



Developments in Combined Gas Chromatography/Mass Spectrometry

Michael A. Grayson
St Louis, MO
Archivist, ASMS

In the late '50s various labs contemplated how the gas chromatograph (GC) and mass spectrometer (MS) could be interfaced to one another. However, the combination of the two was exacerbated by the technology of the time. Chromatographic packed columns were typically quarter inch O.D. with mass flow rates on the order of 20 cm³•atm/min and higher. To compound the problem further, typical mass spectrometer vacuum systems had pumping speeds on the order of 10 l/sec or less; not well-suited for direct connection between the two. Furthermore, MS scan speeds were on the order of 15 to 30 seconds; in some instruments even longer.

EARLY ADOPTERS

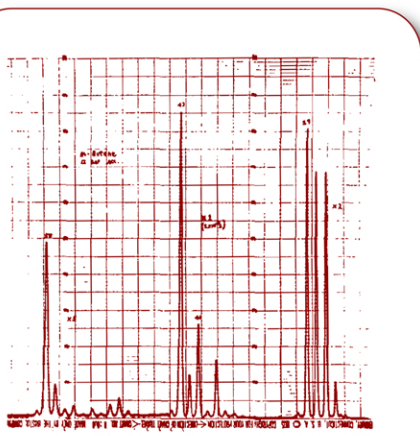
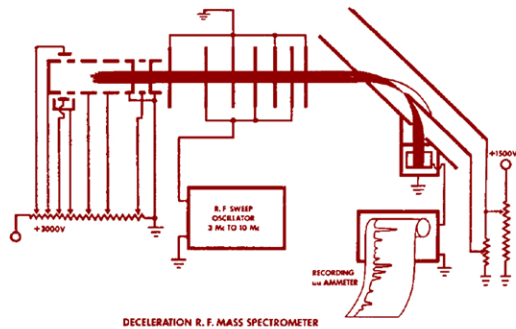
It is generally accepted that Roland Gohlke, working in McLafferty's lab at Dow Midland, was the first to report a combined GC/MS instrument¹ in 1957. Interestingly he chose a, non-magnetic sector mass analyzer; the Bendix time-of-flight mass spectrometer which had only been marketed commercially several years earlier. It had an open ion source, reasonable pumping speed, easily accessible ion source housing and rapid scanning. (*See Poster "The Bendix Time-of-Flight Mass Spectrometer"*) Gohlke used a simple split to route a small portion, typically 0.002%, of the column effluent to the mass spectrometer inlet; the remainder went to a thermal conductivity detector.

Beckman Explores Possibilities

A group at Beckman Instruments reported a combined instrument in 1957³. at the ASTM Committee E-14 meeting in New York City, using a mass spectrometer based on RF technology.

They also reported "A simple inlet system . . . which is easily attached to any gas chromatograph . . ." However, no further details were given nor can be found in the literature. For reasons that are not known, Beckman elected to abandon further development of the RF mass spectrometer and thus their combined GC/MS instrument.

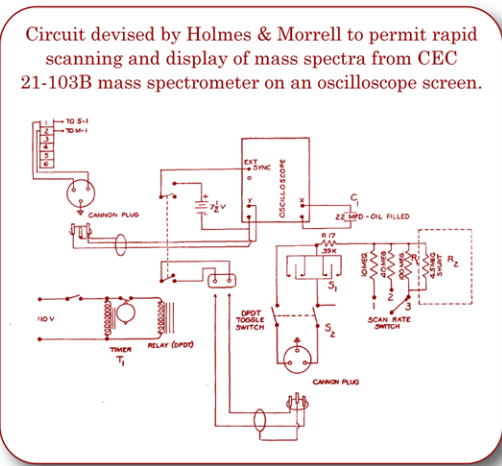
Diagram of Beckman's deceleration RF mass spectrometer



Mass spectrum of n-butane obtained with Beckman RF mass spectrometer in 1954.

