch and a pair of legs that took the resulting stack of cards down the hall to the computation center. I should also admit that a human operator was involved who controlled the speed of the plate carriage, running the screw fast between lines and slowing it down when a line or group of lines approached the center of the display screen of the Gaertner Comparator and speeding it up again when the line(s) had passed. A light sensing device (the phototube of a commercial darkroom light meter) was held (by copious use of electrical tape) to the display screen. The output was fed to a strip chart recorder, not to obtain a density recording on chart paper but to have the pen actuate a microswitch when the optical density started to increase due to a line moving into the light path; the switch activated the card punch which, in turn, recorded the output of an encoder mounted on the axis of the strip chart recorder and of another encoder mounted on the screw of the comparator, thus punching position and optical density as fast as it could. The process thus involved a very sensitive feedback loop from the eyes of the operator watching the lines moving across the screen via the brain to the hand which controlled the speed: fast during the wide intervals from mass to mass but slow enough while lines pass by to punch out a number of density points sufficient to record the accurate line profile. One of the states of this system is shown in Figure 1.

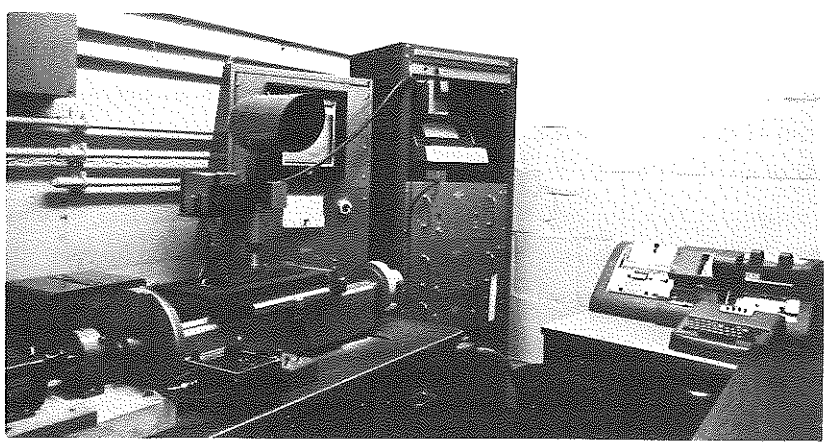

Figure 1. Gaertner comparator with variable speed motor (lower left), density chart recorder (behind screen hood) light measuring voltmeter (in chassis) and card punch (extreme right).

Using this approach it was possible for the first time to record complete high resolution spectra of organic compounds and produce elemental composition data for all ions formed. When applied to a variety of natural products, many of them of unknown structure, two aspects became immediately apparent: 1) the great utility of such a set of data for the determination of the structure of organic compounds and 2) the large volume of data per compound which made it difficult to treat them manually.

For these reasons the concept of the "element map" was developed (1). In contrast to the incorrect usage of this term which is today often applied to a simple listing of elemental compositions by increasing mass, it was a display ordered by distribution of heteroatoms (Figure 2). This arrangement of the data reveals much about the compound type, particularly if its structure is completely unknown. One of the earliest examples was the recognition that the "kokoi venom" isolated from a Columbian frog is a nitrogen containing steroid (2).

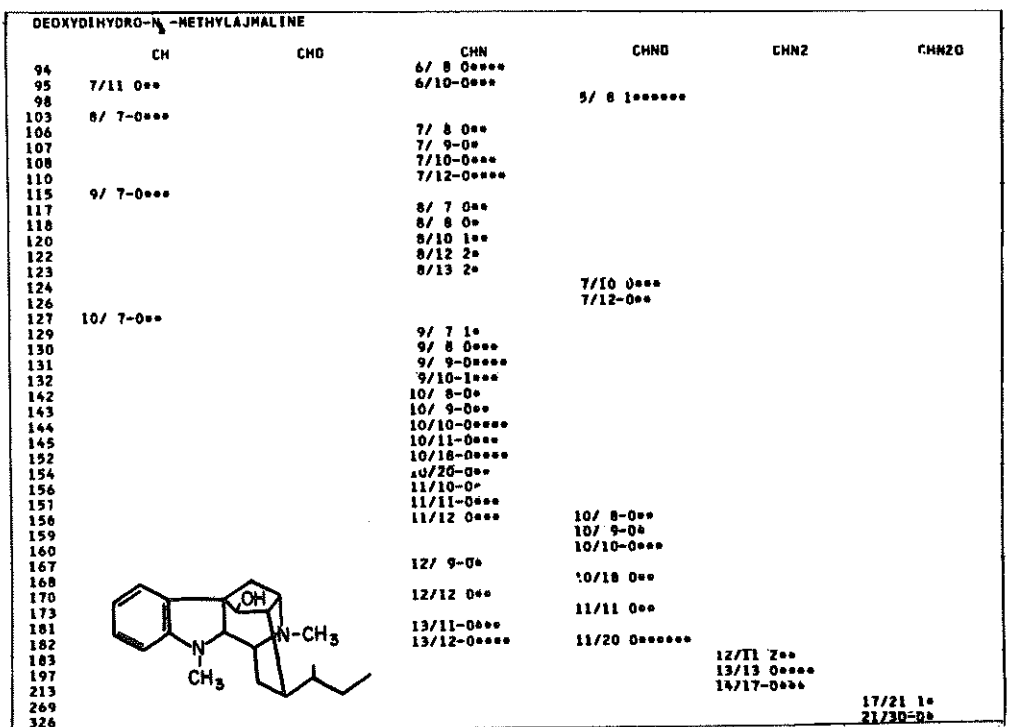

Figure 2. Element map of a dihydroindole alkaloid showing, for example, that there is one nitrogen in an aliphatic system (CHN column, aliphatic C/H ratio) and one in an aromatic system (CHN with aromatic C/H ratio) and that the one oxygen is easily lost with 8 carbon atoms to give $C_{13}H_{13}N_2$ (from ref. 1).

While the photoplate reading system described above can hardly be compared to a present day computer based data system and the processing of the data involved chiefly off-line "number crunching" on a large scale, it triggered the beginning of the use of fast, on-line data acquisition systems as we know them today. A series of four consecutive papers from our laboratory at the twelfth Annual Conference on Mass Spectrometry held in June, 1964 in Montreal described the photoplate reading system, the sample introduction via a vacuum lock, the method for fast calculation of elemental compositions, the recording of high resolution mass spectra of compounds eluting from a gas chromatograph and the interpretation of complete high resolution spectra of organic molecules (3-6). These advances all had been made possible by the use of a Mattauch-Herzog type mass spectrometer which allowed the recording of a complete high resolution spectrum in seconds or minutes on a photographic plate which then could be measured at leisure. Those present at that Conference will remember the shock felt by users or manufacturers of Nier-Johnson type high resolution mass spectrometers. Since these have a focal point rather than a focal plane one would have to record the signal electronically in real time and in computer readable form. Considering the state of the art in digital recording it was clear that this could not be done at high resolution and at a speed compatible with the time-width of a gas chromatographic peak. Thus, the search was on for improved digital recording systems and their interfacing to mass spectrometers. Fortunately, more powerful forces than a bunch of mass spectrometrists pushed for the vast improvements in rate and range of A/D converters, increased cycle speed, size of memory, secondary storage capacity, display terminals, etc. These improvements eventually overtook the requirements of a fast scanning mass spectrometer, but in 1964 they were far behind.

In order to avoid a sudden obsolescence of the MS-9, AEI attempted to devise a method which involved the use of an analog magnetic tape for the fast recording of the raw data which was then digitized off-line, and the digital data fed into a computer via digital magnetic tape. The fact that Prof. Lipsky at Yale had ordered an MS-9 under the condition that such a recording system would be developed provided an additional incentive. Furthermore, his input and the experience of Dr. Walter McMurray, who had joined him from our laboratory, was expected to help in the realization of the project. A paper describing the results of this effort appeared in August, 1966 (7,8). It is of interest to note that a number of papers on the subject of analog or digital recording of fast scanned high resolution mass spectra were presented already at the 1965 ASMS Conference (St. Louis) but

most of them dealt with calculations concerning ways to eliminate peak distortion at fast scan rates or the semi-manual evaluation of data recorded on analog tape followed by slow replay into an oscillograph recorder or A/D converter (9).

The limitation in the speed and accuracy of digitizing devices coupled with the need to transfer the data at some point to a large computer, located usually some distance from the mass spectrometer, hampered the acquisition of high resolution mass spectral data from scanning instruments. Fortunately, the computer technology began to catch up, but at the same time a new application of mass spectrometry had evolved: the on-line recording of mass spectra of compounds emerging from a gas chromatograph (GCMS). Although we had solved this problem, even in the high resolution MS mode, as early as 1964 through the use of photographic plates (10), it soon became clear that the vast majority of the application of GCMS would involve low resolution mass spectrometers. The faster scan rates desired even for packed GC columns (practical capillary GC had still to be invented!) required data acquisition rates that came close to those envisioned for high resolution MS. Because of this quest for rapid digital data acquisition, the stage was set in 1966 for the design of a data system useful for the continuous recording of GCMS data.

For reasons outlined earlier (the remoteness of the computer), the first approach involved digitization of the signal to 12 bits at 3 kHz and writing the digital data on a magnetic tape which was then read in and processed by an IBM 7094 computer in MIT's computation center (11). This system worked well, but the transfer of the data was cumbersome. Fortunately, just at that time computer technology made another step forward with the debut of the first commercial computer which incorporated both a 14-bit A/D converter and up to three removable disc cartridges each having a capacity of 1 Mbyte. Thus, the stage was set to design the type of mass spectrometer data system which is common today: a laboratory computer which directly accepts the analog signal generated by the mass spectrometer and can process and store in real time the large amount of data generated by a mass spectrometer that continuously scans the effluent of a gas chromatograph. At the 4th International Mass Spectrometry Conference held in Berlin in September 1967, we reported (12,13) on the design, operation and application of such a system for GCMS based on an IBM 1800 computer (Figure 3) which had been installed in our laboratory in late 1966, originally for the purpose of acquiring data from the photoplate reader (14,15). It demonstrated the great utility of continuously recorded GCMS data which then led to a number of processing and interpretation algorithms which will be discussed shortly.

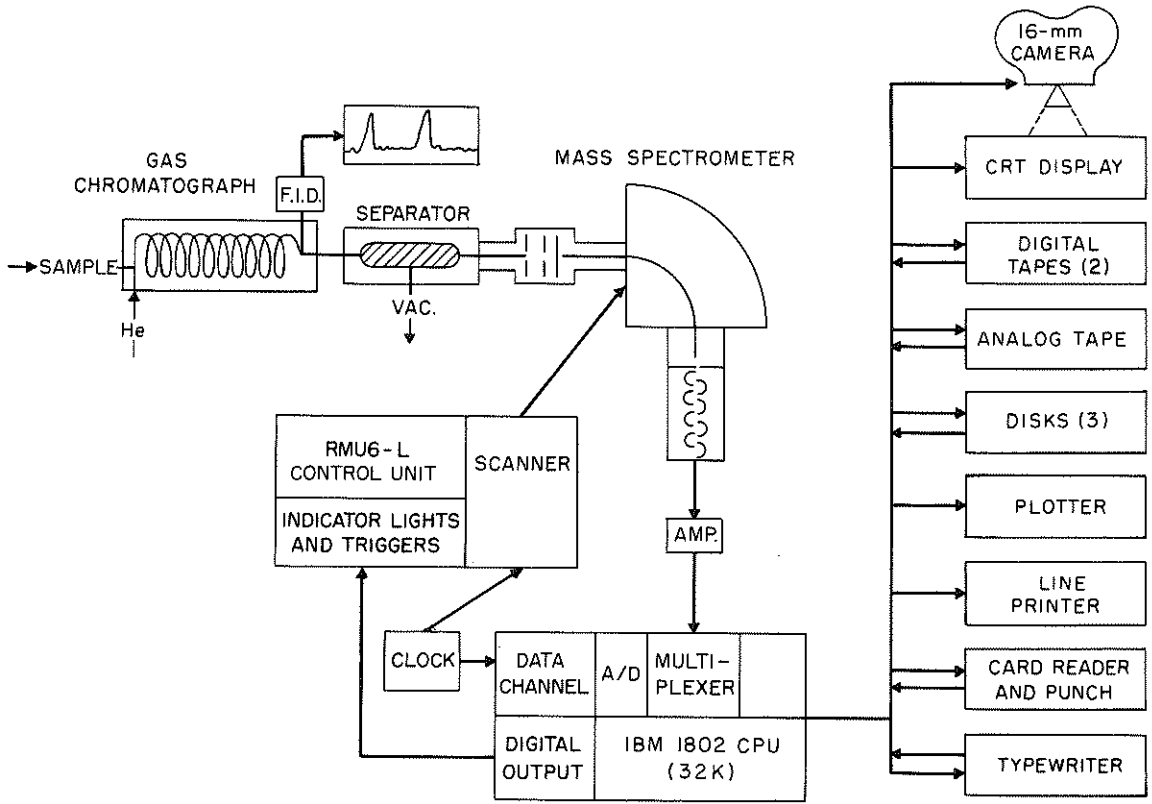

Figure 3. Block diagram of a gas chromatograph-mass spectrometer-computer system with ancillary input-output devices (from ref. 37b).

