

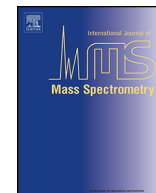


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40 years of Fourier transform ion cyclotron resonance mass spectrometry

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ABSTRACT

This article reviews the development of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in several respects: (a) a strong static magnetic field serves to convert ion mass-to-charge ratio into cyclotron frequency. Because frequency is the most accurately measurable property, ICR MS inherently offers higher mass resolution and mass accuracy than any other mass analyzer. (b) Coherent excitation followed by induced charge detection yields a time-domain signal whose discrete Fourier transform produces a mass spectrum of ions spanning a wide m/z range simultaneously. By simple analogy to weighing objects with a mechanical balance, that “multiplex” advantage can be shown to be equivalent to “multichannel” detection by an array of individual single-channel detectors. (c) FT-ICR MS performance benefits from near-elimination of magnetic field inhomogeneity by inherent ion cyclotron rotation and ion axial oscillation; inherent nearly quadrupolar electrostatic trapping potential and nearly uniform rf electric field homogeneity near the center of the ICR ion trap (both improved even further by recent ICR cell designs); and theoretically optimal excitation and mass selection produced by stored-waveform inverse Fourier transformation (SWIFT). (d) External ion accumulation allows efficient coupling of atmospheric pressure continuous ionization sources (notably electrospray ionization) with pulsed high-vacuum FT-ICR MS excitation/detection, and injection of externally trapped ions through the “magnetic mirror” into the ICR ion trap has been optimized based on ion trajectory simulations. (e) MS/MS can be performed either inside (e.g., electron capture dissociation, infrared multiphoton dissociation) or outside (e.g., collision-induced dissociation, electron transfer dissociation) the ICR ion trap. (f) Finally, FT-ICR MS instrumentation and experimental event sequences have benefited from striking parallels to prior nuclear magnetic resonance spectroscopy developments. Similarly, non-ICR FT MS development (notably the orbitrap) has benefited from FT-ICR precedents.

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1. Introduction

This article represents a personal perspective of the development of Fourier transform mass spectrometry (FT MS), primarily FT ion cyclotron resonance MS. Literature references are therefore illustrative, but not comprehensive. For example, of the dozens of reviews of various stages and aspects of FT-ICR MS technique development and applications, only a few are cited here: early history [1,2], the “teenage” years [3,4], and milestones through the year 2000 [5].

The initial conception of the FT-ICR experiment in 1973 [6] was inspired by analogy to FT-NMR, just as FT-NMR was inspired by prior FT-infrared spectroscopy. It is interesting to note that FT-NMR was introduced [7] almost immediately after the appearance of the Cooley–Tukey fast Fourier transform algorithm [8], which reduced the computational time for discrete Fourier transformation by a factor of (initially) 30 and later 1000. Also, it is not accidental that both FT-ICR MS co-inventors were initially trained as NMR spectroscopists, for reasons that will become clear in Section 2.6.

2. Stages in FT-ICR MS development

2.1. Conversion of ion mass-to-charge ratio to frequency

The first stage in any Fourier transform spectroscopy experiment is to produce and sample a temporal (NMR, MS) or spatial (IR)

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interferogram at equally spaced intervals, so that its discrete Fourier transform yields a frequency-domain spectrum [9]. In mass spectrometry, the property of interest is ion mass-to-charge ratio, m/q , so the first step is to convert m/q to frequency. In the ion cyclotron, that conversion is achieved by placing a moving ion in an applied static magnetic field, B_0 , so that the ion rotates at its cyclotron frequency, ω_c :

$$\omega_c = \frac{qB_0}{m} \quad (1)$$

In mass spectrometry, charge is usually expressed as the number, z , of elementary charges (e) per ion, so that Eq. (1) becomes

$$\omega_c = \frac{zeB_0}{m} \quad (2)$$

The principle behind Eq. (1) was first applied in Thomson's 1897 determination of the m/q ratio of the electron [10]. Subsequent stages in ion cyclotron configurations are shown in Fig. 1. Lawrence and Livingston [11] realized that ion cyclotron frequency is independent of ion speed. They therefore formed ions in one of two opposed D-shaped electrodes, with an accelerating electrostatic potential applied between the electrodes. As soon as the ions crossed from one "D" electrode to the other, the sign of the electrostatic potential was reversed, so that when the ions crossed back to the original "D" electrode, they were further accelerated to higher speed. The potential was switched back and forth so as to continue accelerating ions each time they crossed the gap between the two "D" electrodes, thereby achieving acceleration that would otherwise have required a vastly longer (and higher voltage) linear accelerator.