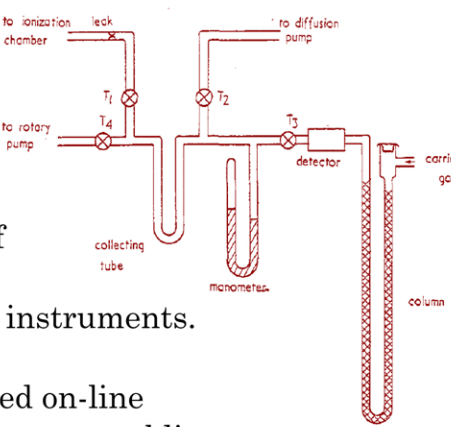
Despite the inherent advantages of the ToF-MS for combined GC/MS, it had several problems, most notably the degradation of resolving power with increasing mass when analyzing organic compounds. Furthermore, the dominant view at the time was that magnetic sector instruments were far superior to the ToF-MS. That, coupled with the fact that most laboratories already had existing magnetic sector instruments, prompted the publication of a large body of literature devoted to interfacing the gas chromatograph to slower pumping and slower scanning magnetic sector instruments.

Some approached the problem by developing sophisticated on-line trapping/introduction systems^{6,7}, to obtain a mass spectrum resembling that obtained with the conventional batch inlet. Others modified the instrument electronics to scan the spectrum more rapidly⁸.



Many of these early adopters interfaced the two instruments as did Gohlke, by the simple expedient of a split⁸⁻¹¹. This situation was acceptable as long as one was interested only in the major constituents of a mixture, but the desire to obtain mass spectra of minor constituents required some means of introducing more of the sample while rejecting as much carrier gas as possible. To this end, several different approaches were explored beginning in 1964 with the description of the molecular jet separator by Ryhage¹² at the Karolinska Institute. The following year, Watson working in Biemann's laboratory at MIT introduced the molecular effusion separator¹³. In both these devices, the mass flow rate of helium carrier gas into the mass spectrometer was reduced relative to the sample. A completely different approach to the problem was proposed by Llewellyn and Littlejohn¹⁴, then at Varian, at the Pittsburgh Conference in 1966 with a device referred to as the solution diffusion separator. In this approach, a thin silicone film served as a barrier to the entrance to the ion source and the chromatographic effluent flowed over the film. The solution and diffusion of helium into and through the film was orders of magnitude lower than for organic compounds, thus, they were preferentially transported into the mass spectrometer. (*See Poster "10th Annual Conference – 1962 – New Orleans"*) In short order, a number of variations on these designs were published in the literature, some of which are noted in the timeline below. (*See also Poster HP 5992 Gas Chromatograph/Mass Spectrometer/Data System.*)

On-line trapping arrangement by Beynon, Saunders and Williams for collecting GC cuts to transfer to the MS.



ENVIRONMENTAL IMPACT

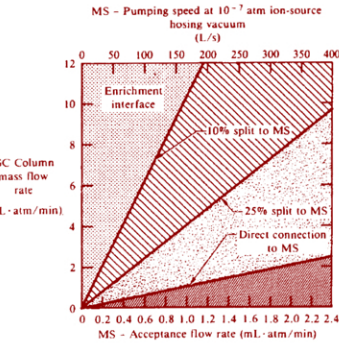
In the early '70s, the Environmental Protection Agency (EPA) was formed and mandated to track the presence of specific pollutants in water. Finnigan Instruments had developed a quadrupole mass filter for use as an analytical mass spectrometer in a combined GC-MS system¹⁵ and wanted to sell it to the EPA. However the price tag was over an order of magnitude higher than the analytical approach that the EPA was considering, primarily gas chromatography. The Finnigan team realized that it couldn't compete on instrument price, but figured that they could compete on cost per analysis¹⁶. Equally, if not more, important was the realization by the EPA's legal staff that the specificity of GC-MS data was more reliable and defensible in court than GC data alone. They ended up ordering the Model 1015/System 150 instruments and as a result it became the standard instrument for analysis of pollutants in water for all of the EPA; as well as for companies that faced potential EPA oversight. Consequently, Finnigan's sales rose dramatically over the ensuing decades and so also did the use of combined GC/MS in many other analytical venues.