In the meantime the development of the real-time acquisition of high resolution data, either from photoplates or scanning, doublefocussing mass spectrometers had been continued and at the same Berlin Conference, A. Burlingame (16,17) reported what was probably the first practical solution to the latter problem. High resolution mass spectral data were digitized at 25 kHz to 15 bits and read into a SDS Sigma 7 computer which thresholded the data and recorded peak profiles on magnetic tape. This was then read into a CDC 6600 computer which processed the peak profiles to time, mass and finally elemental composition. A similar approach was reported by Merritt et.al. (18) but not further developed.

The availability of complete high resolution data led to a period when attempts were made to develop interpretation algorithms utilizing complete elemental composition data (19). These attempts were based on the assumption that this information would be more suitable to the interpretation of a mass spectrum of an organic compound than an integer mass. The algorithms ranged from the identification of the molecular ion (even if absent) (20), to the identification of specific compounds (21) or general compound types (22) and finally even to sequencing of peptide derivatives (23,24). However, none of them found lasting applications, in part because the basic assumption was unrealistic and in part because the vast majority of mass spectra are recorded today at low resolution and are of known compounds which have to be correctly identified. Algorithms for that purpose became available in the late 1960's and have practically taken over these tasks.

This brings us back to the point where, in 1966, the continuous recording of low resolution mass spectra from a GCMS system had been accomplished. The large number of spectra produced during a single gas chromatogram required some time saving device to at least recognize those compounds of which authentic mass spectra were available. This need led to algorithms which are generally known as "library searching" because they compare the unknown spectrum with a set ("library") of mass spectra stored in or accessible to the computer. Before the automatic recording of complete spectra was possible only a small set of peaks (usually the n largest where n = 3-10) were compared (25-29).

With automatic recording it was, in principle, possible to compare the entire spectrum but this was neither necessary nor even possible because the entire library could not be stored without condensation of the spectra to a smaller set of the most significant, but not

necessarily the largest, peaks. Selection of the two largest peaks in every 14-mass unit window were selected as the mass spectrometrically most logical choice and this became the most widely used approach (30). The earliest versions listed the n best fits (usually n = 10) by decreasing similarity index which is 1.000 for an absolutely identical spectrum and 0.000 for an entirely different one (Figure 4).

MVD-24-2-0, METHYLATED	SCAN NO. 179
RESULTS	SIMILARITY INDEX
*METHYL OCTANE-1,8-DIOATE	0.721
METHYL 4-METHYLHEPTANE-1,7-DIOATE	0.390
METHYL 10-METHYL-OCTADECANOATE	0.196
METHYL 14-METHYL-HEPTADECANOATE	0.184
METHYL HEXADECANOATE	0.180
METHYL NONANOATE	0.173
METHYL HEPTADECANOATE	0.168
METHYL PENTADECANOATE	0.168
METHYL TRIDECANOATE	0.165
METHYL 16-METHYL-HEPTADECANOATE	0.161

Figure 4. Result of the computer-comparison of the spectrum of a fraction in a gas chromatogram with a large collection of authentic spectra (from ref. 37b).

It may be noted that the collection of mass spectra in existence in the mid 1960's were in tabular, printed form: the collection of the American Petroleum Institute; the "uncertified" spectra of ASTM Committee E-14 (the precursor of ASMS); various small collections from individual laboratories; and of course, the literature. These had to be punched onto IBM cards and copied onto magnetic tapes. Recognizing this need, a number of groups independently embarked on this laborious task. Fortunately, this duplication was recognized early enough and the Mass Spectrometry Data Center in Aldermasten, England, the Jet Propulsion Laboratory in Pasadena, CA, and we at MIT joined forces to compile the first 8,000 spectra which eventually evolved into the NIH/EPA collection. In parallel, the laboratories of F.W. McLafferty, at that time at Purdue University, Stenhagen and Abrahamsson in Goteborg, Sweden, undertook the same task which produced a collection (using essentially the same sources) which became known as the "Registry of Mass Spectral Data", distributed commercially by Wiley-Interscience, New York, in printed form or on magnetic tape.

While most of these search algorithms check how well the condensed spectrum of the unknown matches each similarly condensed spectrum in the library ("forward search") others check whether all the peaks of the condensed library spectrum are present in the uncondensed unknown spectrum. Such "reverse searches" (31) are most useful if one only wants to know whether a certain ("target") compound is present or not. This approach which is most suitable for mixture spectra forms the basis of the PBM (probability based matching) system which McLafferty (32) originally designed for a fully automatic mass spectrometric identification system (briefly produced by Universal Monitor Corp., Pasadena) which did not involve prior separation by gas chromatography.

Many of these algorithms are nowadays part of the "menue" offered by commercial data systems, sometimes in an improved form but not infrequently also misnamed, misunderstood or misapplied.

A third approach was taken by Heller at NIH who designed an interactive search system (33,34). It worked well but lent itself mostly to the interpretation of a single spectrum. Its chief advantage was the fact that the user could choose any sequence of peaks to interrogate the library and these peaks could be taken just as easily from an oscillograph record as from a computer acquired mass spectrum.

A second consequence of the continuous recording of mass spectra of the effluent from a gas chromatograph was that it provided a three-dimensional data set which contained not only mass number and intensity but also time (see Figure 5). Thus it became possible to display the appearance and disappearance of the signal for any ion in the hundreds of mass spectra recorded consecutively. Since they were recorded continuously and at constant scan rates the sequence numbers of the scans were analogous to retention times. Thus the concept of "mass chromatograms" evolved (35). The same type of display had been generated previously by recording a single mass (or a few masses by alternating the magnetic or electric fields) on oscillograph paper. Such plots were termed "mass fragmentograms" (36). The main difference is selection of the mass to be displayed, before or after the experiment. Unfortunately, this distinction has been lost and the two terms are often used interchangeably.

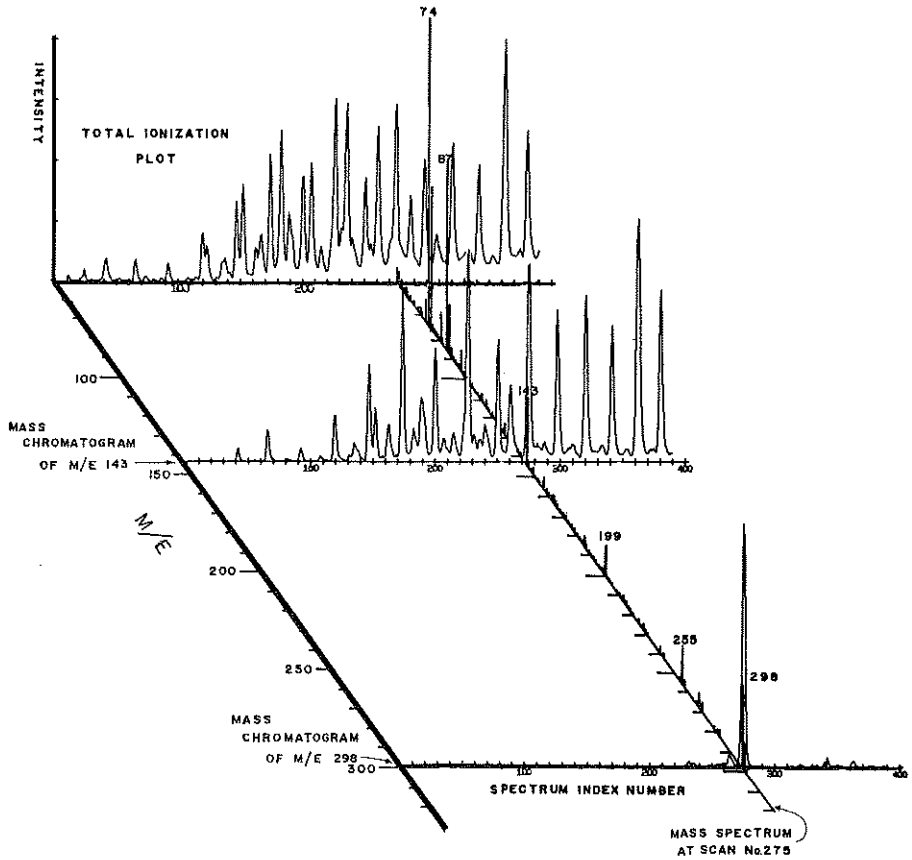

Figure 5. Composite drawing showing the relationship of the data resulting from a continuously scanning GC-MS system: the computer-generated gas chromatogram ("total ionization plot"), two of 422 mass chromatograms (the mass spectrometer was scanned from m/e 28 to m/e 450), and one of the 400 mass spectra (from ref. 37b).

Mass chromatograms turned out to be extremely useful for the interpretation of GCMS data, such as the search for a particular compound or group of compounds giving rise to a characteristic ion of a certain mass. One of the resulting frustrations was the selection of the most informative mass chromatograms when dealing with a mixture of unknown compounds. Working on such problems it was soon realized that the display of a few mass chromatograms chosen by a hit-or-miss approach (which is still today the mainstay of commercial data

systems) is very unsatisfactory. To identify the components of complex mixtures one must have all mass spectra and all mass chromatograms at one's finger tips and this was achieved by automatically displaying one after the other on a CRT screen and recording it on 16 mm microfilm right after the GCMS experiment was completed (37). The investigator could then inspect all these data at leisure using a microfilm reader, completely independent of the computer (time sharing and multi-tasking was available on small computers in the late 1960's but not very practical because of the large overhead). This microfilming system is still in routine operation in our laboratory at this writing and functions well. Although extremely useful it has not been duplicated, to our knowledge, anywhere else (with the exception of a brief period at JPL during the Viking Mission) chiefly for two reasons: it was never described in detail in the literature because we felt that it would soon be outdated by a video taping system which would eliminate the second reason, namely the need for wet-developing of conventional film (although even this is accomplished automatically). However, even to date the resolution of video cameras is quite inferior to the optical camera (Bolex) and the Kodak RAR film and this is an area where technology still has not caught up in the last two decades.

The availability of all mass chromatograms also permitted the resolution of a complex gas chromatographic peak into its individual components and to generate the "pure" spectrum of each component ("reconstructed" mass spectra) by plotting only those peaks that maximized in the same scan (38). The example shown in Figure 6 illustrates that the mass spectra of the gas chromatographically unresolved components maximize separately. A similar approach was then used by the Stanford group (39) and by Henneberg (40); it was also incorporated into Sweeley's MSSMET system which attempts to automatically identify and quantitate the components of complex mixtures (such as urinary acids) for the purpose of clinical diagnosis (41).

Considerable effort has been devoted to the more or less automatic identification of compounds from their mass spectra. For this purpose the search algorithms have been refined to the point that a spectrum can be reliably identified if three conditions prevail: 1) an authentic spectrum of the compound is present in the library and is of good quality; 2) the compound has a unique mass spectrum; and 3) the spectrum of the unknown is of good quality. Of these the first is difficult or impossible to assess at the outset and always has to be

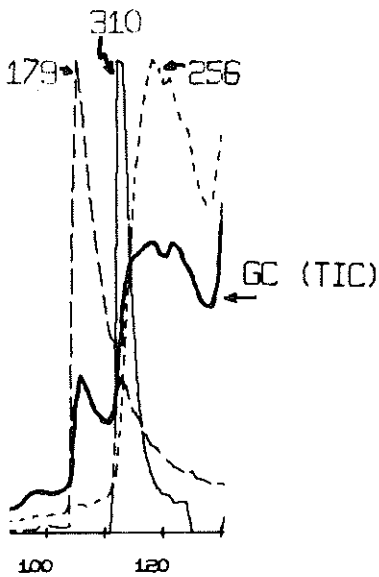

Figure 6.
Small section of a gas chromatogram showing mass chromatogram profiles of three different components (for details see ref. 38).

carefully judged by the investigator based on the answer received. Herein lies the greatest pitfall of this approach because the novice tends to believe what the computer says. Unfortunately, because simple compounds are nowadays easily and correctly identified by matching algorithms without human intervention, the novice has now little occasion to learn the manual interpretation of mass spectra.

Although the number of compounds represented in computer searchable collections of mass spectra has steadily increased and stands now at about 40,000 in the NIH/EPA library and 67,000 in the Registry, there is always a good chance that the compound in question is not represented. Attempts have been made to cope with such situations through algorithms which mimic the human interpreter.

One approach developed by Lederberg, Djerassi and their collaborators at Stanford (42) was based on the capability of a computer program (Heuristic DENDRAL, originally developed by Lederberg) to generate rigorously exhaustive structures of organic molecules of a given

elemental composition, predict the major features of the mass spectrum of each and compare it with the spectrum of the unknown. While this worked, in principle, with simple compounds, like aliphatic ketones (43), for aliphatic amines additional NMR data had to be included and for steroids high resolution mass spectra were required (44). In retrospect, this was a much too ambitious approach for which even the next generation of computers may not be powerful enough. The useful parts of these algorithms are now incorporated in CONGEN, a system that is an aid to the organic chemist who wishes to determine the structure of an organic compound from a wide variety of spectral data and other chemical information (44).

