Enhancing The Sensitivity of Miniaturized Quadrupole Mass Spectrometers

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Abstract -A novel two stage mass filter where the first stage operates in DC/RF mode and second in RF only mode is proposed. This design can be characterized by very high mass resolution and may not require high precision mechanical and electronic design. An ion detector by integrating a VLSI chip with a Faraday cup is described. Extremely low biasing currents, differential and narrow frequency band operation resulted in significant improvement of the signal to noise ratio.

I. INTRODUCTION

Mass spectrometers are used for the fast analysis of a wide range of chemical compounds. Unfortunately, conventional mass spectrometers are large, heavy and have high power requirements. The optimum solution would be to have a miniaturized portable mass spectrometer. There is a significant effort to reach this goal in many leading research institutions. Miniaturization has several advantages but also several drawbacks. Two major drawbacks are: (1) reduced resolution, (2) smaller ion current to be detected. C. Henry in [26] presented a review of these efforts.

II. OPERATION OF THE QUADRUPOLE MASS SPECTROMETER

Mass spectrometers are based upon the trajectory of ions through an electromagnetic field. There are about 20 different types of mass spectrometers, but the prime candidates for miniaturization are the multi-pole mass filter type [16][3][18][15] and the planar ion trap type [4]. For this research we have chosen the multi-pole mass spectrometer, illustrated in Figure 1, which can be easily implemented in double filter form.

The potential distribution in the multi-pole mass spectrometer with four hyperbolic rods can be approximated by:

$$\varphi(x,y) = \varphi_o \frac{x^2 - y^2}{r_o} \qquad (1)$$

where $\varphi_o = U + V\cos(\omega t)$

The biasing voltage, φ_o, is function of both the DC (Direct Current) voltage, U, and an RF (Radio Frequency) signal of radial frequency $\omega = 2\pi f$. Ion movement is described by the set of differential equations:

$$\frac{d^2x}{dt^2} + [a + 2q\cos(\omega t)]x = 0; \quad \frac{d^2y}{dt^2} - [a + 2q\cos(\omega t)]y = 0; \quad \frac{d^2z}{dt^2} = 0 \qquad (2)$$

where

$$a = \frac{8eU}{m r_0^2 \omega^2} \quad \text{and} \quad q = \frac{4eV}{m r_0^2 \omega^2} \quad \text{note} \quad \frac{a}{q} = \frac{2U}{V} \qquad (3)$$

and m is ion mass, e is the electron charge, and $2r_o$ is the distance between hyperbolic rods.

