LOW COST HIGHER FREQUENCY RF POWER SUPPLIES FOR QUADRUPOLE ION GUIDES IN FT-ICR INSTRUMENTS WITH EXTERNAL ION SOURCES

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INTRODUCTION

In the past, various external ion source types have been interfaced to FT-ICR MS instruments using a diversity of ion guide designs. Some ion guide design considerations include:
(a) efficient guiding of ions from a low magnetic field (~ 0.01 T) into a high magnetic field (*e.g.*, 3+ T) ICR cell
(b) overcoming the magnetic mirror effect
(c) reducing or eliminating time-of-flight (TOF) effects
(d) RF or ion guide parameter optimization for *wide mass range* and high ion transfer transmission efficiency

EXTERNAL ION SOURCE FT-ICR MS ION GUIDES

(a) RF only quadruple and multipole ion guides: First reported, used, and theory of operation discussed by McIver and co-workers [1] beginning in the mid 1980's.
Strength: relatively simple mechanical design (quadrupole), capable of "very high" ion transmission efficiency
Weakness: mass dependent ion transmission efficiency, hard to vary frequency at will if using LC tank circuits

(b) Electrostatic ion guide lenses: First reported and theory of operation first discussed by Kofel *et al.* [2] in 1985
Strength: little or no mass dependent ion transmission efficiency
Weakness: Complex array of flight tubes, lens elements, and decelerators

(c) Other methods: wire ion guides [3]; ions or electrons guided by stray magnetic field lines [4]; stacked-ring electrostatic ion guides [5]; hybrid RF multipole/electrostatic ion guide [6]; off-axis injection into ICR cells [7].

A more complete discussion on ion guides is provided in our recent review article [8].

GOAL

Our goal was to acquire GC/FT-ICR mass spectra from external ion source electron impact ionization (EI) and/or chemical ionization (CI) experiments that included m/z range below 100. Our two FT-ICR instruments share a common 9.4 tesla superconducting magnet and are equipped with external ion sources (EI/CI [9] and ESI) and quadrupole ion guides. The original manufacturer's 1.1 MHz (optional 2.5 MHz for GC side only) RF supply yields a low mass cutoff limit of ~m/z 100 at 2.5 MHz and is unacceptable for detection of low molecular analytes by external EI ionization/FT-ICR MS. To overcome the low mass cutoff of the quadrupole ion guide, we have constructed and evaluated higher-frequency (> 4 MHz) RF power supplies using low-cost components. The schematics (Figure 1), physical set-up (Figure 3), and mass spectral results (Figures 4-7) for the RF configuration(s) are presented.

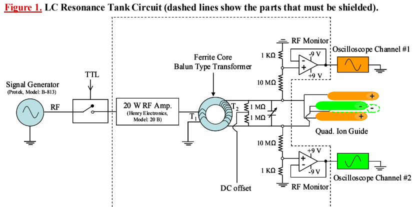


Figure 1. LC Resonance Tank Circuit (dashed lines show the parts that must be shielded).

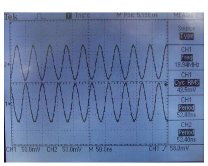


Figure 2. Read outs on the two legs of T_2 of transformer monitored on Tektronix TDS 210 oscilloscope using a home-built RF monitor.

EXPERIMENTAL

Circuit Designs:

1) LC Resonance Tank Approach: The design is based on the previously reported LC tank circuit [10]. The components of the circuit are shown in Figure 1. RF signals with desired frequencies are generated using a signal generator (Protek, NJ, Model: B-813). The output from signal generator is amplified by a fixed gain amplifier (Henry Electronics, CA, Model: 20 B) which derives the primary stage of a Balun type transformer. The stored energy in the primary stage (T_1) of the transformer is inductively transferred to the secondary stage (T_2) of the transformer (where a high voltage RF signal develops) through a ferrite toroidal core (Amidon Associates, CA). The secondary stage of the transformer is a part of the LC resonance tank circuit including capacitance of quadrupole ion guide and BNC cables.
The resonance frequency of the circuit is determined by total capacitance load (C_{total}) on the transformer secondary stage and inductance (L) of the secondary stage:

$$f = \frac{1}{2\pi\sqrt{L \times C_{total}}} \quad \text{equation 1}$$

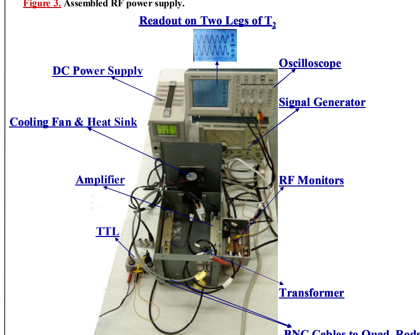
2) Brute Force Approach [11]: An alternative approach for generating high frequency voltages was explored using high power RF amplifiers. A 300 watts RF Ham radio amplifier was purchased for $450. A wave generator connected through a TTL controlled relay switch was used as the input to the amplifier. The output of the amplifier drove a transformer with a center-tapped secondary which produced the high voltage waveform along with its inverted waveform. The benefit of this approach is that a wider range of frequencies could be selected compared to LC resonance tank approach. However, several challenging problems arose including:

(a) The input impedance of the transformer must be approximately matched with the output impedance of the amplifier. 300 watts RF Ham radio amplifier is designed to shut off when the impedance of the load does not match the amplifiers output impedance. This impedance mismatch causes RF interruption.
(b) Other drawbacks include the size of the amplifier, heat generation and distorted waveforms resulting from mismatched impedances.