A more practical and useful method was developed in McLafferty's laboratory: the Self-Training Interpretive and Retrieval System (STIRS) (45). In a nutshell, it uses common features of the mass spectra of compounds having the same functional groups and checks the spectrum of the unknown for those spectral features. The result is a listing of structural entities most likely present in the compound which give rise to mass spectrum to be interpreted. Figure 7 illustrates that the lower range of the mass spectrum indicates the presence of a disubstituted benzene ring, the middle a monosubstituted benzoyl moiety and the neutral loss from $M^{\ddagger}$ implies the presence of a propyl ester. The algorithm has been developed and refined over the years using mass spectra from the spectral library as "unknowns" but there are hardly any examples in the literature of its use for real unknown compounds.

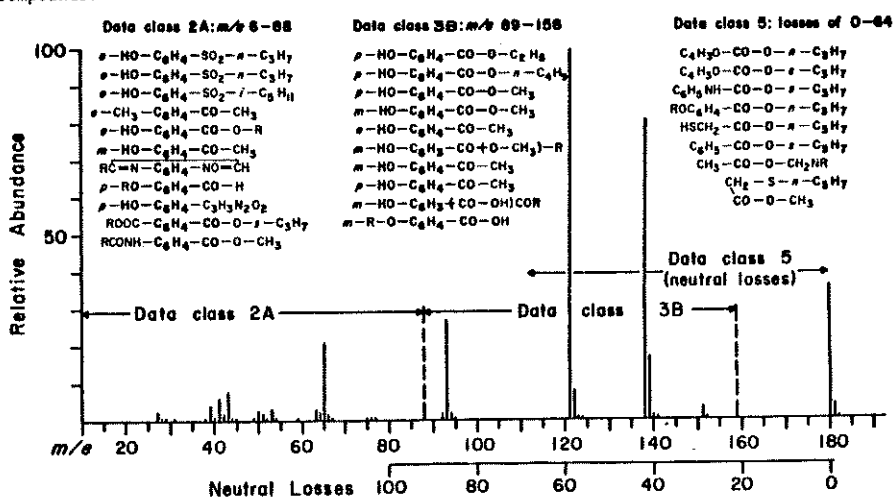

Figure 7. Output of STIRS (from ref. 45).

There is one area where it is not possible to use the library search approach but which is well suited to straight forward computer interpretation: the determination of the amino acid sequence in a peptide, suitably derivatized for mass spectrometry. To construct a complete collection of such mass spectra is an unsurmountable task because of the large number (millions) of even small peptides theoretically possible. On the other hand, the highly restrictive, structural constraints for protein-derived peptides (which all represent a linear chain of α-amide bonds bearing the side chains of the 23 protein amino acids) makes it possible to devise a relatively simple algorithm for the interpretation of their mass spectra which fortunately also exhibit a very characteristic, uniform fragmentation pattern. To date the algorithm (46) for the determination of the sequence of small peptides based on the mass spectra of the O-TMS derivative of the corresponding polyamino alcohol is the only practically useful and used example for the computer aided interpretation of mass spectra (in contrast to the matching algorithms discussed earlier).

The last decade saw a consolidation and refinement of the developments of the period of 1962-1974 during which the basic groundwork was laid for the computer-based acquisition and processing of mass spectra as outlined in the preceding recapitulation of events. The most distinguishing aspect of these two periods were the relationship of the tempo of the developments in mass spectrometry and computer hardware: the demands of high resolution mass spectrometry and GCMS first exceeded what computers and ancilliary equipment could do for a price (and size) that was compatible with a mass spectrometer, while the last decade saw a dramatic increase in the capability of computer related hardware and a decrease of cost and size. This threw the field wide open and led to the situation mentioned at the very outset of this story, namely the fact that modern mass spectrometers now come with finished data systems which incorporate most, if not all the useful components and capabilities that had been developed in the 1960's and 1970's. The increase in processing speed and decrease in size represented by microprocessors allows now much more to be done in real time. Acquisition processors consisting of a series of microprocessors provide practically final mass spectra to the host computer which then carries out the manipulation of the data that can now be displayed and interrogated while the GCMS experiment is still in progress. Large disk storage capacity at affordable cost make it possible to store and access complete mass spectra from much larger libraries. Previously, much effort in programming and algorithm design had to go into the efficient condensation of data without loss of information.

There are a few more recent developments in mass spectrometry which needed and still need new approaches: acquisition, processing and display of linked scans on MS/MS data is one area; another is the handling of mass spectral data beyond about m/z 2000, now accessible due to the development of fast atom bombardment mass spectrometry. In the latter area, the problem is the need to use high resolution mass spectrometry (with respect to resolving power) at practically unit mass resolution. The conceptual problems have been alluded to, but the computational consequences have still to be resolved (47).

One variant of mass spectrometry needs to be mentioned which would not have been possible were it not for the explosive growth in the power of computers since the early 1970's: Fourier transform ion cyclotron resonance mass spectrometry, FTMS. The pioneering work of Comisarow and Marshall (48) laid the groundwork for the exploitation of the many and unique capabilities of ICR-MS and extended it to extremely high resolution. This is a typical example where advances in one field open possibilities in another one which otherwise would have remained difficult or even impossible to accomplish.

One of the most complex examples of computer aided mass spectrometry was the Viking Molecular Analysis Experiment carried out in 1976. Seven years earlier, NASA had recognized the uniqueness of mass spectrometry as a method to detect and identify organic compounds. The author had proposed an experiment to search for the presence of organic compounds in the surface of Mars, a planet to be explored by a landed experiment package first planned for a 1973 launch but postponed to 1975. It contained, as one of ten experiments a GCMS system capable of detecting organic compounds at the sub-part per billion range in the surface material of the planet. None were detected at that level-to be sure-but the experiment worked well and beyond a shade of doubt (49). The instrument was also used to analyze the atmosphere of the planet for the minor constituents and their isotopic distribution (50).

The most remarkable accomplishment of this mission, aside from placing a miniaturized GCMS on the surface of another planet (and have it work) was the data acquisition and transmission. The instrument's operating parameters were controlled by command from Earth to execute a complete atmospheric analysis or GCMS experiment, the data (17 megabits for a GCMS) were recorded, stored and then transmitted to an orbiter which flew 1500 km over the lander once a day. The data were stored there and transmitted twice over more than 300 million km

to one of the three Deep Space Network stations on Earth, and then to JPL, Pasadena, CA. From there they were sent by cable and airplane to MIT for detailed analysis on the PDP 11/45 system which by that time had just begun to replace the IBM 1800 computer at our laboratory. Results were sent back via telephone lines to JPL. This was probably the most elaborate acquisition, transmission and processing of mass spectral data achieved to date, and most likely for some time to come.

There are many other functions of mass spectrometers which were greatly improved by certain data acquisition modes or by the computer processing of the raw data. Although important, many of them are consequences of the basic developments reviewed in this paper. Quantitative analysis using GCMS is one of these areas which today represents a large fraction of the utilization of mass spectrometers. Environmental chemical analysis and quantitation in pharmacology, toxicology and clinical chemistry fall in these categories. Computer controlled or computer-aided tuning of quadrupole mass spectrometers and the mass analysis of time-of-flight instruments are another area. And, last but not least, the tremendous efforts that have gone into the hardware and software developments of commercial mass spectrometers need to be acknowledged. They are not included because they are difficult to trace objectively and are mainly based on the developments described in this review.

In retrospect, 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. It is a fascinating story worth recording and remembering.

BIBLIOGRAPHY

1. Biemann, K., Bommer, P. and Desiderio, D.M., "Element-Mapping, A New Approach to the Interpretation of High-Resolution Mass Spectra", Tetrahedron Letters, 26, 1725 (1964).

2. Biemann, K., "High-Resolution Mass Spectrometry of Natural Products", J. Pure and Appl. Chem. 9, 95 (1964).

3. Bommer, P., McMurray, W. and Biemann, K., "Techniques in the High-Resolution Mass Spectrometry of Complex, Polyfunctional Organic Molecules", 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, June 1964, p. 428.

4. Desiderio, D. and Biemann, K., "Computer Techniques for the Fast and Facile Conversion of Line Positions to Elemental Compositions of Ions Recorded on Photographic Plates", 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, June 1964, p. 433.

5. Watson, J.T. and Biemann, K., "High-Resolution Mass Spectra of Compounds Emerging from the Gas Chromatograph", 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, June 1964, p. 438.

6. Biemann, K., McMurray, W. and Bommer, P., "High-Resolution Mass Spectra of Organic Molecules and their Use for Structure Determination", 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, June 1964, p. 442.

7. McMurray, W.J. and Lipsky, S.R., "Computer Techniques for Fast Scanning High Resolution Mass Spectrometers", 14th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, May 1966, p. 297.

8. McMurray, W.J., Greene, B.N. and Lipsky, S.R., "Fast Scan High Resolution Mass Spectrometry". Anal. Chem. 38, 1194 (1966).

9. Merritt, C., Issenberg, P., Bazinet, M.L., Green, B.N., Merron, T.O. and Murray, J.G., "Fast Scanning of High Resolution Mass Spectra", Anal. Chem. 37, 1037 (1965).

10. Watson, J.T. and Biemann, K., "High-Resolution Mass Spectra of Compounds Emerging from a Gas Chromatograph", Anal. Chem. 36, 1135 (1964).

11. Hites, R.A. and Biemann, K., "A Computer-Compatible Digital Data Acquisition System for Fast-Scanning Single Focussing Mass Spectrometers", Anal. Chem. 39, 965 (1967).

12. Hites, R.A. and Biemann, K., "Computer Recording and Processing of Low Resolution Mass Spectra" in Advances in Mass Spectrometry, 4, The Institute of Petroleum, London, 1968, p. 37.

13. Hites, R.A. and Biemann, K., "A Mass Spectrometer-Computer System Particularly Suited for Gas Chromatography of Complex Mixtures", Anal. Chem. 40, 1217 (1968).

14. Cone, C., Fennessey, P., Hites, R., Mancusco, N. and Biemann, K., "Recent Developments in the Acquisition and Interpretation of Mass Spectrometric Data", 15th Annual Conference on Mass Spectrometry and Allied Topics, Denver, May 1967, p. 114.

15. Biemann, K., "Interpretation of High Resolution Mass Spectra", in Advances in Mass Spectrometry, 4, The Institute of Petroleum, London, 1968, p. 139.

16. Burlingame, A.L., "Data Acquisition, Processing, and Interpretation via Coupled High-Speed Real-Time Digital Computer and High Resolution Mass Spectrometer Systems", in Advances in Mass Spectrometry, 4, The Institute of Petroleum, London, 1968, p. 15.

17. Burlingame, A.L., Smith, D.H. and Olsen, R.W., "Real-Time Data Acquisition, Display, and Subsequent Processing in High Resolution Mass Spectrometry", Anal. Chem. 40, 13 (1968).

18. Merritt, C., Issenberg, P. and Bazinet, M.L., "Design and Performance of a Direct-Coupled Real Time Spectrum Digitizer and a Rapid-Scanning High-Resolution Mass Spectrometer", in Advances in Mass Spectrometry, 4, The Institute of Petroleum, London, 1968, p. 55.

19. Venkataraghavan, R., Board, R.D., Klimowski, R., Amy, J.W. and McLafferty, F.W., "Automated Acquisition and Interpretation of High-Resolution Mass Spectral Data", in Advances in Mass Spectrometry, 4, The Institute of Petroleum, London, 1968, p. 65.

20. Biemann, K. and McMurray, W.J., "Computer-aided Interpretation of High Resolution Mass Spectra", Tetrahedron Letters, 11, 647 (1965).

21. Mandelbaum, A., Fennessey, P. and Biemann, K., "An Approach to the Computer-Interpretation of High Resolution Mass Spectra", 15th Annual Conference on Mass Spectrometry and Allied Topics, Denver, May 1967, p. 111.

22. Biemann, K., McMurray, W.J. and Fennessey, P.V., " 'Ion Types', a Useful Concept in the Interpretation of High-Resolution Mass Spectra", Tetrahedron Letters, 33, 3997 (1966).

23. Biemann, K., Cone, C. and Webster, B.R., "Computer-Aided Interpretation of High Resolution Mass Spectra II. Amino Acid Sequence of Peptides", J. Am. Chem. Soc. 88, 2597 (1966).

24. Senn, M. and McLafferty, F.W., "Automatic Amino-Acid-Sequence Determination in Peptides", Biochem. Biophys. Res. Commun. 23, 381 (1966).

25. Abrahamsson, S., "The Use of Computers in Low Resolution Mass Spectrometry", Sci. Tools 14, 29 (1967).

26. Pettersson, B. and Ryhage, R., "Mass Spectral Data Processing. I. Computer Used for Identification of Organic Compounds", Ark. Kemi 26, 293 (1966).