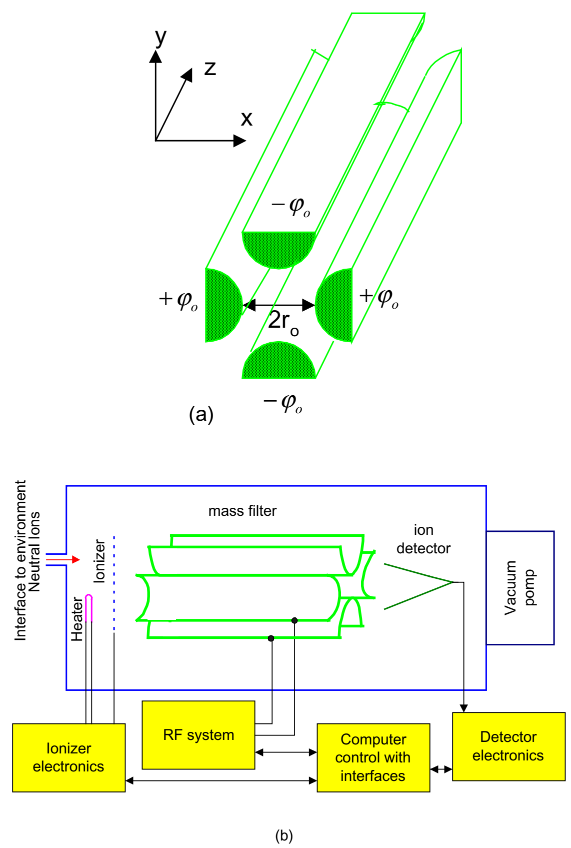
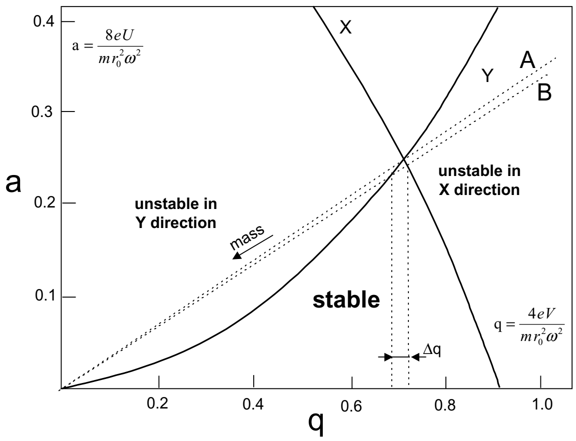
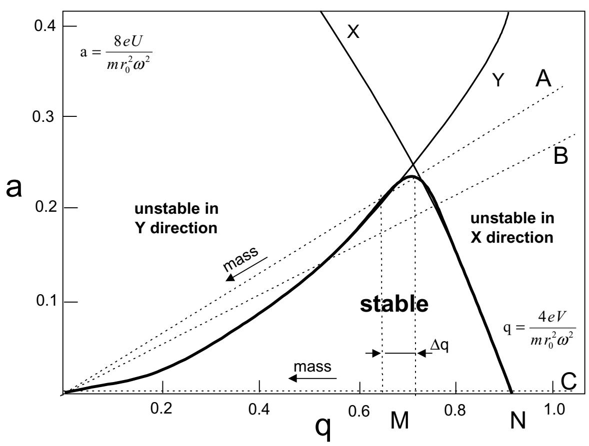


Fig. 1. Multi-pole Mass Spectrometer. (a) quadrupole mass filter and (b) multi-pole mass spectrometer implementation.



(a)



(b)

Fig. 2 Filtering action of multi-pole mass spectrometer (a) theoretical curves for stable operation and (b) actual stable region, as affected by mass filter dimensional tolerances and other undesirable effects, such as initial random radial velocity or the proximity effect.

Figure 2a shows the stable region, delineated by curves X and Y, in which ions are held in the space between the quadrupoles. To the right of curve X, light ions hit the left or right poles and are neutralized. To the left of curve Y, heavy ions hit the upper or lower poles and are neutralized. Fixed values of the DC voltage, *U*, and the RF amplitude, *V*, yield a constant a/q ratio (Equation 3), so the operating regime of the mass filter can be drawn as a straight line of slope a/q that passes through the origin, such as line B in Figure 2a. The segment of the line that falls to the right of curve Y and to the left of curve X corresponds to the range of ion masses that are stable within the quadrupole filter.

From Equation 3, and noting that $\omega = 2\pi f$, we can see that this single mass and the corresponding RF amplitude are given by:

$$m = 0.1384 \frac{V}{f^2 r_o^2} \qquad \text{(a)}$$

$$V = 7.225 m f^2 r_o^2 \qquad \text{(b)} \qquad (4)$$

where frequency f is given in MHz, dimension r_o in cm, and ion mass m in atomic mass units (amu). The equation (4) describes the intersection of X and Y curves.

In a real quadrupole, the value of r_o varies slightly due to less-than-perfect fabrication techniques. Also, initial radial velocities are random and ion-ion repulsion (the proximity or space charge effect) causes ion trajectories to deviate from the assumed behavior.

The reduction in area between the poles means the number of detected ions will be reduced, so smaller ion currents would be detected. To improve the signal/noise ratio, the number of detected ions could be increased by using higher efficiency ionizers or by using a larger number of poles [16][15]. The most direct approach to improving the signal/noise ratio would be to increase the sensitivity of ion detectors.

