The Hewlett Packard HP5930A Mass Spectrometer

Leo Weibel

PPD, Inc

8551 Research Way, Suite 160

Middleton, WI 53562

Ned Kuypers

Agilent Technologies

Santa Clara, CA

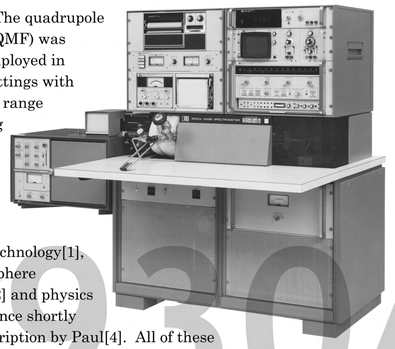
Michael A. Grayson

Washington University in St Louis

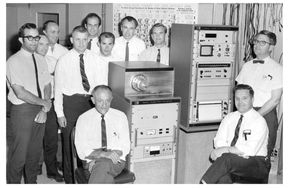
St Louis, MO 63130

QMF:

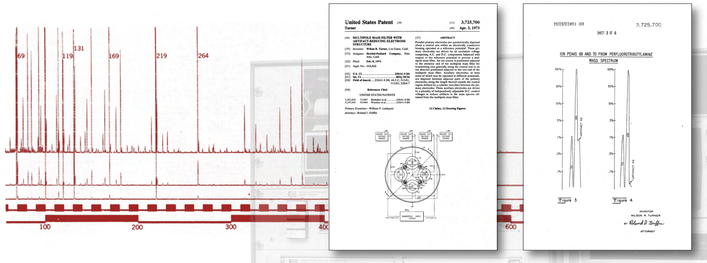
The quadrupole mass filter (QMF) was originally employed in analytical settings with limited mass range and resolving power. It had been used for specialty applications in vacuum technology[1], upper atmosphere exploration[2] and physics research[3]since shortly after its description by Paul[4]. All of these applications required an instrument with unit mass resolution over a limited mass range, typically 2 to 100 Da.



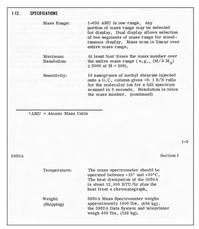
By the late '60s, combined gas chromatography/mass spectrometry (GC/MS) had been refined in the laboratories of early adopters to the point that instrument companies saw a lucrative market and embarked on the design of commercial units for GC/MS applications. At the time, magnetic sector instruments were the standard for analytical mass spectrometry, but were not particularly well-suited for GC/MS due to the relatively slow scan speeds imposed by the magnet. The Bendix Corporation had introduced the time-of-flight (ToF) mass analyzer in 1955[5]and it was well suited for the GC/MS application since it had no scan speed limitations. However, the resolving power of the instrument degraded above 300 daltons and it had a non-linear mass scale.



A number of companies turned to the quadrupole mass filter as the mass analyzer for an inexpensive analytical mass spectrometer for the GC/MS market. The Finnigan Corporation (1968); a venture capital company, Olfax (1973)[6]; and Hewlett Packard (1971) were among the earliest. In this presentation, we focus on the Hewlett Packard entry into this market, the HP5930A, which was first marketed in the summer of 1971.



SPECIFICATIONS:



One of the attractive features of the QMF as a mass analyzer is that it has a linear mass scale. This helps to simplify data processing to convert the raw data into a mass-marked spectrum.

The definition of Resolving Power, misnamed Maximum Resolution in the specifications, is complex. Eventually this was simplified to unit mass resolving power over the mass range. The sensitivity specification is typical for mass spectrometers of the period.

Paul's theory[7] for the separation of ions of different mass was posed in terms of a quadrupole with hyperbolic elements. Obviously, the machining of an approximation to a hyperbolic surface is not only costly, but extremely difficult. Therefore, most quadrupoles used circular rods as a first order approximation to hyperbolic rods. Finnigan was marketing an instrument with circular rods at the time the HP5930A was introduced. The introduction of a QMF based on dodecapole technology was an attempt by Hewlett Packard to produce a better instrument than one based on circular rods alone. According to H-P literature, "The four extra pairs of electrodes in the mass filter enhance the resolution attainable over quadrupole mass filters (with circular rods) and in addition, permit electronic tuning of peak shapes." Essentially, the "blades" added to the analyzer region provide a means of overcoming artifacts at the base of the mass peak that arise from the use of circular rods.