Finnigan introduced the OWA as an updated version of the 1015 that was specifically designed for the analysis of pollutants in water.

An important event on the chromatography side of the combination was underway at the same time that the first GC-MS combinations were being reported; the development of capillary columns by Marcel Golay¹⁷. Operating at mass flow rates on the order of 1 cm³•atm/min, most or all of the column outlet could be introduced directly into the mass spectrometer^{11,18}. Even though this column technology was commercially available in the early '60s, it was not readily accepted in the analytical community. As differentially pumped mass spectrometers and a greater variety of stationary phases for capillary columns became available, their popularity increased and a direct connection from the chromatograph to the mass spectrometer became standard. By the mid '80s, reports in the literature using capillary GC-MS-DS instrumentation exceeded 100 per year. The era of separator interfaces was long gone. (*See Posters "The Hewlett Packard HP5930A Mass Spectrometer"*)

Why Separators are no longer needed

A plot in a paper by Grayson¹⁹ sums up pretty clearly the conditions for which a separator interface is needed based on the column mass flow rate, pumping speed of the mass spectrometer vacuum system and the fraction of the effluent that is required to enter the mass spectrometer. For capillary column flow rates and modern vacuum systems with appropriate pumping speed, a direct connection is simplest and best.



1958	1960	1961	1962	1964	1966	1967	1968	1969	1970	1971	1972	1974	1975	1979	1983	1985	1988	1991	1992	1995
Golay describes 'open and coated tubular columns' in Amsterdam GC Symposium	Biemann & Vetter report MS determination of sequence in peptide derivatives by GC-trapping-MS	Henneberg reports using MS as GC detector by measuring ion current at only one mass	McFadden and co-workers report "Use of Capillary Gas Chromatography with a ToF Mass Spectrometer" at ASTM E-14 Conference	Ryhage uses two jet separators in tandem for GC-MS interface	Sweeley and co-workers describe MS method of detecting unresolved components in chromatographic peaks	Grayson and Wolf compare performance of molecular separators	Hites and Biemann describe 'Computer recording and processing of low-resolution mass spectra' in Advances in Mass Spectrometry	Bruneel describes 'variable conductance' separator	Oro and co-workers report GC-MS analysis of lunar samples from the Sea of Tranquility	Arsenault and co-workers report GC-MS with alternate EI-Cl scans	McNair and co-workers report analysis of sterol hormones by direct GC-MS	Biemann reports test results of Mars Viking GC-MS	Lovett reports GC-MS analysis of Apollo 16 & 17 lunar samples	Budde and Eichelberger publish 'An EPA manual for organics analysis using gas chromatography-mass spectrometry'	Drew and co-workers report on 'A man portable GCMS for explosives detection'	Preston & Owens describe GC-MS for carbon-13 measurements with isotope ratio mass spectrometer	EPA describes GC-MS for analysis of polychlorinated biphenyls and chlorinated pesticides in water, soil and sediment	Chan and co-workers describe application of GC-MS for drug analysis at 1988 Olympic Winter Games in Calgary	Shoemaker and co-workers use GC-MS to exonerate mother of poisoning her infant with ethylene glycol	Bertsch & Holzer review application of GC-MS in the analysis of accelerants in fire debris
						Cree describes molecular effusion separator using porous silver membranes	Simmonds and co-workers report palladium-hydrogen separator for extraterrestrial GC-MS system					Harris & co-workers report on 'Direct analysis of water samples for organic pollutants with gas chromatography-mass spectrometry'	Dandaneau & Zerenner report use of fused silica capillary tubing for support coated open tubular columns							

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