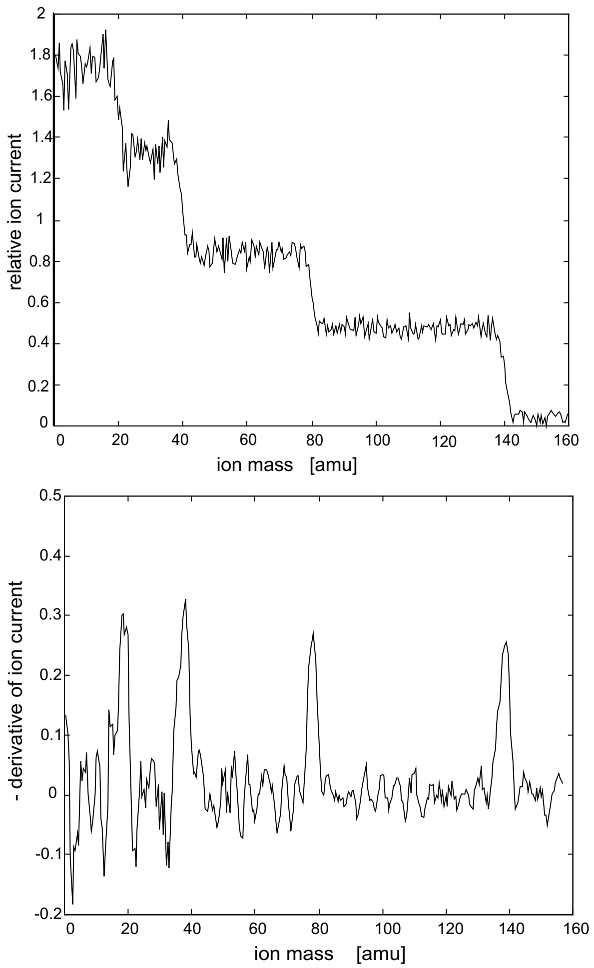
Electron multipliers use an avalanche multiplication phenomena that has an inherent noise component. This limits the minimum ion current that can be detected. In this research, we propose development of a VLSI amplifier with a 10^7 to 10^8 current gain, integrated with a Faraday cup. The sensitivity of such system should be about 100 to 1000 times greater than electron multipliers, and, in contrast to an electron multiplier, the gain should be stable.

III. TWO STAGE MASS FILTER

The first task is to improve the design of the mass filter. As described later, our proposed mass filter will consist of a traditional RF/DC multi-pole filter followed by an RF-only filter. This design will make the miniature mass spectrometer less sensitive to dimensional fabrication errors.

Fig. 2(a) shows the theoretical stability diagram for a quadrupole mass spectrometer. The slopes of the operating lines are set by choosing the proper ratio between the DC and RF signals (see Eq. (3)). In the ideal case (line A), U/V=0.1679. In practical applications, the slope must be slightly less (see B line on Fig. 2(a)). Note how sensitive the selectivity of the mass filter is to the ratio of a/q or to the ratio of DC voltage, *U,* to RF voltage, *V*.

Quadrupole operation in RF-only mode is sometimes used [5][10][7][18]. In this mode of operation *U*=0 (a=0) and the operating line lies on the q axis (see line C in Fig. 2(b)). The quadrupole assembly operates as a high mass filter. The threshold mass corresponds to the intersection of the X curve and the q axis. Ions that are lighter than this mass strike the poles and are neutralized, while heavier ions are retained between the poles. This type of mass filter is relatively insensitive to dimensional tolerances. Fluctuations in mechanical tolerances may shift the threshold or it can make the threshold less sharp. The shift in the threshold can be easily corrected if dimensional errors are stationary, so the filter can be recalibrated.