GC/FT-ICR MS & GC/FID:

Samples were injected on a 60-m {0.28 mm i.d., 1.0-µm cross bonded 100% dimethylpolysiloxane stationary phase coating} MTX-1 capillary column {Restek Corporation, Bellefonte, PA} housed in an SRI model 8610C GC equipped with flame ionization detector (FID) {SRI Instruments, Las Vegas, NV}. A home-built post-column splitter was used to direct the GC effluent to both the FID detector and to external ion source (EEI)/FT-ICR MS using transfer lines made from lengths MXT guard columns (Restek Corporation, Bellefonte, PA). The transfer line from GC to EEI was maintained at 185 ºC.
Mass spectra were acquired with an FT-ICR mass spectrometer equipped with an open-ended cylindrical Penning trap (IonSpec Corp., Irvine, CA) and recently upgraded 9.4 tesla superconducting magnet (Cryomagnetics Inc., Oak Ridge, TN).

Figure 3. Assembled RF power supply.



RESULTS and DISCUSSION

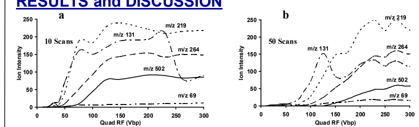


Figure 4. The quadrupole ion guide efficiency in (a) 7.0 tesla magnet and (b) 9.4 tesla magnet for fragment ions of FC-43 at RF frequency of 2.5 MHz.
Note: Commercially available RF frequencies (IonSpec Instrument) for the quadrupole ion guide: ~1.0 or 2.5 MHz
Comparing the NIST FC-43 mass spectral abundances [*e.g.*, m/z 69 (100%), m/z 219 (67%)] with the data in Figure 4 reveals severe mass discrimination towards low mass ions [*i.e.*, m/z 69 (~2%), m/z 219 (100%)] for quadrupole RF voltages >85 V_{bp}. Quadrupole RF voltages <60 V_{bp} modestly improved the ion guide efficiency for low mass ions (m/z <100) but at the expense of heavier ions (m/z >130) and much lower total ion signal. Experimental results suggest that higher RF frequencies are needed for efficient guiding of lower mass ions. Comparisons between Figure 4a and 4b reveal more sever effects of stray magnetic field in 9.4 tesla magnet on the ion transmission efficiency (*i.e.*, to yield the same ion intensity with 7.0 tesla and 9.4 tesla magnet, 5 more scans were needed when 9.4 tesla magnet was used).

Table 1. Bench test results of three types of ferrite toroidal cores.

Ferrite Toroidal Core (AMIDON part #)	A_L values (mH/1000 turns) (AMIDON data)	Capacitive Load on T_2 (pF)	T_1:T_2 (turns*)	Resonance Frequency (MHz)	Output Voltage (V_{pp})
FT-61-114	79.3	259	2:6	4.8, 7.5	350, 230
FT-61-114	79.3	259	2:6	3.0	440
FT-61-114	79.3	250	2:12	13.0	425
FT-61-114	79.3	130	2:6	12.0	300
FT-61-114	79.3	67	2:6	16.5	150
FT-61-114	79.3	67	2:12	7.8	425
FT-61-114	79.3	50	2:6	18.0	100
FT-67-114	25.4	250	2:12	26.0	50
FT-67-114	25.4	67	2:6	23.3	65
FT-67-114	25.4	67	2:12	15	150
FT-77-240	3130	250	2:6	0.6-1.4	60
FT-77-240	3130	250	2:6	23	40

*To estimate the # of turns on T_2, the inductance (L) was calculated based on the total capacitive load and desired frequency (see equation 1). The calculated L was then used to estimate the # of turns using the following formula provided in an AMIDON Associates technical bulletin on Iron-Powder and Ferrite Coil Forms (December 2001): # of turns = 1000 $[L/A_L]^{0.5}$.