27. Crawford, L.R. and Morrison, J.D., "Computer Methods in Analytical Mass Spectrometry", Anal. Chem. 40, 1464 (1968).

28. Knock, B.A., Smith, I.C., Wright, D.E., Ridley, R.G. and Kelly, W., "Compound Identification by Computer Matching of Low Resolution Mass Spectra", Anal. Chem. 42, 1516 (1970).

29. Pettersson, B. and Ryhage, R., "Mass Spectral Data Processing", Anal. Chem. 39, 790 (1967).

30. Hertz, H.S., Hites, R.A. and Biemann, K., "Identification of Mass Spectra by Computer-Searching a File of Known Spectra", Anal. Chem. 43, 681 (1971).

31. (a)Abramson, F.P., "Extended Automation of a GC/MS Data System by a New Compound Identification Program", 21st Annual Conference on Mass Spectroscopy, San Francisco, May 1973, p. 76; (b)Abramson, F.P., "Automated Identification of Mass Spectra by the Reverse Search", Anal. Chem. 47, 45 (1975).

32. McLafferty, F.W., Hertel, R.H. and Villwock, R.D., "Probability Based Matching of Mass Spectra", Org. Mass. Spec. 9, 690 (1974).

33. Heller, S.R., "Conversational Mass Spectral Retrieval System and Its Use as an Aid in Structure Determination", Anal. Chem. 44, 1951 (1972).

34. Heller, S.R., Fales, H.M. and Milne, G.W.A., "A Conversational Mass Spectral Search and Retrieval System-II: Combined Search Options", Org. Mass. Spectrom. 7, 107 (1973).

35. Hites, R.A. and Biemann, K., "Computer Evaluation of Continuously Scanned Mass Spectra of Gas Chromatographic Effluents", Anal. Chem. 42, 855 (1970).

36. Hammar, C.-G. and Holmstedt, B., "Mass Fragmentography. Identification of Chlorpromazine and Its Metabolites in Human Blood By a New Method", Anal. Biochem. 25, 532 (1968).

37. .(a)Biller, J.A, Hertz, H.S. and Biemann, K., "The Application of a GC-MS-Computer System and Various Interpretive Programs to Problems in Natural Products Chemistry", 19th Annual Conference on Mass Spectrometry and Allied Topics, Atlanta, May 1971, p. 85; (b)Biemann, K., "Data Acquisition in Mass Spectrometry", in The Applications of Computer Techniques in Chemical Research, The Institute of Petroleum, London, 1972, p. 5.

38. Biller, J.E. and Biemann, K., "Reconstructed Mass Spectra, A Novel Approach for the Utilization of Gas Chromatograph-Mass Spectrometer Data", Anal. Letters 7, 515 (1974).

39. Dromey, R.G., Stefik, M.J., Rindfleisch, T.C. and Duffield, A.M., "Extraction of Mass Spectra Free of Background and Neighboring Component Contributions from Gas Chromatography/Mass Spectrometry Data", Anal. Chem. 48, 1368 (1976).

40. (a)Henneberg, D., "Ein kontinuierliches Verfahren zur massenspektrometrischen Bestimmung gaschromatographisch vorgetrennter Substanzgemische", Z. fur Anal. Chem. 170, 365 (1959); (b)Henneberg, D., "Eine Kombination von Gaschromatograph und Massenspektrometer zur Analyse organischer Stoffgemische", Z. fur Anal. Chem. 183, 12 (1961).

41. Gates, S.C., Dendramis, N. and Sweeley, C.C., "Automated Metabolic Profiling of Organic Acids in Human Urine. I. Description of Methods", Clin. Chem. 24, 1674 (1978).

42. Lederberg, J., Sutherland, G.L., Buchanan, B.G., Feigenbaum, E.A., Robertson, A.V., Duffield, A.M. and Djerassi, C., "Applications of Artificial Intelligence for Chemical Inference. I. Number of Possible Organic Compounds. Acyclic Structures Containing Carbon, Hydrogen, Oxygen, and Nitrogen", J. Am. Chem. Soc. 91, 2973 (1969).

43. Duffield, A.M., Robertson, A.V., Djerassi, C., Buchanan, B.G., Sutherland, G.L., Feigenbaum, E.A. and Lederberg, J., "Applications of Artificial Intelligence for Chemical Inference. II. Interpretation of Low-Resolution Mass Spectra of Ketones", J. Amer. Chem. Soc. 91, 2977 (1969).

44. Gray, N.A.B., Smith, D.H., Varkony, T.H., Carhart, R.E. and Buchanan, B.G., "Use of a Computer to Identify Unknown Compounds: The Automation of Scientific Inference", in Biochemical Applications of Mass Spectrometry, Supplement 1, Waller, G.R. and Dermer, O.C., eds., John Wiley & Sons, Inc., 1980, p. 127.

45. Kwok, K.-S., Venkataraghavan, R. and McLafferty, F.W., "Computer-Aided Interpretation of Mass Spectra. III. A Self-Training Interpretive and Retrieval System", J. Am. Chem. Soc. 95, 4185 (1973).

46. Herlihy, W.C. and Biemann, K., "Advances in Gas Chromatographic Mass Spectrometric Protein Sequencing. III-Automated Interpretation of the Mass Spectra of the Polyamino Aclohol Derivatives", Biomed. Mass Spectrom., 8, 70 (1981).

47. Yergey, J., Heller, D., Hansen, G., Cotter, R.J. and Fenselau, C., "Isotopic Distributions in Mass Spectra of Large Molecules", Anal. Chem. 55, 353 (1983).

48. Comisorow, M.B. and Marshall, A.G., "Fourier Transform Ion Cyclotron Resonance Spectroscopy", Chem. Phys. Lett. 25, 282 (1974).

49. Biemann, K., Oro, J., Toulin, P., Orgel, L.E., Nier, A.O., Anderson, D.M., Simmonds, P.G., Flory, D., Diaz, A.V., Rushneck, D.R., Biller, J.E. and Lafleur, A.L., "The Search for Organic Substances and Inorganic Volatile Compounds in the Surface of Mars", J. Geophys. Res. 82, 4641 (1977).

50. Biemann, K., Owen, T., Rushneck, D.R., Lafleur, A.L. and Howarth, D.W., "The Atmosphere of Mars: Detection of Krypton and Xenon", Science 194, 72 (1976).

OBSERVATIONS ON SOME OF THE EVENTS LEADING TO THE FORMATION OF ASTM COMMITTEE E-14 TWENTY YEARS AGO

Harold F. Wiley

(Presented at the Banquet for the 20th Annual Conference on Mass Spectrometry and Allied Topics, June 4-9, 1972, Dallas, Texas.)

Several years ago Mrs. Wiley and I were traveling in Anatolia, Turkey, which is one of the oldest continuously inhabited areas on earth. There is a legend that Konya, a major city in central Anatolia, was the first city to emerge after the flood. Paintings and stone engravings have been found there which go back to at least 7000 B.C. Anatolia entered the Copper Age sometime in the 4th Millennium. In the year 1900 B.C. the Hittites arrived there. Greeks settled along the coast about 1000 B.C. Then came the Seljuk Turks, and finally the Ottoman Turks who arrived in the 13th Century. In that region, the 13th Century is like yesterday.

After this very recent immersion into the ruins, excavations, museum displays, and history of the civilizations and societies of Anatolia, I am now asked to survey the ancient ruins, poke into the moldy excavations, translate the strange dialects, and otherwise reconstruct the history of a quite different society - known to us today as the "American Society for Mass Spectrometry".

I have seen inscribed tablets found in the vicinity of what is now Pittsburgh, which reveal that the formal beginnings of a mass spectrometry society were established there in the year 1952 A.D. In that city's meeting place - or Forum - then called "The William Penn Hotel", nine days before the Ides of March, one hundred and three followers of the cult of mass spectrometry engaged in a strange, legalistic ritual known as "forming an E Committee". It was the fourteenth committee with this particular structure so, following the custom of that age, it was called "Committee E-14".

Its full name was "American Society for Testing Materials Committee E-14 on Mass Spectrometry". The establishment of this committee twenty years ago, and the inauguration of annual meetings sponsored by it, are the events we are commemorating this evening.

The cult of mass spectrometry is, of course, much older than twenty years. It originated, as we all know, over a half-century ago in a land across the seas, within a strange order of intellectuals called "Physicists". They occupied part of a famous temple of learning, the remains of which still can be seen today, and in it they erected a metal and glass goddess, the object of their intense devotion, which they named "Mass Spectrograph". Almost at the same time, in another famous temple of learning on the shores of Lake Michigan, a somewhat different glass and metal goddess was enthroned, and thus the cult of Mass Spectrometry was established among the physicists of this country.

It was not long before this cult spread to other temples of learning, here and abroad, and soon manuscripts and pronouncements about the beliefs and practices of Mass Spectrometry began to appear in the esoteric journals of the physicists of that time.

As long as the cult of Mass Spectrometry was practiced by just a few cloistered physicists, the idols they worshipped tended to be different from each other, although certain materials such as sealing wax, beeswax and resin, and some time later, Glyptol, were used for ritualistic decorations on each one.

This all started to change when an offshoot sect who called themselves "Geophysicists", and whose temple at that time was a small suite of rooms

over a drug store, wanted to establish an oracle that would tell them where oil could be found. They consulted a high priest of physics about it, and he suggested that they adopt the cult of Mass Spectrometry. And so they did. The goddess they first erected was not a thing of beauty by any standards, but its most devastating deficiency was like that of the Oracle of Delphi. It gave only ambiguous answers. As a geophysical oracle, it was a total bust.

A world war was underway by then and suddenly there was huge demand for aviation gasoline. The processes for making 100 octane gasoline were very tricky to control, and it was obvious that supernatural intervention would be mighty helpful. The geophysicists that I just mentioned heard about this problem and they decided to try Mass Spectrometry for invoking this intervention. They erected a new mass spectrometer, and they developed a new ritual, and after many months of fasting they began to get some helpful answers. So it was that in 1942, thirty years ago, this new goddess of Pasadena, called the "CEC Model 21-101" was reproduced and its first offspring was shipped to the Atlantic Refining Co. in Philadelphia.

Because of wartime restrictions, many events in Mass Spectrometry in the early 1940's were kept secret. The outstanding example, of course, was the Manhatten Project and the critical role of mass spectrometry in that huge undertaking. Secrecy made it impossible, of course, for anyone connected with this project to reveal what they were doing. Therefore, this activity had no visible effect on the developing social organization of Mass Spectrometry in that early period.

CEC, followed very soon by Westinghouse, began to supply mass spectrometers to a few research laboratories such as NACA, Bureau of Mines, Bureau of Standards, Bell Labs, etc., but most of them went to petroleum companies. This meant that the cult of Mass Spectrometry started to be infested with chemists - not just physical chemists who were true believers anyway - but also by organic chemists. Worse still, most of these organic chemists were employed by industry. Imagine how that started to upset the social order!

One of the first signs of change occurred in the spring of 1944 when a group of about ten people met for an afternoon in Pasadena, California. All except the hosts were recent converts to the cult, and all of them were worried. Worry number one was the demanding, indeed overwhelming new ritual that they had to learn and follow. Worry number two was the temperamental and usually nasty disposition of the new goddess that was, or soon would be, enthroned in their laboratories.

These people found comfort and reassurance in being able to talk in everyday, earthy language to one another about their new goddess, and they were greatly relieved when no one was striken deaf and dumb when they criticized her more obvious shortcomings. We know today, of course, that mass spectrometers have to be both sweet-talked and chastised. Unquestioning adoration will get you nowhere.

The next meeting of the Group took place during an ACS meeting in New York City in September, 1944. Unfortunately this is remembered mainly because a violent hurricane swept the east coast that week, and very few people were able to attend. The third meeting was held in Philadelphia in December, 1945. Attendance swelled to 37 people representing 16 laboratories. Five scheduled talks were presented, in addition to the informal discussions that occupied most of the two days. Also, CEC unveiled a new Electrical Computer for solving twelve simultaneous linear equations. From then on, CEC Group Meetings were held annually, and the principle was established of holding the meeting each year in a different part of the U.S.

Those annual meetings were supplemented by the exchange of limited circulation reports among the true believers. These "CEC Group Reports" ranged in subject matter all the way from service hints to formal, landmark

papers which were later published in technical journals, and almost all were contributed by users. Anyone with a bent toward the ancient history of Mass Spectrometry will find a reference to some of these Group Reports in the First Annual Review of Analytical Chemistry, published in January, 1949.

As far as I know, no written record of those early meetings still exists, but there are many legends about them that have been kept alive by word of mouth. For example, there are numerous legends about the problems of feeding the goddess. The miniscule portions that she could take in at any one time created all sorts of difficulties, so there was intense interest in feeding methods and systems. Then there were elaborate rituals that were suggested for avoiding or overcoming a digestive malady delicately called "gas sensitivity". Sometimes these strange, primitive cures worked just fine. I suspect they may offer clues for curing certain internal ills, mentioned a time or two this week, as affecting some of today's goddesses.