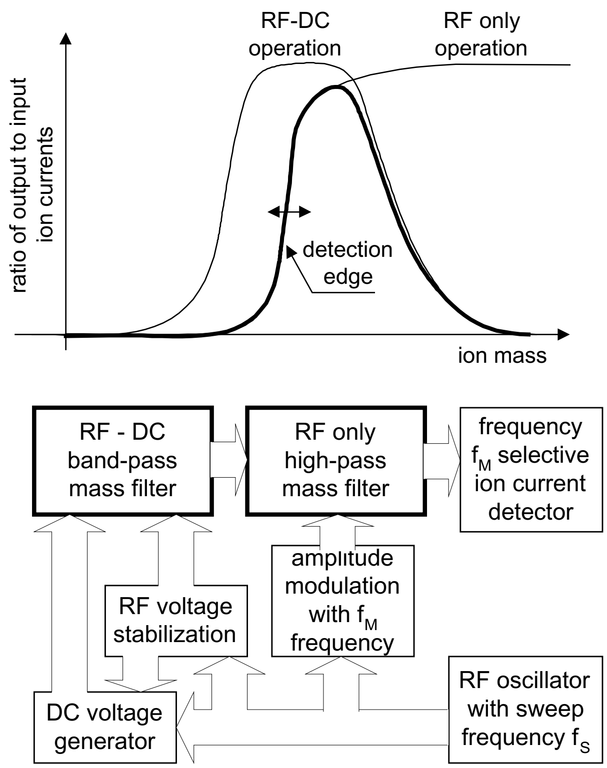


(a) (b)

Fig. 3. Typical output current in mass spectrometer operation in RF only mode (a) measured current and (b) derivative of the current.

Figure 3(a) shows a typical ion current versus mass for an RF-only mass filter. The measured current consists of ion currents for all ions with heavier mass than a threshold. The curve in Fig. 3(b) is the derivative of the curve in Fig. 3(a). In Fig. 3(b), detected ions appear as peaks, and the spectrum is very similar to those that would be obtained from a conventional RF/DC quadrupole.

The RF-only mass filter works well only for heavier masses because the step height for a heavy ion (right hand side of Fig. 3a) is a large fraction of the total detected ion current. For light ions, the step height may be too small as compared to the total detected current, and the signal/noise ratio may be lower, especially if a large number of ions are present. This problem can be solved using a two stage mass filter. The first filter operates in RF/DC mode. The ratio of the RF and DC voltages is set for a relatively wide mass range. The second filter operates in RF-only mode, with a threshold mass near the center of mass range of the first filter. The combined filtering action of these two stages is shown in Fig. 4a. The function of the first filter is to narrow the range of masses that enter the second filter. This improves the detection of a small, light ion current on a large background current by eliminating ions with larger masses that cause background noise in the RF-only mass filter.



(a) (b)

Fig. 4. Double filter mass spectrometer with cascade of band-pass and high pass mass filters: (a) characteristics and (b) block diagram.

The system block diagram shown in Fig. 4(b) is capable of measuring directly the derivative of the ion current with a respect to the threshold mass. This is possible by introducing the AC amplitude modulation in the RF-only high-pass mass filter. Such an approach has two advantages. First, it is possible to measure directly the derivative of the high-pass filter, thereby generating results that are readily comparable to conventional quadrupole mass filters. Second, this approach allows the use of AC detector circuits that have much better signal to noise ratio than DC circuits. While the modulation technique is used for the detection of a current corresponding to a given mass, both filters are tuned simultaneously and the entire mass spectrum is swept.

IV. INTEGRATED HIGH CURRENT GAIN ION DETECTORS

It was shown already that many parameters of electronic system can be significantly improved when a dedicated VLSI chip is designed [2][23][24]. We propose to build an integrated Faraday cup with a VLSI current amplifier. This should greatly increase detector sensitivity, thereby overcoming the problem of small ion current. One way to increase the spectrometer sensitivity is to use a multi-pole array design [15]. The 4 X 4 pole array has 9 channels between the poles, so the ion collection area is 9 times greater than the conventional quadrupole design. However, there are several anticipated problems with this design. Each channel in the multi-pole array, due to dimensional and electrical tolerances, is expected to have slightly different mass filtering characteristics. Since the detected signal is the sum of the ion currents from all of the channels, the cumulative effect of all of the errors in all of the channels will cause imprecise mass filtering. The multi-channel design also complicates focusing ion beams onto a detector.