Analytical instruments exploited cyclotron rotation differently. In the "omegatron" (Fig. 1), ions are irradiated by a fixed-frequency rf oscillating electric field in an applied magnetic field. One can think of the linearly oscillating rf field as the sum of two counter-rotating equal-amplitude components, one of which accelerates ions of that cyclotron frequency continuously forward in their orbits while leaving ions of other m/z values unaffected. Thus, "resonant" ions (i.e., ions whose m/z value matches that of the applied rf electric field) spiral outward until they hit a "collector" electrode, and the detected charge is proportional to the number of those ions. By keeping the rf excitation frequency

constant, and slowly scanning the applied magnetic field, ions of successively higher m/z could be detected [12]. The omegatron was suitable for "residual" gas analysis (i.e., simple low molecular weight gases).

Wobbschall instead measured the power absorption by resonantly excited ions, again at fixed marginal oscillator frequency as the applied magnetic field was swept slowly through resonance (see Fig. 1) [13]. His design was later commercialized by Varian Associates, and applied by John Baldeschwieler's group to measurement of ion–molecule reaction pathways, rates, and equilibria [14]. Baldeschwieler (who also started his independent research career in NMR) realized that cyclotron acceleration of ions of a given m/z ratio could increase their speed (and thus reactivity), and subsequent scanning across the full m/z range provided a means for detecting and quantitating ion–molecule reaction product ions. By analogy to NMR, the experiment was initially called "double resonance" (i.e., initial resonant excitation of reactant ions followed by resonant frequency scanning to detect product ions) [15]. Today, such experiments would be called "tandem" MS or MS/MS, and are typically used to fragment large ions by collisions with inert neutral small gas atoms or molecules (as in gas-phase peptide or protein sequencing).

2.2. Coherent excitation followed by broadband detection: the "multiplex" advantage

FT-ICR MS experiments are conducted at fixed applied magnetic field. Ion cyclotron motion is initially spatially incoherent (i.e., ions are distributed randomly about a small-radius orbit). Coherence is produced by applying an rf oscillating electric field excitation, during which each packet of ions of a given m/z spirals outward to a final orbital radius of a few centimeters. The first FT-ICR MS experiment (Fig. 2) employed a single-frequency rf pulse of duration, T , which could excite ions whose cyclotron frequencies spanned a (narrow) range of $\sim 0.1/T$ Hz (see Fig. 3) [6]. For the next dozen years, broadband excitation was produced by a linear frequency sweep [16,17]. The most versatile excitation is produced by a time-domain voltage generated by inverse Fourier transform of the desired frequency-domain excitation profile (stored waveform inverse Fourier transform, or SWIFT (see Fig. 3)

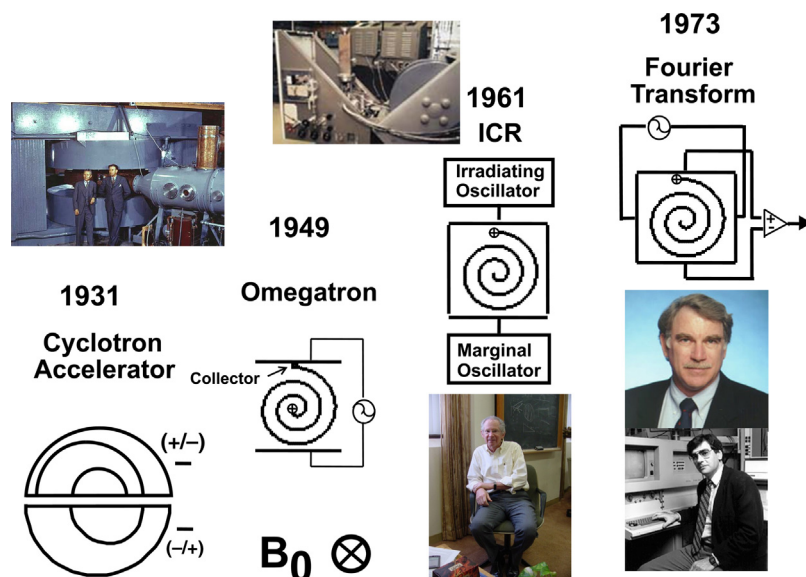


Fig. 1. Stages in cyclotron development history. The individuals shown are Lawrence and Livingston (cyclotron accelerator) [11], John Baldeschwieler (marginal oscillator) [14], and Melvin Comisarow/Alan Marshall (Fourier transform) [6]. Each stage represents a different experimental configuration/event sequence (see text).

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