As time went on the attendance at the meeting so increased and the scope so broadened that it became evident to CEC that a different form of organization was needed for planning and sponsoring the meetings. Also - it was never talked about openly - but very strong pressure for change came from the legal departments of several large companies whose employees participated in the Group Meetings. "Close cooperation among competitors during the war years was just fine," they said. "But now we have to worry about the anti-trust implications. Get under the wing of an established technical society."

A more vocal campaign for change was undertaken by the General Electric Co. G.E. supplied the Manhatten Project mass spectrometers on a contract basis, and they entered the commercial MS business several years after Westinghouse dropped out. G.E. was on the outside looking in as far as the CEC Group Meetings were concerned, and they worked hard, particularly in 1951, to establish annual meetings under the sponsorship of a so-called "National Committee" or of an existing technical society. ISA and SAS were two that were approached.

The events of 1951 and early 1952 that finally led to the formation of ASTM Committee E-14 are quite well documented. For example, it is matter of record that on Monday, June 25, 1951, the late E. B. Tucker of the Whiting Research Labs of American Oil made the first suggestion that an ASTM "E" Committee be formed for mass spectrometry. It is a matter of record that on January 14, 1952, a conference was held at ASTM headquarters to consider whether a national group should be formed, and whether if formed, it should be set up as an ASTM "E" Committee. A steering committee with Bill Young of Atlantic Refining as Chairman was established at that meeting.

The 1952 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy was selcted as the vehicle for launching the new organization. A special effort was made to solicit papers on mass spectrometry and as a result, twenty-one papers were presented at that conference. It is interesting to note that the first of the three MS sessions was presided over by Jack Sharkey, Jr., and that the first paper was "Recent Developments in Mass Spectrometry" by Al Nier.

The strong technical program helped to insure that many mass spectroscopists would attend the conference and so would also the attend the special evening meeting called to formally establish Committee E-14 and to elect its officers. Bill Young was elcted chairman. The secretary was John Hutton of G.E.. Vice-Chairmen were Jack O'Neal of Shell, Fred Mohler of the Bureau of Standards, Harold Kelley of DuPont, and myself representing CEC. Various committee chairmen were appointed soon after that.

The following year the technical sessions were held jointly with the Pittsburgh Conference. The first conference entirely under the sponsorship of Committee E-14 was held late in May, 1954, at the Jung Hotel in New Orleans.

There is a lot more to tell, of course, but I am sure you will forgive me if I don't tell it tonight. Invite me to speak at the 40th anniversary dinner and I'll continue the story. In fact, I'll skip the dull details because now you've heard them, and I'll recite more of the legends of this strange cult we call "Mass Spectrometry". Until then, thanks, and may your filaments burn brightly forever and forever and forever.

"Early" Days at Humble, Circa 1960

by Thomas Aczel

These are some scattered memories of mass spectrometry as it was practiced in an industrial research laboratory around 1959 when I first came in contact with this fascinating art. The place was Humble Oil and Refining Company, later to become Esso, Enjay, Enco, Exxon Research; my mentors were Earl Lumpkin, and two highly skilled research technicians, Jack Taylor and Glynn Taylor (called Tee, for not to confuse him with the other Taylor, no relation). Both were in mass spectrometry for over twenty-five years, operating at that time an already venerable CEC 21-103c instrument and calculating analyses. Incidentally, Glynn (Tee) Taylor worked with Earl to construct our first, all-glass heated inlet system with facilities for solids introduction, a system that became widely adapted by several manufacturers, and is still in use today in modified form.

Operation was a rather arduous affair. One of my first tasks was developing the long photographic charts on which the spectra were recorded. The instrument had a circle-like door on the top left panel; the operator had to put a black sleeve on his left arm, put the sleeve over the door, open it, take out the chart, hold it under the sleeve, and walk it to a nearby closet, used as a dark room. Here he had to take off the black sleeve, retrieve the chart, fold it as an accordion (still in the dark!) and immerse it in the developing solution, making sure that it came in contact with all the folds of the accordion-chart. If not, the spectrum would contain blank-spots, could not be counted or measured well, and woe to the unhappy developer! The wet, developed spectrum had to be then dryed on a hot, sizzling rotating drum, another ordeal. Needless to say, I never became an expert in this procedure; my charts seemed to always have blank, bald, and burned spots; hence my subsequent liking for automatic data acquisition systems and computers!

One oft-repeated story related to this modus operandi is the case of the captive cockroach. These creatures are ubiquitous in the south, and apparently survive even in the innards of a mass spectrometer, however well cared for and cleaned. One of our operators was taking out a chart to be developed holding it within his black sleeve when suddenly he felt a creeping movement on his forearm. It was our prehistoric friend; a giant specimen trapped in the dark with the chart. The operator faced a terrible dilemma: get rid of the cockroach and expose and lose the chart, or grin and bear it until he could reach the darkroom. Needless to say, bound to duty, he selected the latter; chart and cockroach were both taken to the dark room. The chart was developed all right. The fate of the cockroach is unknown; it is still growing in our tales.

Peak numbers (nominal masses) were "counted" out, often using major fragments at every 14 mass units in hydrocarbon spectra as mileposts. Peak heights were measured with a ruler - fifty to a hundred per spectrum, many spectra per day. But thanks to human ingenuity, this work was soon facilitated by using transparent rulers, graduated in multiplets of 1, 3, 10, and 30, as the galvanometer record, so that at least multiplication was eliminated. One tedious weekly calibration job, however, remained: to check the galvanometer responses, and to calculate and use the required correction factors if the sensitivity ratios were not exactly theoretical.

Incidentally, our first high resolution spectra, vintage 1963-66 or so, were also recorded on charts; at first photographic, then a great advance, on a UV sensitive Visicorder, that at least did not have to be developed! To "compensate", high resolution, low voltage spectra (most of our work), were rather long, as manual mass measurement and pattern recognition required a distance of at least one or two inches per unit mass, from m/e 60 to about m/e 700 (50 to 100 feet per spectrum, and chart paper and UV sensitive paper were expensive!). Nevertheless using ^{13}C isotopes of molecular ions at each mass as mass/distance calibrations, we were able to measure masses with an accuracy of 10-20 ppm, routinely. Traffic in our hallways had to be stopped several times as we proudly displayed some long spectra representing significant, albeit now forgotten, achievements (not to every fellow employee's enthusiastic approval!).

Many of these spectra contained several hundred or even a thousand molecular ions, each to be measured, and input manually in a computer program that determined concentrations and related properties. We ran literally thousands of them; we finally acquired an IBM 1800 for automatic data acquisition in around 1966 or 67 making everybody's life easier and disposition happier.

Many of the early low resolution spectra were used in mixture and compound type analyses, containing five to twenty or more components. Calibration spectra were obtained in replicate for each; a matrix was developed that contained a characteristic peak for each component and the interferences of each component to the peaks used for all the others. Thus, we obtained a set of simultaneous equations, that when solved, gave very reliable quantitative results for concentrations in an unknown sample. Solutions were generally via an inverse and we inverted 20 by 20 matrices by hand, using a noisy Frieden calculator. The procedure, with the required checks, confirmations, and blanks required about a week of constant pounding on the calculator keys. Those Frieden calculators were, however, a boon, even with all the noise pollution (an unknown concept then). They were well suited for calculating standard deviations, for example. We used them even for converting times and/or distances to precise mass measurements in the early sixties, looking up natural logarithms by hand; and I remember my elation when first acquiring a Wang terminal which finally had a built-in logarithmic function.

Life is easier now, with computer terminals in our offices and homes, and essentially completely automated data acquisition and handling systems. But I expect, that in twenty years or so, somebody will reminisce about our first generation computer programs, bugs and all, in the same nostalgic but relieved way that we now talk about manual calculations.

Recollections of mass spectrometry in Britain and the USA

by John H. Beynon,
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When I joined ICI's Research Department in 1947 I was overwhelmed by being asked to build a mass spectrometer. I had had no previous experience in this field but soon found out that mass spectrometers had begun to be used in the petroleum industry in USA during the second world war. They were used exclusively for the analysis of petroleum samples and for this work it was essential that the 'cracking pattern', as the relative heights of the peaks making up the mass spectrum was called, remained constant as a function of time and that the same cracking pattern was obtained for any particular hydrocarbon in any of the mass spectrometry laboratories. To ensure this, the tungsten filament of the mass spectrometer was carefully conditioned before use so that the emitting surface consisted of tungsten carbide and, after conditioning, only hydrocarbons were ever examined.

In 1947, mass spectrometers were under construction in Manchester, England, by Metropolitan Vickers Electrical Company Ltd. (now Kratos Analytical Instruments) but ICI decided that to ensure continuous development of the instrument and its applications it would be wise to undertake construction themselves and two instruments were eventually built, one in my own laboratory and the second in another Division of the Company. The design was based on a paper that had been published by Graham, Harkness and Thode; the flight tube was of glass, with a flattened copper tube where the ions passed through the magnetic field. The pumping system included a home-made mercury-diffusion pump, also made of glass. The tungsten ribbon filament was mounted at the end of a long glass tube. Changing the filament involved cutting the glass and re-sealing while keeping the filament in position at the ion chamber. The detector was a Faraday cup, the lead to which was sealed through the end of the glass flight tube. The ion current was measured using a 10^{11} ohm resistor and an RCA 'acorn' electrometer valve connected in a D.C. amplifier. A feature of the design, of which we were very proud, was a variable exit slit operated by rotating an iron bar connected to a screw thread by means of a magnet manipulated outside the vacuum system. The instrument had a resolving power of about 250. Ions of m/z up to 200 could be transmitted at the full accelerating voltage of 2kV. One difference between our method of obtaining spectra and that of the people in USA was that we always scanned the magnetic field; they scanned the accelerating voltage.

It was intended that our instrument should be used for measuring gas samples labelled with ^{13}C, ^{15}N or ^{18}O obtained in studies of the metabolism of various pharmaceutical products being developed by ICI. However, it was soon found that the instrument was valuable for the qualitative identification of organic compounds and this application soon accounted for the great majority of the instrument time. At first, the magnetic field was scanned by hand. Two people were required to produce a spectrum, one to scan slowly through the spectrum and call out the peak heights and the sensitivity factor, the other to write down these values and normalise the spectrum using a mechanical calculator. Peaks were seen as deflections of a galvanometer spot on a curved, 2 metre long transparent scale. We looked forward to the day when we could buy a pen-recorder and automate the plotting of spectra, but when our recorder was delivered we found it a mixed blessing. It had the unpleasant habit of periodically going into violent oscillation and spraying ink across the laboratory.

Occasional mass spectrometry meetings were being held in Britain and the first of these was organised by the Institute of Petroleum in Manchester at the laboratories of Metropolitan Vickers, in 1950. The fourteen lectures, the discussions following each lecture and a Bibliography of mass spectrometry papers published between 1938 and 1950 were published in book form. The topics covered fell under the headings : Ionization and dissociation of molecules; Instrumental aspects; Applications; Preparation of standard gases. It is my recollection that about 40 people attended this 2-day meeting.

Our own research had resulted in a slow but steady improvement in the performance of our mass spectrometer. Our optimum resolution was, by 1953, about 600 so that we were able to resolve some simple doublets such as CH_4-O and our mass measurement accuracy for molecular ions was about 25 ppm. We were clearly able to see the potential of this improved performance in the characterisation of organic substances, but the performance still fell woefully short of what we would have wished. We approached Metropolitan Vickers and asked if they would consider building us a double-focusing instrument after the design of Nier and Johnson. They were confident that they could easily achieve our suggested resolution of 2,500 but

equally sure that we would quickly destroy the performance with what they called the 'organic muck' that we wanted to analyse. In the end, they agreed to build an instrument based on a 6" radius magnetic sector and ICI agreed to accept it whatever the actual performance achieved.

1955 was a memorable year in my life. Not only was the instrument delivered but within a short time we achieved a resolution of 13,500. The decision was taken not to manufacture any copies of this instrument (which had been called the MS8) but instead to manufacture an instrument of double the size - the MS9. Parallel developments were taking place in USA where Consolidated Electrodynamics Corporation, makers of the first commercial mass spectrometers, also decided to market a double-focusing instrument but based their design on the Mattauch-Herzog geometry with a photographic-plate detector on which ions of all m/z ratios could be focused simultaneously.