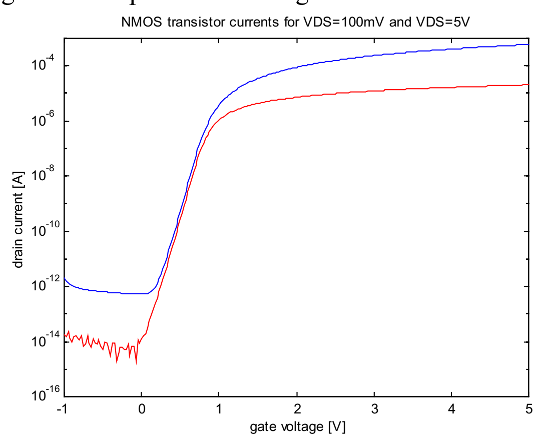
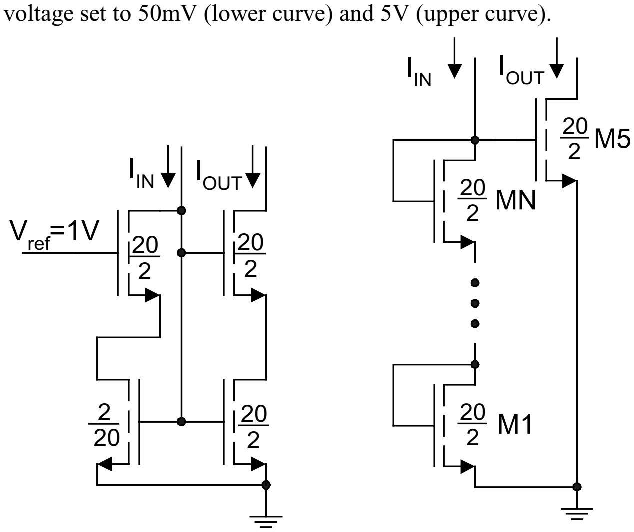


Fig. 5. Measured integrated NMOS transistor characteristics in low current range with gate voltage sweep from -1 to +5 volts and drain voltage set to 50mV (lower curve) and 5V (upper curve).



(a) *(b)*

Fig. 6. Asymmetrical low current amplifiers: (a) linear amplifier and (b) logarithmic amplifier.

The most promising approach is to use a quadrupole mass filter and increase the low current sensitivity of the detector. Several approaches will be investigated, including: (1) low DC current measurement with a Faraday cup and an integrated VLSI amplifier, (2) amplitude modulation of the RF signal and narrow band detection to increase signal to noise ratio, (3) the use of beam deflection and a two piece Faraday cup to provide an ac signal to an integrated VLSI amplifier (Figure 8a), and (4) the use of a logarithmic current amplifier to allow the detection of a wide range of ion currents.

Figure 5 shows typical characteristics for an NMOS transistor, with channel length L=2µm and channel width W=4µm, fabricated with MOSIS 2µm n-well process, as measured in the low current region. Note, that with a small drain voltage, the transistor can correctly operate at drain currents as low as 10fA (10^{-14} A). Such low current operation is not possible for a larger drain voltage where the hot carrier phenomenon [21] leads to larger leakage currents in the range of 1pA (10^{-12} A). The hot carrier phenomena could be eliminated by using special low voltage design. In such designs all drain-source voltages must be lower than corresponding energy gap and trap levels. Several such low current and low voltage designs are presented in Figure 6.

Simulation results for these circuits are shown in Fig. 7. Note that for the circuit on Fig. 6(b), with 3 transistors in cascade, the gain in 1pA range is about 100,000,000 or 10^8. The concept of an integrated Faraday cup and VLSI amplifier is not new [1][9][2], but previous detectors were designed to measure the spatial resolution of an ion beam and were not designed for low current detection.

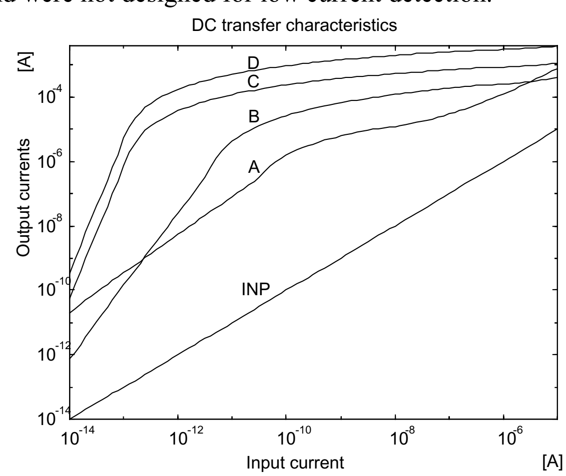


Fig. 7. SPICE simulation of DC transfer characteristics of several circuits for A - circuit of Fig. 6(a), B - circuit of Fig. 6(b) with cascade of 2 transistors, C - circuit of Fig. 6(b) with cascade of 3 transistors, and D - circuit of Fig. 6(b) with cascade of 3 transistors and with W/L of M5 changed to 100/2.