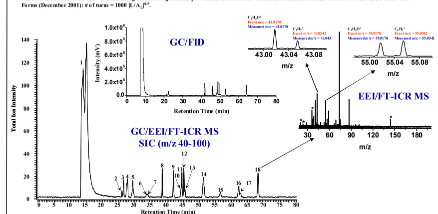


Figure 5. GC/FID and GC/EEI/FT-ICR MS of a 0.5 µL Grob test mixture (Supelco Analytical, Bellefonte, PA). Temperature program: 1 min at 40 ºC, ramp at 5 ºC/min to 180 ºC, 51 min at 180 ºC; Injection port temperature: 150 ºC; GC He head pressure: 15 psi. Split ratio: unknown (GC splitter not calibrated but the split ratio is variable using a manual needle valve). Quadrupole ion guide RF frequency: 5.5 MHz (DC offset: -42 V) (*: noise).
GC/EEI/FT-ICR MS peak identities: (1) Methylene chloride (solvent); (2) Impurity; (3) 2,3-Butanediol; (4) unassigned, (5) unassigned, (6) assigned, (7) unassigned; (8) Undecane; (9) 1-Octanol; (10) 2-Ethylhexanoic acid; (11) Nonanal; (12) Decane; (13) 2,6-Dimethylphenol; (14) 2,6-Dimethyl aniline; (15) Dicyclohexylamine; (16) Methyl Nonanoate; (17) Methyl decanoate; (18) Methyl undecanoate. Note: unassigned .. mass spectra lacked high mass peaks for positive identification.

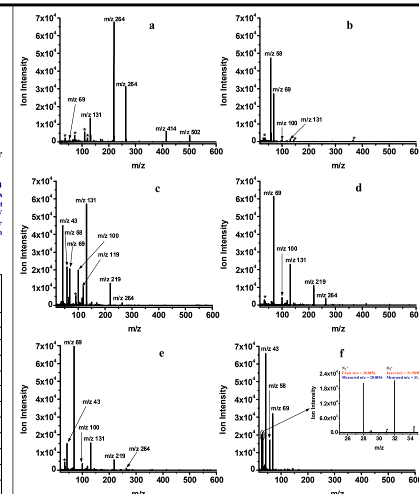


Figure 6. EEI/FT-ICR mass spectra (average of 10 scans using optimized parameters for high S/N ratio) of FC-43 and acetone acquired using quadrupole ion guide RF frequency of (a) IonSpec 2.5 MHz (DC offset, -10 V), (b) 3.2 MHz (DC offset, -33 V), (c) 4.2 MHz (DC offset, -25 V), (d) 4.6 MHz (DC offset, -33 V) , (e) 4.8 MHz (DC offset, -40 V), and (f) 5.8 MHz (DC offset, -40 V) (*: noise). The transformer ferrite toroidal core used (please refer to Table 1) was FT-61-114 with T_1:T_2 = 2:12.

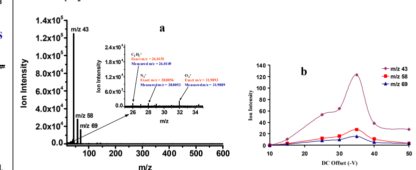


Figure 7. (a) EEI/FT-ICR mass spectrum (average of 10 scans using optimized parameters for optimal S/N ratio) of FC-43 and acetone acquired using quadrupole ion guide RF frequency of 10 MHz (DC offset, -35 V). (b) Effect of DC offset voltage on the ion intensity at 10 MHz RF frequency. The transformer ferrite toroidal core used was FT-61-114 with T_1:T_2 = 2:6.

COSTS (EXCLUDES LABOR & DEVELOPMENT)

Table 2. RF power supply parts list and cost.

Part Name	Price (USD)	Vendor	Comments
Ferrite toroidal cores	2.00	AMIDON Associates	FT-61-114 for frequency range of 3.0-10.0 MHz
20 watt amplifier	475.00	Henry Electronics	Model: 20B
DC power supply	97.00	MPJA	0-120 V @ 3A Benchtop Power Supply
Cooling fan	2.00		
Signal generator	400.00	Protek	Model: B8110
16 Gauge insulated copper wire	77.20/1383 feet	ESSEX	
RF Monitor	10.00	Home-built	
TTL switch	20.00	Home-built	
Total Cost	986.20		

CONCLUSIONS

• As expected, there is a significant difference between 7.0 tesla and 9.4 tesla magnet for ion transmission efficiency and 2.5 MHz (highest available on IonSpec Instrument) RF frequency is too low to transfer, trap, and detect ions below m/z 100.

• Current results show that the home-built RF power supply based on LC tank circuit can be used to efficiently guide and transfer ions from external ion source to ICR cell with m/z as low as 26.

• Due to impedance mismatching between transformer input and Ham radio amplifier output, we were unable to utilize the brute-force approach for building a high frequency and high voltage RF power supply.

• With the current setup we are able to generate different RF signals (*i.e.*, frequency range of 3-10 MHz) with stable ion trajectories, however, we are not able to change the frequency "on-the-fly" during the ion transmission event. We plan to explore using digital RF input as a means of improving mass spectral appearances (*i.e.*, wider mass range ion transmission) by averaging signals from two or more mass spectra.

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