The Sun and Solar Wind: A Search for the Beginning

APPENDIX B

Mass Spectrometry A Historic Technique for Analysis That is of Great Importance to Genesis

The analysis of materials by the technique of mass spectrometry played a seminal role in the development of the Standard Model of the Sun. It was through the mass spectrometric determination of the exact mass of helium that it was realized that the mass of an atom of helium was 0.8 percent less than the mass of four hydrogen atoms. This observation was at odds with the view suggested by the English chemist William Prout nearly 100 years before that the atomic weight of any element is an exact multiple of the atomic weight of hydrogen. That Prout's suggestion was not correct gave Arthur Eddington, a leading physicist of the 1920s, the necessary clue that he needed to propose that the furnace in the interior of stars is fueled by sub-atomic energy. Eddington did not know of the existence of neutrons, so his theory was incomplete in its details, but his fundamental idea was correct. Mass spectrometric techniques have continued to play an important role in science (particularly in chemistry) and it is very satisfying to recognize that this old and historically important technology is likely to play a major role in the final phase of the Genesis project.

The instrument called a mass spectrograph was developed in 1919 by Francis Aston in Cambridge, England. The importance of this technology was immediately recognized, and Aston was awarded the Nobel Prize for his work in 1922. So, what does a mass spectrometer do and how does it work? In the following few paragraphs the classical technology will be described, and then a few words will be devoted to modern instrumentation of the type that may be used for analysis of Genesis samples when they are returned to laboratories here on Earth in 2003.

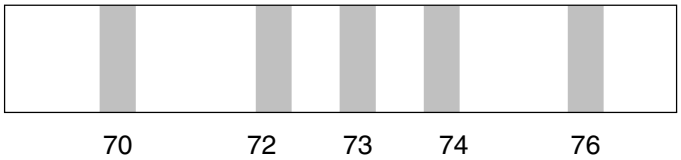
Mass spectrometers permit the experimental determination of atomic and molecular masses with great accuracy. Aston's mass spectrometer had a precision of one part in 10,000, which was sufficient for him to discover the isotopes of many elements. Modern instruments are even more precise.

Mass spectrometers operate under conditions of high vacuum, typically 10^{-8} Torr. (In comparison the pressure in outer space may be in the order of 10^{-12} Torr.) Under these conditions samples are fed into the spectrometer's ionization chamber where they are exposed to a beam of rapidly moving, energetic electrons generated by an electron gun. The samples can be in the form of a gaseous element such as neon, the vapor of a solid or liquid element such as mercury, or even the vapor of a molecule such as water or methane. With modern technology it is possible to introduce a wide variety of materials, including mixtures, into a mass spectrometer. When an atom or molecule is introduced into the ionization chamber it encounters the accelerated electrons and during the collision an electron is knocked out of the sample, leaving it with a positive charge. In other words, electrically charged cations are formed in the gaseous state.

The ions so formed are then pushed out of the ionization chamber by an electric field applied between two metal grids. This is a simple application of Coulomb's law in that the positive grid repels the positive ions and the negative grid attracts the positive ions, giving them a net acceleration toward the negatively charged grid. The negative grid, which is full of holes, allows the accelerated ions to pass through it and exit the ionization chamber. The speeds reached by the ions as they are accelerated by the electric field is determined by their masses, with the lighter ions reaching higher speeds than the heavier ones.

The accelerated beam of cations, which generate a magnetic field of their own—in common with all moving charged particles—is then passed through an externally applied magnetic field. The magnetic field of the cations interacts with the external field, with the net result that the trajectory of a charged particle is circularly bent to an extent that depends on its speed (and therefore its mass) If the beam of a mixture of ions having different masses is then allowed to impinge on a photographic plate, it will be seen that ions of different masses converge at different points, corresponding to the different radii of the semicircular paths. The mathematical equation that describes this phenomenon is: $m/e = H^2 r^2 /2V$, where m is the mass of the ion, e is the charge of the ion, H is the magnetic field strength, r is the radius of the semicircle, and V is the accelerating potential.