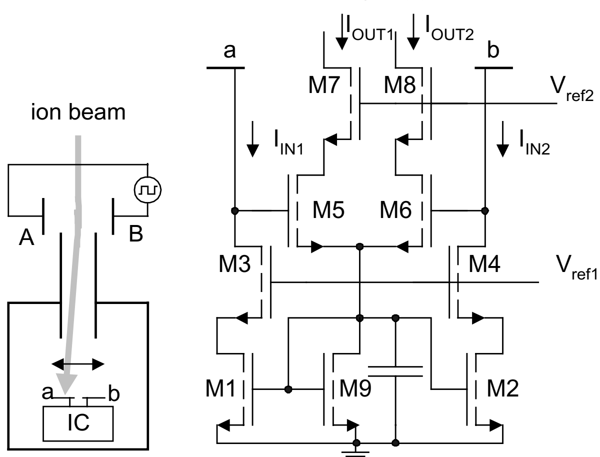
V. IMPROVEMENT OF SIGNAL TO NOISE RATIO

High stable gain is the only one side of the story. Often more important is the signal to noise ratio. In this respect, the VLSI ion detector is much superior to the electron multiplier in which the noisy avalanche multiplication phenomenon is employed. The MOS transistor has three major noise components: thermal noise, shot noise and flicker noise [26]. Thermal noise is associated with series transistor resistances and it is negligible. The shot noise and the flicker noises are function of drain current and in the subthreshold conduction mode may be expressed as:

$$I^2_{D\_shot} = \frac{8kT}{3} g_m \Delta f \approx 2qI_D \Delta f$$

$$I^2_{D\_flicker} = \frac{K_F I_D^{A_F} t_{ox}}{\varepsilon_{ox} L^2} \frac{\Delta f}{f} \qquad (6)$$

where k is Boltzmann constant, T is absolute temperature, Δf is frequency bandwidth, g_m is transconductance, q is electron charge, $K_F \approx 10^{-26}$ is flicker noise coefficient, $A_F \approx 1.2$ is flicker noise exponent, L is channel length, t_{ox} is oxide thicknesss, ε_{ox} is permittivity of oxide, and f is frequency. Both noise components decrease with transistor current and increase with amplifier bandwidth. Flicker noise can be also reduced by increasing channel length L, by increasing operation frequency f, and by decreasing oxide thickness t_{ox}. Note that for DC operation ($f \rightarrow 0$) flicker noise becomes very large and dominates. Further improvement and elimination of induced noise (from the surrounding electromagnetic field) is possible in the AC differential mode operation as in the circuit shown in Fig. 8(b).



(a) (b)

Fig. 8. Integrated chopped ion detector: (a) chopping concept and (b) symmetrical amplifier with automatic adjustment of polarization currents.

Most high gain integrated circuit amplifiers use symmetrical modes of operation in the input stages. This leads to elimination of many undesired effects such as temperature effects, long term parameter drift, and common mode signals, which often introduce large noise signals. A similar concept can also be applied to a very low level ion current detector. This concept is illustrated in Fig. 8(a). The ion beam is slightly deflected by an AC signal applied to electrodes A and B. As result, the differential current component occurs on inputs a and b of the integrated differential amplifier (Fig. 8b). The solution shown in Fig. 8 has many advantages. First, a differential mode of operation is used. This allows the use of AC amplification, which is less sensitive to parameter and temperature fluctuations. Furthermore, by chopping the ions at high frequency, the amplification can be moved to a higher frequency range where the flicker 1/f noise is much lower.