It was decided that I should visit the United States and I gave a lecture at the third annual meeting of ASTM Committee E-14 on Mass Spectrometry. The meeting was held at the Mark Hopkins Hotel in San Francisco. I was able to spend a month in USA and I made the most of the time setting foot (mainly in airports) in 29 States. I was able to visit people whose work I had been able to admire only through their publications - Fred McLafferty who was working in the same general area of qualitative identification as I was and who was located at Dow Chemical Company, Midland, Michigan, where his right-hand men were Vic Caldecourt and Roland Gohlke; Al Nier, who was already a legend and who was measuring atomic masses to great accuracy with Walter Johnson. His spectrometer, I remember, had a resolving power of 30,000; Harry Svec who showed me how to be innovative in instrument design and who was located, as he is today, in Ames, Iowa; Vernon Dibeler and Fred Mohler who were working at NBS, Washington, on isotope analysis and the provision of isotopic reference standards; Austin Wahrhaftig and Henry Rosenstock from the University of Utah, two of the authors who had published the momentous paper on Quasi-equilibrium Theory a few years before; Lou Friedman of Brookhaven National Laboratory who was studying how QET could explain fragmentation patterns of various classes of organic compound; Bill Hickam of Westinghouse Research Laboratories who was using low-energy electrons to study the formation of negative ions; Jack Sharkey and Gus Friedel of the Bureau of Mines, Bruceton, Pa., who were extolling the virtues of trimethylsilyl derivatives in analysis; Mark Inghram and Robert Gomer of the University of Chicago who told me about field ionization and with whom I also discussed the method of measuring the translational energy with which fragment ions are formed in an ion source. Mark had, the year before, co-authored a Handbook on Mass Spectrometry with C.J. Hayden - in my opinion, a masterpiece; Charlie Judson of American Cyanamid, Stanford, Conn., who was looking at rearrangements in the mass spectra of amines; Fred White of Knolls Atomic Laboratory, Knolls, NY, who told me about his 3-stage analyser; R.F.K. Herzog of the Air Force Research Centre, Cambrdige, Mass., of undying 'Mattauch and Herzog' fame, who talked to me about double-focusing; Lincoln Smith of Brookhaven National Laboratory who showed me the very high accuracy with which his 'mass synchrometer' could measure atomic masses and who discussed its use as a high resolution instrument for organic chemical work. On my visit to Consolidated Engineering Corporation, I met Harold Wiley, Charlie Robinson, Bill Brubaker, Harold Washburn and Cliff Berry, the counterparts of John Waldron, Robert Craig and Alan Errock at Metropolitan Vickers back in Britain. I learned about the commercial version of the 'cycloidal' spectrometer of Bleakney and Hipple which they were manufacturing (and was so impressed that ICI later purchased one); I saw the new Mattauch-Herzog mass spectrometer, the rival to my own MS8, and was again very impressed; Cliff Berry told me about the Z^2/R abberation, due to magnetic fringing fields, on which he was going to speak at the San Francisco meeting. My visits to various oil companies opened my eyes to the developments in computer techniques for matrix inversion necessary for the analysis of complex mixtures of hydrocarbons and the possibilities of automated data processing. Perhaps the most impressive set-up was at Esso, Linden, New Jersey, where Bill Priestley and Dude Dudenbostel showed me around. They also took me to my first baseball game - the Brooklyn Dodgers against the N.Y. Yankees - and I saw my first homer, hit by Mickey Mantle. Another of the leading mass spectrometry laboratories that I visited was that of the Humble Oil and Refining Company in Baytown, Texas, though there is really no-one humble in that State. There, I was shown around by Earl Lumpkin. In Whiting, Indiana, I visited Sy Meyerson at the Standard Oil laboratories. He was working with ^{13}C and deducing mechanisms of ion fragmentation reactions and postulating new rearrangements and structures. At Shell Oil Company in Houston, Texas, I met Archie Hood and Jack O'Neal. Jack had been responsible for the invention of the gallium inlet system that had greatly extended the range of volatilities of samples that could be examined. There were many other visits that I paid - to chemical manufacturers, government laboratories, tobacco firms and other places where mass spectrometry and related techniques were in use.

This was, perhaps, the period most productive of new ideas that I have seen and I went to the meeting in San Francisco expecting to learn a great deal more. I was not disappointed. All the above people were there as well as many others - about 200 in all, including people from Canada, Germany, Holland and Britain. There were 69 papers over a period of 4 days and no parallel sessions, so that one could learn about everything going on. There was to be no publication, but photography was allowed and, in common with others, I photographed important slides so that I could write up as comprehensive an account as possible on my return home. Several traditions were already being established; papers lasted only 20 minutes, hospitality suites were there in abundance (some even served breakfast!), sub-committees met at the end of each day and there were instrument clinics on the Friday. A difference was that the meeting included an exhibition of mass spectrometers and associated equipment.

I attended the meetings regularly from then on. Indeed, in 1961 I was appointed to the Committee as Member-at-Large. But nothing has since approached the thrill of my first visit to USA. And although travel has become faster since my first trip; there is no longer the need to warm up the piston engines before take-off, to circle from Denver to gain the necessary height to cross the Rockies or to spend 16 hours on a flight from New York to London as I did; nothing will surpass the thrill of that visit. And when I come to think of it, mass spectrometry has progressed too, just as air travel has. But nothing has surpassed for me the challenge and thrill of being involved in mass spectrometry in those early days.

REFLECTIONS

Every year there are fewer persons who can remember what a 21-101 mass spec was. Historically it was the Model T of mass spectrometers - a successful unit that survived. In the years following, innovations and upgrades led to the newer, improved workhorse for many of us. This 21-103C is acquainted with most of the finest mass spectrometrists. My exposure with a 21-101 saw the luxury of 30 cycle/second, 4 galvanometer recording system. Linearity and calibration sometimes took hours, since film development, measure and study were done with each adjustment. It was "a piece of cake" for the experienced man. Incidently, there were few female practitioners in those early years. And the four coil magnet was a thermal monster. The high currents (for hi masses) were the last runs of each day, typically, and unpleasant 'exotics' were the Friday nite specials.

Our local service engineer for C.E.C. (Consolidated Engineering Corporation) was one Clyde Bateman, a gentle giant with hands twice mine. He was most capable, even though an L.A. tackle in size and spirit. One of many who performed miracles of a sort.

These early days were spent under the steady hands of R. W. Law and R. C. Childs, at Allied Chemical and Dye Corporation. The year was 1952, and they had just moved their mass spectrometer from downtown Philly out to their research center, way out in Glenolden, Pennsylvania (Barrett Division, it was). This relocation to suburbia was among the early attempts to create a research environment apart from plant and production operations. I came to the aforementioned tutors from the Frankfort Plant of Barrett, way up 'North Philly', across from the Arsenal. Just getting there was a daily test of courage across the length of Erie Avenue.

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. This was especially true with Barrett, and its coal and coal-tar chemicals, with the prime reference being a limited set from Koppers. All was related to physical distillation, acid-base character, or some such (with melting points or refractive index reserved for 'pures'). It was an adventure to see so many unknown or impure spectra among the knowns. Inference was paramount at a time when literature references were near-nonexistant. Things are really different now, for unknowns are still being evaluated at ever-increasing rates really, with massive libraries, correlative powers and hyperspace tuned to help. Emphasis is regularly redirected, in this and in most endeavors, but the encounter with the unknown is exponential, it seems. The modern, diverse application front finds increasing numbers of scientists pursuing their volumes of terminal printouts of complicated spectra.

C.E.C. in 1954 had eleven sales and service offices (including Philly, Buffalo, and Seattle), probably concentrated by equipment density. Much travel was by auto, so engineers serviced you with avengeance - something like 12 hours continuously until the unit was back fully operational, so they could make another long drive to the next challenge. It was also common to have several upper echelon of C.E.C. drop in, take off their coats and help. I distinctly remember this happening on several occasions, both at Allied, and a few years later, at Colgate.

By 1956 the sweet smell of the big city called, and I joined Colgate-Palmolive-Peet Co. in Jersey City, looking across the wharves and the Hudson to the present locale of the Twin Towers. In this venture into soaps, fats, essential oils, and detergents, there were a great many influential persons, with none moreso than a most talented co-worker for many years, Bill Casazza. Bill was prematurely gray when I finished with him, and he went into being recognized for his own achievements. This reflection of Bill must in no way suggest that there were not countless more who all went into making my job easier, and far richer.

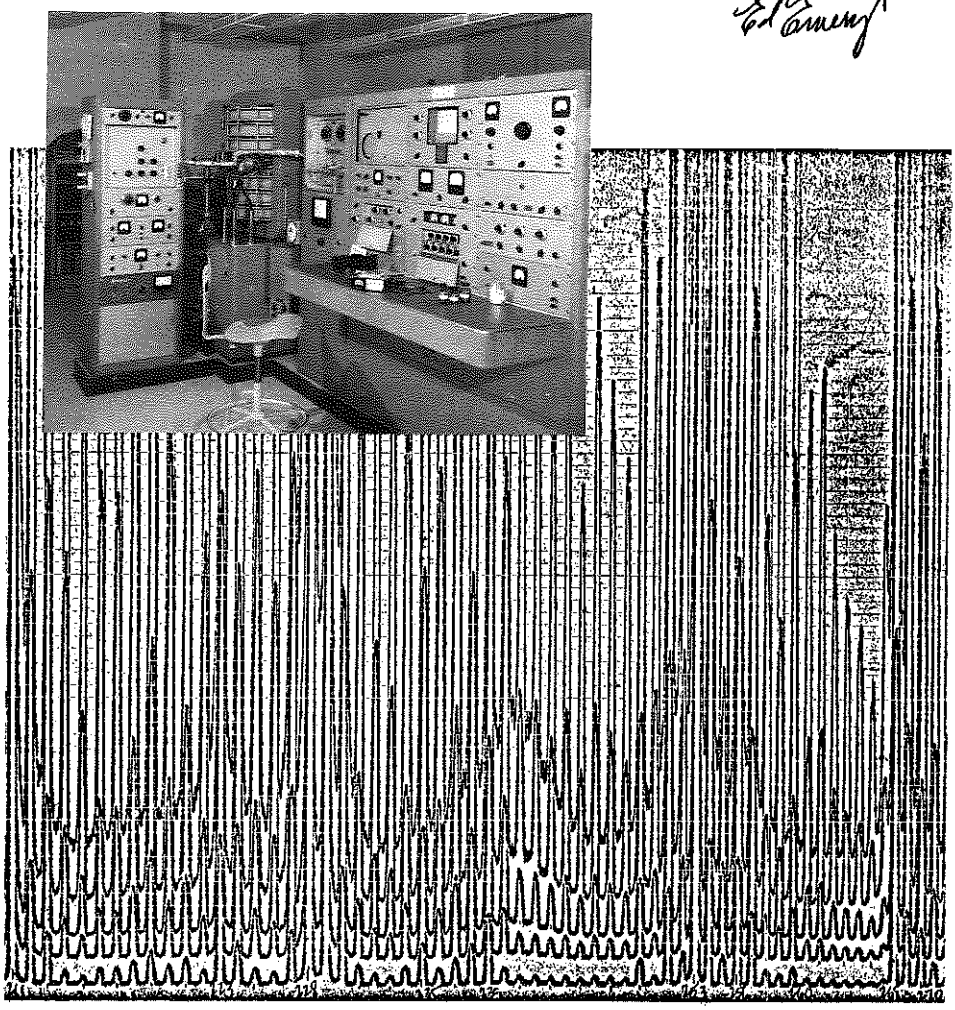
Every place has its skeptic. This doubter gave me two samples, asking only for molecular weights. The first was so-called "dodecylbenzene", a mixture of homologs and isomers - which, to his mind, was c-12-alkylbenzenes only. The resultant spectrum easily showed many other chain lengths.

The second was a pet sample that he had painstakingly synthesized and purified. Here too the spectrum was clear, distinctive and a real cinch once the mass scale was established. This man became one of the strongest proponents for mass spectrometry, since his pure sample was, and in effect proved that the other sample was as complex as indicated. He, and others, have been rewarded often by the power of the technique.

Below is a composite picture made up of a copy of a portion of an oscillographic record (the trace fades with time, so preservation for reports were via copies) with a 21-103C in mint-condition after 16 years (1972). Only the need for GC/MS, faster throughput, and ever poorer parts replacement made this a reflection.

The distinguished representatives of mass spectrometry history, Nier, Honig, Svec, Meyerson and Biemann at ASMS, were but a very few from so very many.

Ed Lamey



CHEMICAL PHYSICS MASS SPECTROMETRY AT THE HUMBLE OIL AND REFINING CO.

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In thinking about an appropriate topic for discussion in an ASMS Bound Volume whose theme is a retrospective look at earlier activities in mass spectrometry, I came to the idea of describing very briefly the chemical physics mass spectrometric activities of the Refining Technical and Research Division, Humble Oil and Refining Company, Baytown, Texas. I should state at the outset that this retrospective comes solely from my memory, and it is written, in the classic words of Dorothy Parker, sans peur et sans research. I emphasize that it is concerned with chemical physics mass spectrometry, for at Humble in those days was also a major effort in analytical mass spectrometry with which one associates the names Ben Thomas, Earle Lumpkin, Sam Hastings, and Tom Aczel, but that is another story.