4-24. The Dodecapole structure is shown in Figure 4-5. Small dc voltages are applied to the "blades" inserted between the rods and it is found that sharp, symmetrical peaks can be obtained. The significance of this development is two fold. By obtaining sharp, symmetrical peaks, the data system works better, and there is no question of overlap or unresolved lines. Adequate resolution may be easily obtained and can also be maintained as the structure and/or source becomes contaminated by column bleed or sample background, thus reducing the frequency of necessary mass filter cleaning.

The Electronics:

By 1970, Hewlett Packard had established itself as one of the premier brands for electronic equipment used in metrology, signal generation, recording and power supplies. The QMF, a mass analyzer whose performance depended solely on electronic components was a natural technology for Hewlett Packard to pursue. H-P had successfully entered the analytical instrument market with the purchase of the F&M Scientific Corporation in 1965, a gas chromatograph supplier[8]. Development and marketing of the QMF for GC/MS applications was a natural move for the company.

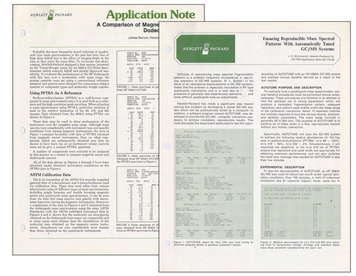
ACCEPTANCE: In the late '60s, magnetic sector instruments dominated the field and were in a horsepower race to produce the mass spectrometer with the highest resolving power. The QMF was seen as an inferior mass analyzer for analytical mass spectrometry and, despite being endorsed by the Environmental Protection Agency, it was not readily accepted. Further, Eichelberger and co-workers,[9] pointed out that the intensity of ions above mass 100 Da in spectra from the QMF were not as intense as those in the spectra from magnetic sector instruments. Since compound identification by comparison of sample spectra with standard libraries of spectra taken on sector instruments was a primary analytical objective of GC/MS/Data Systems, this shortcoming required attention.

Eichelberger and co-workers chose decafluortriphenylphosphine (DFTPP) as a calibrant compound and showed that the variation in the mass spectra of DFTPP among 11 laboratories using the same model QMF instrument was far greater than that among 4 laboratories using sector instruments from different manufacturers! These differences were traced to the manner in which the QMF was 'tuned' by the operator. By selecting tuning parameters that produced a DFTPP spectrum similar to that obtained with sector instruments, standardization of tuning could be obtained, and QMF spectra could be successfully searched against a database of magnetic sector spectra.

Applications:

The acceptance of the QMF as an analytical mass spectrometer did come after tuning issues were resolved. These instruments were generally smaller and less expensive than their magnetic sector competition and were able to scan even more rapidly to meet the challenge of continually improving chromatographic resolution and sharper GC peaks. Applications in environmental analysis, forensic science, analysis of drugs of abuse, and other small molecule analytical areas grew. Within a decade of introduction, the QMF was accepted as a legitimate analytical mass spectrometer. Subsequent developments, such as the triple quadrupole MS/MS instrument in the late '70s, sealed the reputation of the quadrupole mass filter as a viable mass analyzer in the analytical mass spectrometer market.

Tuning for reproducible spectra



Hewlett Packard elected to use a different compound for tuning their QMF instruments; perfluorotributylamine. These two "Application Notes" from the mid '70s indicate the importance of the QMF tuning problem. The 'Autotune' system was developed for the successor to the HP 5930A, the HP 5985 GC/MS/Data System instrument. This ensured reproducibility of spectra from day to day and from instrument to instrument.

1924 — CTR Corporation under the management of Thomas J. Watson changes its name to International Business Machines Corporation

1937 — Atanasoff-Berry Computer, considered to be the first electronic digital computer, created on the Iowa State University Campus

1938 — Dave Packard moves into house at 367 Addison Avenue, Palo Alto. Bill Hewlett rents the cottage behind the house. The two begin part-time work in the garage with $538 in working capital

1939 — Hewlett & Packard form partnership on January 1st. Coin toss decides company name.

1946 — ENIAC developed at Penn by Mauchly and J. P. Eckert

1947 — ENIAC patent filed

1950's — IBM becomes chief contractor for United States Air Force SAGE Interceptor system, requiring the company to design and produce a digital computer

1952 — A. J. P. Martin and Richard R. L. Synge receive the Nobel prize for "for their invention of partition chromatography"

1953 — Wolfgang Paul publishes "A New Mass Spectrometer without Magnetic Field"

1957 — Ken Olsen and Harlan Anderson form Digital Equipment Corporation (DEC)

1959 — F & M Scientific Corporation formed to design, produce and market gas chromatographs

DYMEC, Incorporated becomes DYMEC Division of Hewlett Packard