The radius of the semicircular path clearly is proportional to the mass of the particle. A photographically detected mass spectrum of natural germanium obtained under conditions of constant magnetic field and accelerating potential would look like the figure shown below:



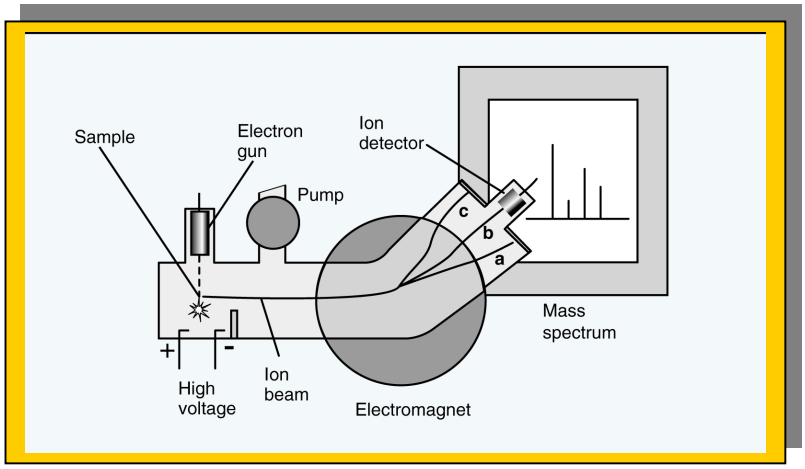
The relative abundances of the ions can be determined from the densities of the photographic images they produce.

Since H, V, and r can be varied or determined experimentally, the ratio m/e can be determined in one of several fashions. In a typical modern mass spectrometric experiment the strength of the external magnet is slowly varied, causing the paths of the various ions to sweep past an exit point where the mass spectrometer's ion detector is located. In other words, a signal is produced at the detector when the magnetic field is just strong enough to bend the pathway of ions of a given mass so that they arrive at the detector. The mass of the ion detected is then calculated from the accelerating voltage and the strength of the magnetic field required to produce the signal. The mass spectrum is a graph of detector signal versus the magnetic field strength. The positions of the peaks on the graph are used to calculate the masses of the ions, and the relative heights of the peaks indicate the relative proportions of the ions of various types that were in the sample. If the ion has a charge of one, then the mass is determined uniquely. Note that a dipositive ion of 64 gives rise to the same value of m/e as a monopositive ion of mass 32. Under the usual conditions for operating a mass spectrometer most of the ions produced are singly charged.

Alternatively, it is possible and actually more convenient to vary the accelerating voltage while keeping the magnetic field constant, leading once again to a spectrum that can be analyzed to provide ion masses and relative abundances. Modern mass spectrometers are hooked up to computers that do the analysis and produce a graph (spectrum) having mass in amu's or **atomic mass units** plotted on the x-axis and relative intensity on the y-axis. The relative intensity is a measure of how many cations of a given mass are detected. Note also that the units of daltons are sometimes used in place of amu's: 1 amu = 1 dalton. With modern low-resolution instruments, one can expect to obtain accuracy of plus or minus 1 amu up to 1000 mass units. High-resolution instruments can provide 2-3 parts per million (ppm) accuracy up to masses of 3000 amu.

There are many variations on the theme of mass spectrometry, but all of them are fundamentally based on the principles outlined above. Of particular note is a time-of-flight instrument in which the ions are produced in spurts and allowed to diffuse toward the detector in a straight line. No magnetic field is used. The heavy ions move more slowly than the light ones and the spectrum is a plot of intensity versus time of flight of the particle.

Mass spectrometers no doubt will play a major role in the final phase of Genesis when the samples are returned to Earth for analysis. By that time the technology may be significantly improved over what is now available.



Adapted from: P. Atkins and L. Jones. "Chemistry. Molecules, Matter and Change, 3rd Ed." W.H. Freeman, New York, 1997, p 9.