The large amount of activity in mass spectrometry at Humble in the period from about 1945-1965 is illustrative of the major role in mass spectrometry played by American industry, and particularly the petroleum and chemical industry, in those early days. In the early 1940's Consolidated Engineering Corporation of Pasadena, California began to market a commercial mass spectrometer, the CEC Model 101, and during the 1941-1945 war Westinghouse Electric Corp. developed the Type LV mass spectrometer for analytical purposes in the synthetic rubber development effort. These instruments were impossibly expensive by university standards (the Westinghouse Type LV cost $15,000, the CEC 101 cost $35,000), for aside from this extremely high price, no federal funding for basic research in universities was in those years available. The oil companies were for the most part the only organizations who had the need and the money for mass spectrometry. People and companies in addition to the group at Humble which come to mind in this regard are John Hipple and Dave Stevenson at Westinghouse and later Dave Stevenson at Shell Development, Rick Honig at Socony Mobil, Sy Meyerson at Standard Oil of Indiana, Norm Coggeshall at Gulf, Fred McLafferty at Dow, and so on. Until about 1955 ASTM E-14 mass spectrometry meetings were almost completely industrial gatherings; the influx from academe did not begin until the late 1950's after funds for equipment began to become available, and incidentally,

after the sceintific value of the field had been established by industrial workers. The contribution of these workers was very great, and it resulted as a development from the important empirical analytical utility of mass spectrometry. In those early days the situation with mass spectrometry was somewhat analogous to the situation with respect to the steam engine a hundred years earlier: science benefited much more from the steam engine than the steam engine ever benefited from science.

Chemical physics mass spectrometry at Humble originated with Joe Franklin. Joe was a chemical engineer who was involved almost completely in the ptetroleum engineering jobs that made the money at the refinery, but he had a passion for trying to understand phenomena at the most basic level possible. In 1949-50 he was concerned with understanding the product distribution in sulfuric acid catalyzed alkylation of olefins. To achieve this understanding he made the unprecedented and highly original step of turning to the very small amount of information then available on the energies of gas phase carbonium ions. This information came primarily from the appearance potential measurements of Hipple and Stevenson. The energies of the gaseous ions helped him to make some interesting and useful rationalizations of alkylation behavior, but it became very apparent that much more data were needed.

My introduction to mass spectrometry also involved Humble, for it had donated an obsolescent Westinghouse mass spectrometer to the University of Texas where I had just joined the staff. Research funds and equipment were in almost vanishingly short supply, and so I undertook to set up and operate this mass spectrometer even though I had no previous experience in the field, and neither had any one else at the University of Texas. I started a research program in measuring appearance potentials, which Joe Franklin learned about, and he invited me to work at Baytown for the summer of 1951. One thing led to another and I joined the company the next year. Joe and I continued the project of measuring appearance potentials using another surplus Westinghouse mass spectrometer that Humble had kept for itself.

Joe was a convincing promoter of basic mass spectrometric research as well as a skillful participant in it, and the project flourished, thanks in large part to Joe's success in convincing the Humble management of the value of this basic research, as well as several other kinds of basic research. In 1954 Fred Lampe joined the group; in 1957 Jean Futrell joined to work in related projects in radiation chemistry;

and in 1961 Burnaby Munson joined the group.

In 1956 we convinced the management of Humble to provide funds for the Humble chemical physics mass spectrometer, which was designed to be an all purpose instrument for research in chemical physics mass spectrometry. The instrument cost somewhat more than $100,000, which would translate into approximately $600,000 in 1984 terms. I thought then, and I think now, that the vision of the Humble management in supporting this outlay of money for equipment to be used solely for basic research was exemplary and commendable. The manager of Humble R and D at the time was Art Draeger, and, of course, much credit should again go to Joe Franklin for his convincing management to support the project.

Those were particularly exciting days, for serious studies of ion-molecule reactions were just being undertaken, and every time one screwed up one's courage and put up the pressure in the mass spectrometer a little above the standard electron ionization pressure one was rewarded with observing new and strange reactions. In designing the chemical physics mass spectrometer I made the happy choice of calling for what in those days was an extremely high capacity differential pumping (300 liters per second on both source and analyzer), and thus we were able to achieve higher ion source pressure than had heretofore been used. This in turn enabled us to extend the kinds of ion-molecule reactions which we could observe and led directly to the discovery of chemical ionization.

This chemical physics mass spectrometric research began to wind down at about 1960. Jean Futrell left the company to satisfy a military obligation; Fred Lampe went to Penn State; Joe Franklin was appointed the first Robert A. Welch Professor at Rice University; I transferred to Esso Research and Engineering at Linden, New Jersey, and the chemical physics mass spectrometer went with me; and finally, in 1967 Burnaby Munson went to the University of Delaware and the project ceased. Neither is space available nor is it appropriate to give here a wash list of the scientific accomplishments of the laboratory, but one can say that they were extensive and significant. It seems to me that it comprises an interesting case of support of basic research by private funds. It is also interesting to speculate on the economics of the operation. 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. Certainly some indirect benefits accrued to the company, but making a cost accounting of the value of these is beyond my abilities. I think it quite clear, however, that whatever the benefit to the Humble Company, society as a whole profited. I think it not at all inappropriate that Humble made this contribution, and I rather suspect that the company management felt the same way.

Early Developments of the Quadrupole Mass Spectrometer

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The quadrupole mass spectrometer (QMS) was invented independently and virtually simultaneously in the early 1950's by Professor Wolfgang Paul of the University of Bonn, FRG and by Dr. Richard Post of the University of California, who was working with Professor Ernest O. Lawrence at the time. The work of Post is little known because he reported results of his QMS invention and experimental results in a University of California Radiation Laboratory report—UCRL 2909—during 1954, but not in the published literature. Both Paul and Post were attempting to use the QMS for strong focussing and separation of ions in particle accelerator experiments.

Significant breakthroughs in quadrupole mass spectrometry did not occur until 1958 when K. R. Shoulders of Stanford Research Institute (SRI) initiated work on a unique research program in microelectronics. Shoulders proposed a detailed program covering the development of a thin-film deposition and micro-machining technology that would ultimately permit the fabrication of complete electronic systems (with a density of 10^{11} components per cubic inch) entirely under contaminant-free ultra high vacuum conditions. Shoulders saw that in order to reliably monitor the thin-film manufacturing process, a small non-magnetic type mass spectrometer was needed which was capable of being baked out to 900°C under ultra-high vacuum. After reading the patent of Paul, Shoulders decided to use the QMS for this purpose.

Together with several colleagues, who included C. A. Rosen, W. J. Fies, and C. E. Blahnik, Shoulders designed and built a number of QMS during the period 1959-1962. By the end of 1960 this group had produced a practical QMS which gave excellent sensitivity over the mass range 1 to 500 dalton. Figure 1 shows the early SRI quadrupole mass filter, which was similar in size and utilized radio frequencies approximately equal to most of those being used in commercial QMS systems today. The SRI micro-electronics program is described in depth in several publications and SRI reports.[1,2,3,4]

I joined SRI in 1962 to found a process controls research group together with P.M. Uthe. Both Uthe and I became extremely interested in the work of Shoulders and in the QMS as a potentially excellent detector for measurement and feedback control of industrial processes. We attempted unsuccessfully to interest several petrochemical companies and instrument manufacturers in sponsoring research to develop the QMS for the process control application. In 1963, Uthe and I left SRI to form a new operation for Electronics Associates, Inc. (Scientific Instruments Division located in Palo Alto, California) of which I was director. We immediately started an evaluation of the QMS for possible use in process control. In 1963, we built several QMS for SRI from their "breadboard" drawings; Shoulders' group was no longer involved in constructing quadrupoles by that time. Based upon interest from several other potential users, we built prototype models of a commercial QMS in early 1964. Our first commercial product was the Quad 200 Residual Gas Analyzer (RGA) which was intended for use by physicists and physical chemists in a diversity of applications including space research, ultra high vacuum measurements, Knudsen cell experiments, etc. We delivered the first Quad 200 in the fall of 1964 to the Nuclear Sciences Department of the University of California Berkeley. It is shown in Figure 2.

The Quad 200 RGA, made up of the quadrupole filter and associated power supplies, had a mass range from 1 to 500 dalton with unit resolution over this range, and had a minimum detectable partial pressure of 1×10^{-15} torr. It could scan the entire mass range in 10 ms. This was an unusual performance for an instrument selling for $10,000 in 1964 and it was immediately recognized as a sound value by scientists working on the NASA space program, as well as by research scientists in many other diverse fields. Initially, we literally could not keep up with orders we received and in the ensuing four years EAI sold more than four hundred Quad 200 Series worldwide.

In 1965, we introduced the Quad 150 RGA, a solid state quadrupole residual gas analyzer with lower specifications on mass range and sensitivity than the Quad 200 and a considerably lower price. It also experienced an excellent reception and was instrumental in solidifying the position of the quadrupole as the accepted instrument for residual gas analysis applications. In 1966, we introduced the Quad 300 QMS system which was our first complete mass spectrometer system equipped with vacuum pumping and sample inlet systems. It did not include a gas chromatograph (GC) interface. Five Quad 300's were delivered in 1966 including one to the Analytical Instrument Division (F&M) of Hewlett-Packard Company.

In early 1967, I left EAI and together with Roger Sant, T. Z. Chu, M. S. Story, and W. J. Fies co-founded Finnigan Instruments Corporation. Our sole objective was to develop, manufacture, and market a gas chromatograph/mass spectrometer system (GC/MS) utilizing the QMS. We felt that its inherent advantages of simplicity, low cost, compactness, capability of operating at relatively high ion source pressures, and most importantly, ease of computerization would make it a logical choice for the GC/MS application. At that time the only GC/MS commercially available was the LKB 9000, which had just been introduced into the U.S. market.

Design of our first GC/MS system, the Model 1015, was completed in one year, and we delivered the first prototype system to the Stanford Medical School Genetics Department in January 1968. The Model 1015 had a mass range from 1 to 750 dalton with unit resolution over this mass range, scan speeds as fast as 50 ms., and sensitivity of 1 microgram for full scan (using methyl stearate and cholesterol as standards). The Model 1015 used a single-stage glass jet separator for interface to the gas chromatograph, the design of which was given to me by Professor E. Stenhagen of University of Goteborg, Sweden.

From the beginning of our GC/MS development program, I was convinced that our ultimate success was dependent upon successful computerization of the quadrupole GC/MS, in order to meaningfully handle the enormous amounts of data being generated. In part my conviction was based upon observing the success which Stanford Medical School had in computerizing the first Model 1015 GC/MS.

During early 1968, we accepted an order from Professor E. Horning of Baylor Medical College for a computerized GC/MS system to be delivered by year-end 1968. About the same time, Dr. E.V.W. Zschau, a professor in the Stanford Business School (now the U.S. Congressman from Silicon Valley), approached me for product ideas for a new company he was just forming. I suggested that they develop a data system for our Model 1015 GC/MS. This product, the System/150, subsequently became the first product of System Industries, Inc., now a successful computer peripherals company located in Milpitas, California.

The first commercial GC/MS/DS, the Model 1015/System 150, is shown in Figure 3. Following its introduction in 1969, GC/MS was poised to take off as a principal analytical tool for chemists working in environmental, biomedical, and forensic sciences.

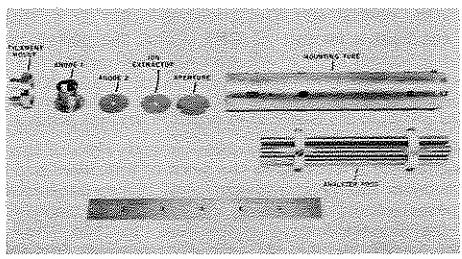

Fig. 1 The SRI Quadrupole Mass Filter (Circa 1960).

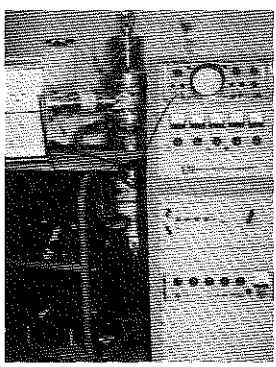

Fig. 2 The Quad 200 Residual Gas Analyzer (circa 1964).

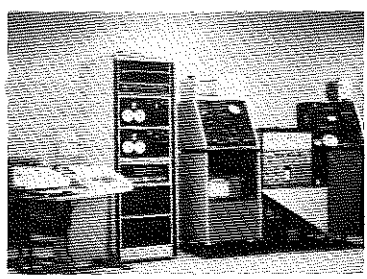

Fig. 3 The Model 1015 GC/MS/DS Prior to Delivery in 1969.

References

1. K.R. Shoulders, "Research in Microminiaturization Using Electronic Machining Techniques," SRI Report, Division of Engineering Research, (1958).
2. K.R. Shoulders, "Microelectronics Using Electron-Beam-Activated Machining Techniques," Advances in Computers, Vol. 2, Franz Alt, Ed., Academic Press (1961).
3. K.R. Shoulders, "Toward Complex Systems," Microelectronics and Large Systems, Spartan Books, Inc., John H. Wiley and Sons (1965).
4. John Kelly, "Research in Microminiaturization Using Electron-Activated Machine Techniques," SRI Report, Division of Information Science and Engineering, (1967).