VI. RF CIRCUITS

Measurements of ion masses are normally carried out by fixing the RF frequency for a range of masses and then by sweeping the RF and DC voltages. In the case where r_o = 0.33cm, f=3.3MHz, and mass range is from 1 to 300 amu, the required RF voltage (eq. 4(b)) would be from 7.225V to 2167.0V and required RF power (proportional to V^2, see eq. 5) changes 90,000 times! Such an approach is very difficult to implement, therefore typical mass spectrometers operate in much smaller amu ranges. A different approach would be to keep the RF voltage constant, for example 100V, and change only frequency from 11.764 MHz down to 0.6792 MHz for full mass range from 1 to 300 amu.

The second approach is much easier to implement. This would simplify the control circuitry by eliminating the need for precise RF voltages over a wide range. The frequency can be precisely controlled using the PLL (Phase Lock Loop) concept that employs a crystal oscillator with a fixed stable frequency and a digitally-controlled frequency divider. A disadvantage of such an approach is that the detected ion mass is a nonlinear ($1/f^2$) function of frequency. The control software can be designed to overcome this problem. If r_o is reduced from 0.33 cm to 0.1 cm the required RF voltage is reduced from 100V to 10V, and this reduces RF reactive power 100 times. Another approach is to design a dedicated peak detector employing the concept shown in Fig.9.

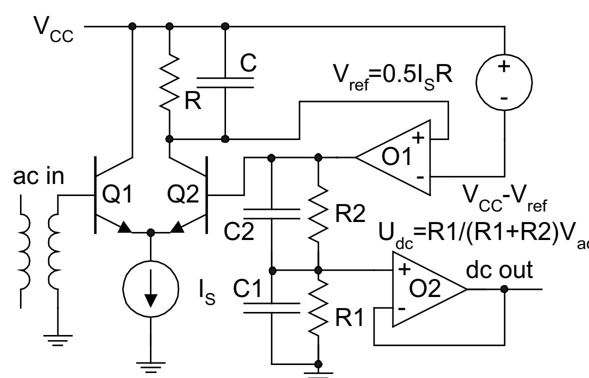


Fig. 9. Circuit diagram of temperature-compensated, accurate, high frequency, peak detector.

VII. IONIZER DEVELOPMENT

There are a number of ionization techniques, but the majority of commercial mass spectrometers use electron impact (EI) ionization. In this technique, electrons are boiled off a hot filament and accelerate, in vacuum, toward an anode. Sample gas molecules are ionized by the impact of these electrons. A negatively charged ring will then pull the positively charge ions towards the entrance of the mass filter. Some mass spectrometers have been used to detect negative ions, but the majority of mass spectrometers are designed to detect only the positive ions.

Brown [6] found that the ionization probability for a number of gasses is at a maximum at an electron energy near 70 eV. Consequently, 70 eV has become the standard electron energy for EI mass spectrometers. This impact energy is substantially higher than a typical molecular bond energy (a few eV), so electron impact frequently causes molecular decomposition. Cracking patterns are sensitive to ionization conditions, but the use of a standardized electron energy has led to the development of a substantial body of literature [13][14] that may be used to interpret mass spectra. The second most common ionization technique is chemical ionization (CI). This technique uses two gasses; a reactant gas, and a sample gas. There are several varieties of CI, but the general approach is to ionize the sample gas by mixing it with an ionized reactant gas. The ionization of the sample gas in CI is less energetic than in EI, so there is less fragmentation of the sample gas molecules. This can be an attractive means of analyzing large, complex, organic molecules. Chemical ionization relies on gas phase molecular collisions, so the ionization section must be operated at a higher pressure than the mass filter section, which operates in the molecular flow regime.

Harrison [8] compared the ionization efficiencies of EI and CI and found, at the same mass filter pressure under typical operating conditions, that CI will generate substantially more ions. Poths and Chamberlin [19] used a microwave plasma ion source [20] to measure isotopic distributions of Kr and Xe in a gas stream that was predominately argon.

VIII. CONCLUSION

The proposed design is expected to increase sensitivity and resolution 100 to 1000 times compared to conventional mass spectrometers. This type of ion detector, of course, will more than offset the potential ion current loss due to miniaturization.

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