REPORT ON THE HISTORICAL WORKSHOP AND EXHIBIT

In conjunction with the retrospective theme of the San Antonio meeting, a workshop entitled "Mass Spectrometers of Yesteryear" was held. The attendance at the workshop was good (> 100) with a good cross-section of ages represented. There were three scheduled presentations, two dealing with the early history of commercial instruments, given by Bob Finnigan and Mike Story of FINNIGAN/MAT, and Sid Evans of KRATOS. The third presentation was by Harry Svec and dealt with instrumentation prior to the availability of commercial instruments.

All three presentations were well received with the commercial instrument history generating much conversation among the audience members who were involved in mass spectrometry in those early years. The newer members of the discipline seemed to find the history prior to commercial instrumentation especially intriguing. There were several comments after the workshop by graduate students in mass spectrometry about how interesting and informative this presentation was and to how something like this would be beneficial to and enjoyed by future newcomers to the field.

At the conclusion of the workshop, a brief discussion was held on whether the society should take an active part in trying to preserve historical documents and hardware. Almost unanimously the attendees of the workshop felt that this would be a very worthwhile endeavor on the part of the society. At a minimum, it was felt that historical documents should be collected. Also, there was strong sentiment for a permanent display of historical hardware if space could be found somewhere. It was suggested that maybe a committee on history could be formed in order to help sustain the enthusiasm generated at this meeting for preserving the history of our discipline.

From the feedback of some viewers of the historical exhibit, the exhibit was well received. The exhibit included: some early documents from ASMS; some recent "firsts" in mass spectrometry; some early metastable spectra; photographs of preparative mass spectrometers; and some hardware from early instruments. Without question, the most talked about aspects of the exhibit were the 1940's vintage flight tubes brought by Professor Harry Svec and the photographs of the preparative mass spectrometers (calutrons).

While the flight tubes were extremely interesting in their own right, the few people who were fortunate enough to hear Prof. Svec and Prof. Nier explain exactly what was involved in doing mass spectrometry with this hardware certainly gained several orders of magnitude more appreciation for these flight tubes. The calutrons proved to be interesting because most people did not realize that preparative mass spectrometry was ever done and because of the size of the calutrons--much, much larger than any conventional mass spectrometer.

To conclude this report, I would like to once again thank all the people who contributed to the historical display and participated in the workshop, and I would like to make a few comments about preserving our history. In trying to organize this exhibit, it became obvious that there is a general lack of motivation for preserving our history (although subsequent to the meeting where much interest was generated, this is probably less so, for the time being). Also a problem exists in determining what is historical. It is my feeling that most hardware probably falls into the category of surplus or junk before it becomes historical , and thus much is thrown out to make room

for new equipment. It is hoped that one outcome of this meeting will be to make people pause and think if material might be of historical value before discarding it. If we as a society are going to act on preserving our history we must act soon as much of the early hardware and documents are already lost and we cannot expect most people to hold onto old equipment forever with laboratory space generally at a premium. So, if you are interested in this topic, now is the time to get involved.

Submitted by:

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VIEWING A MOMENT IN THE HISTORY OF ASMS

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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 Comittee E-14. It was voted on and is today as so many now know it to be.

Mass Spectrometers of Consolidated Engineering Corp. and its Successors

Charles M. Judson

The first commercial mass spectrometer was delivered by Consolidated Engineering Corp. to Atlantic Refining Co. in late 1942. It was a five inch radius, 180 degree magnetic deflection mass spectrometer.

The principles of mass spectrometer analyser design were well established at this time; double-focusing analysers capable of exact mass measurements had been built (Mattauch & Herzog), and instruments for accurate isotope ratios were available (Nier). However, reproducibility of spectra of organic molecules, even simple hydrocarbons, was insufficient to provide a capability to analyse the components of a mixture.

Consolidated Engineering Corp., a geophysical exploration company, undertook in the late 1930's the development of mass spectrometer to analyse 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.

The problem of C-1 to C-4 hydrocarbon mixture analysis, and particularly the butane isomer analysis in the catalytic cracking process for the production of aviation fuel was a critical problem in the war effort. The existing method was a time-consuming method involving distillation in a Podbielniak column. The problem was not simple. Because compositions were calculated with solutions of simultaneous equations, reproducibility of fragmentation patterns was more critical than in typical modern mass spectrometry where separations can be made by gas chromatrography.

War-time production of mass spectrometers was under strict priority control and was restricted to laboratories engaged in petroleum analysis. Even with unrestricted sale after the war, the applications continued to be mainly to the petroleum field until the mid-1950's. However, in the early 1950's, heated inlet systems were available, and spectra of volatile organic compounds of all kinds were being obtained.

The first commercial mass spectrometer was a model 21-101. The 21-101, 21-102, and 21-103 followed as well as the 21-103A, B, and C. Complete convertability up to the 21-103C were available, and most of the 21-101, 102 and 103 instruments were upgraded to the 21-103C design. In the late 1960's, approximately 25 years after the first 21-101, the 21-104 was developed, retaining the 5 inch radius, 180 degree analyser, but abandoning the convertibility in the interest of cost.

Two hundred of the 21-101/102/103 instruments were sold over a twenty-five year period. Due to over 100 patents in mass spectrometry, the only major competition in U.S. sales until the 1960's, for the organic analysis market, was the Westinghouse instrument in the early 1940's before the patents had issued.

The name of the company was changed from Consolidated Engineering Corp. to Consolidated Electrodynamics Corp. but was better known as CEC. It operated in the 1960's as a subsidiary of Bell and Howell, but retained its continuity of management until it was sold to the DuPont Company in 1970.

The company introduced in the early 1960's the Mattauch-Herzog instrument, which was designed to be alternately a high resolution organic instrument, and a spark-source instrument for trace inorganic analysis. About 100 of these instruments were sold. These instruments were very popular in the high resolution version prior to the development of computer data-acquisition systems, when photoplate acquisition was the only way to acquire complete high-resolution spectra.

The company's last product, the 21/490/491/492, was a 4 inch radius 90 degree instrument, convertible to double focusing, which was the successor to the 21-100 series. Over 200 instruments of this model were sold; 50 by CEC and the remainder by DuPont.

At first the oscillograph records had to be read by hand, then semiautomatic methods of reading oscillograph records were developed, and then in the 1950's a digitizer was developed and digitized spectra were obtained with a "Mascot" at a rate of 2 amu per second. Speed of scanning was compromised for convenience.

For analysis of mixtures, without the benefit of GC separations, calculations involving simultaneous equations were required. An analog computer with 144 potentiometers in 12 rows on a rotating wheel was developed. By successive approximations, simultaneous equations in 12 unknowns could be solved. But the accuracy was marginal and the maintenance difficult. When digital computers became available in the 1950's, one of the first tasks of scientific calculation was the solution of simultaneous equations for the mass spectrometer laboratory.

In addition to the mainstream products described, CEC manufactured isotope ratio instruments, both surface ionization and gas analysis, a process control instrument, and residual gas analysers, and was a major manufacturer of mass spectrometer leak detectors.

The author was a user of a 21-103 from 1953, one of the early users in the chemical research laboratory, and was Director of Engineering of the CEC Analytical Instruments Division from 1963 to 1970.

TRACING OUR ROOTS ANECDOTE

THE SINGING OF "THE EYES OF TEXAS"

Contributed by Earle Lumpkin (Emeritus Charter Member)

The mixer preceeding the Wednesday night banquet of ASMS is at full voice. People wandering about the room with drink in hand or gathered in small groups for idle or earnest conversation are distracted by voices raised in song. And the song is "The Eyes of Texas." The moment passes, but tradition has been saved.

Before there was an ASMS, organized in 1969, and before there was an ASTM Committee E-14, 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 preceeded by a mixer.

For several years, CEC hired an accordionist to accompany the usual sing-song at the mixer. As the group was composed mostly of petroleum company representatives with a large contingent from Texas, the final song was "The Eyes of Texas." No alma mater connotations were implied. It was a song all Texans knew. As the years passed the sing-song session was abandoned, but Archie Hood, Chuck Robinson, and I, among others, made sure that at least we sang "The Eyes of Texas."

Joe Franklin and Burnaby Munson, both native Texans, joined us but Joe didn't have a real good singing voice. The Texans were becoming diluted as the then ASTM E-14 Conference attendance grew, so we judiciously 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. I am pleased that Catherine Fenselau, ASMS president for 1982-4, has been aware of this annual event. She asked me to lead ALL of the attendees in singing "The Eyes of Texas" Wednesday night at the barbeque at the 1984 Conference held in San Antonio at the Lone Star Brewery in the Lone Star state. And I did it. Our roots grow deeper! Keep it up!

How I got into Mass Spectrometry

Amos S. Newton
Lawrence Berkeley Laboratory

In June 1941 I received a Ph.D. in Physical Chemistry from Michigan, doing my research work with Professor Kasimir Fajans on a problem involving use of radioactive tracers. I then went to work for Eastman Kodak in their Manufacturing Experiments Department in Rochester. In May 1942 Prof. Fajans, having been approached by the Manhattan Project, approached me to work with him in Chicago on that project. As Fajans was not yet a citizen, his appointment at Chicago was held up. Frank Spedding at Ames and Chemical Director at Chicago at the time asked me to come to Ames for a few weeks to help set up some radiochemical work. I was given a leave of absence from Kodak and went to Ames in May 1942 expecting to go to Chicago's Metallurgical Laboratory soon thereafter. I stayed 4 years in Ames.

In late 1945 everyone in the Manhattan Project was searching for a permanent position. I could have gone back to Rochester or stayed at Ames. At that time C.E.K. Mees, director of research at Kodak, met Fajans at a meeting and mentioned that he and E.O. Lawrence were considering placing a Kodak man at Berkeley to keep informed in the field of nuclear science. Fajans recommended that I be that person as I was already a Kodak employee. I came to Berkeley in May 1946 as a "consultant without salary" but in all other respects to be treated as a laboratory scientist.

At Berkeley I did some radiochemistry and I kept up with progress in radiation chemistry. In 1948 I was given a beautiful laboratory in a new central research laboratory building and started actual work in radiation chemistry. Analysis of gaseous radiation chemical products were difficult and analysis of the lower vapor pressure liquid products virtually impossible. The laboratory had a GE mass spectrometer which had been used for isotope analysis in the Calutron development at Berkeley. We tried to adapt this instrument to organic analysis but had no success.

After consultation with some scientists at the research laboratory of the Standard Oil Company of California, I approached Ernest Lawrence with the request that we buy a CEC instrument, the Model 21-102. He said "Go ahead, see Wally Reynolds (the laboratory's business manager) and he will find you the money." It was not, however, this simple, for even with the money specifications had to be written and the purchase put out to bid. Both GE and CEC responded to the requests for bids and GE came in some 2K under the CEC bid of 32.5 K. Both companies claimed to accurately analyze and identify gases in a mixture. Because of our failure with the old GE instrument, I requested that each prove their performance. Therefore a mixture was made up as follows: H_2 - 22.1%, C_2H_6 - 24.4%; Ethylene oxide - 13.4%, n-C_4H_{10} - 17.0%, and i-C_4H_{10} - 23.2%. This was divided equally into two bottles and I took one to Schenectady, walked into the GE laboratory, handed them the sample and said "Analyze it. I'll wait." At noon they had run the sample, but had no analysis at 4 p.m. when one of the GE people took me to New York so we could see an instrument at Standard of New Jersey the next day. That instrument was not yet working. I took a flight to LA. The following day at 9 a.m. I walked into CEC and handed them their sample. Sybil Rock was in charge of the analytical laboratory at CEC. By 11 a.m. she had a provisional analysis, but was confused by the identity of the ethylene oxide. Sybil knew it was not propane or acetaldehyde. Later that day by phoning some of CEC's customers she had identified it as ethylene oxide and had calculated an excellent fit with the known composition. Sometime later GE sent an analysis which was far from correct. They never identified the ethylene oxide. They reported the presence of 6% H_2 as opposed to the 22.1% added and reported far too much of each butane. Needless to say we purchased the CEC instrument. It was delivered in November, 1949 and the final acceptance test was completed Jan. 15, 1950. The instrument magnet was numbered 73, the serial number was 146L6.

The CEC-21-102 had a sealed ion source which was returned to Pasadena for cleaning and filament replacement. We had trouble with this arrangement because the laboratory business office decided we must get back the same ion source we sent, which would greatly increase the turn around time. To trade ion sources, each of which carried its own serial number, was interpreted as the selling of government property, which the laboratory was forbidden to do. After some hassle this requirement was finally relaxed.

The CEC-21-102 had an all glass inlet system and the inlet line from the inlet cabinet to the mass spectrometer analyzer in the magnet was a straight piece of 15 mm glass tubing. Shortly after installation, Berkeley had a very minor earthquake, but one sufficient to snap the inlet line and let the system up to air, burn out the filament, fill our trap with liquid air, etc. This was solved by making the inlet line a loop of glass some 18 inches high next to the inlet cabinet. We never had another inlet line break with this arrangement, even though Berkeley had quakes as large as 5.5 on the Richter scale.

The instrument was converted to a Model 21-103 B in 1954 and in 1964 was remodeled to include an all metal vacuum system. By 1965, i.e., 15 years of operation, we had run 13,500 samples on the instrument.