Instrumentation for Negative Ion Detection

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The instrumentation and practical circuitry required for the detection of negative ions exiting the mass analysis section of a mass spectrometer is examined. The potentials needed to bias the electron multiplier when detecting negative ions from a low ion-energy mass spectrometer, e.g., a quadrupole, are contrasted with the biasing requirements of a mass spectrometer having high ion-energies, e.g., a magnetic sector.

Methods of decoupling the biasing high voltage on the signal lead of the multiplier in pulse counting measurements are discussed in detail so that normal, ground referenced input, pulse preamplifiers may be used. Easily understood, practical rules for determining the values of circuit components are given together with a simplified theory of transferring pulse signals from multiplier collector to pulse preamplifier.

The changes in circuitry needed when attempting to detect ions by current measurement methods from an electron multiplier are detailed. The effects of leakage currents into the input of the current preamplifier and their avoidance by using triaxial shielding on vacuum feedthroughs are explained. The article suggests possible methods of decoupling the high voltage referenced input and the ground referenced output of a current measuring preamplifier.

Introduction

The instrumentation required to detect negative ions is partly determined by the source of those ions but largely by the signal-handling method to be used; that is, is the signal output in pulse counting or analog current form? Negative ion production is usually via an electron attachment process where a large electron population is thermalized by admixing a high pressure of some diluent gas with the sample molecules. This creates two problems for mass spectrometric analysis and detection. First, the excess electrons have the same charge sign as the ions of interest, and a suitable separation must be effected between them before the ions can be detected. Second, the high gas pressure of the ion source must be interfaced to the low pressure requirements of the mass spectrometer.

Reducing the ionizing chamber's gas pressure to something acceptable to the mass spectrometer means placing a barrier between the two sections pierced with a small diameter orifice. The charac-

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teristic dimensions of this orifice and the gas flow rate through it, frequently produce conditions where the transit time of the electrons through the orifice is less than their diffusion time to the walls under the prevailing diameter, pressure, and space charge conditions. The orifice then acts as a partial separator of electrons and negative ions. For electrons that are not so separated, the common practice is to induce perturbing trajectories with small magnets ahead of ion focussing elements causing the electrons to spiral to the vacuum chamber walls. This is usually sufficient to eliminate electron induced noise from the system, particularly if the electron multiplier is physically isolated from the chamber in which the excess electrons are being dumped.

Detection of Negative Ions

For the detection of negative ions, the importance of establishing complete circuitry, that is, ensuring that dc voltage and current returns and ac bypasses exist, cannot be overemphasized. The precaution is necessary, of course, for positive ion detection, but errors seem more common in nega-

tive ion circuitry design presumably because of the unusual bias voltages required.

Detectors fall into two classes; the passive ion collection cup directly connected to an electrometer capable of measuring extremely small currents; and the active electron multiplier in which an incident ion is converted into a large number of electrons. The latter device allows the use of either pulse techniques or fast preamplifier/electrometer combinations increasing the system sensitivity and speed of response.

Faraday Cups

The mechanical and electrical characteristics of effective Faraday cups for positive ion detection are established in the literature. The details largely concern the suppression of secondary electrons created by the ions impacting into the surfaces of the cup. When detecting positive ions, loss of these electrons from the measuring circuit produces a false increase in the true ion current. When detecting negative ions the loss causes a false reduction in the true ion current. For a poorly designed Faraday cup, electrons may be ejected and lost at the same rate that negative ions impact. The measured ion current under these conditions would be zero.

Secondary electron suppression may be accomplished by the use of ad hoc magnets or by designing the Faraday cup as a tube with a narrow entry for ions and a closed far end. Apart from ensuring adequate screening of the signal cable there is little electronic information that is needed to give ion detection.

Electron Multiplier

As the name states, this device multiplies electrons and is, therefore, not symmetrical in its biassing requirements for positive or negative ion detection. The energy of the impinging ion must be high to induce secondary electron emission from the cathode or first dynode. But no matter what is done to the multiplier potential at the front surface to induce this ion energy, the electrons must see an increasing positive potential from first dynode to anode or final collector. It must be carefully noted that the potential does not increase only from first to last dynode but also between the last dynode and collector. This point is a frequent source of error in connecting multipliers for negative ion detection. Since the anode is a Faraday cup detector of electrons, all the considerations on Faraday cups are applicable in determining its design.

Figure 1 shows the typical potentials and interconnections applied to an electron multiplier attached to a mass spectrometer having a low ion energy, e.g., a quadrupole mass filter. This elaboration is unnecessary for magnetic mass spectrometers with ion energies of 5 to 8 kV at the mass of interest as the effective ion energy to the multiplier is the algebraic difference between the mass spectrometric ion accelerating voltage and the first dynode potential. As long as this exceeds, say 1 to 2 kV, with a sign identical to the ion under analysis, ion impact will cause secondary electron emission.

The +3 kV bias shown on the first dynode is larger than required for adequate secondary electron production from negative ions. It has been demonstrated that 600-800 V impact energy is sufficient. The +3 kV is recommended, however, when the possibility of reduced ion collection exists due to the mechanical arrangement of the mass spectrometer. For example, the off-axis multipliers used by quadrupole manufacturers can lead to lower collection efficiency at low first dynode potentials.

The resistor chain establishes a bias of approximately 150 V per dynode with the last dynode pegged at +5.8 kV. The collector is then placed at a positive potential above the last dynode by referencing the preamplifier to +6 kV.

Decoupling the Signal from the High Potential

Faraday cup detectors are unpolarized in general, and the signal due to ion current appears on a lead that can be at virtual ground for either ion sign. That is, the impedance of the signal source is very high, but it need not be more than tens of millivolts from ground potential at any time since signal currents are small and the input impedance of the preamplifier is relatively low. But as there are no bias potentials required, the output lead from the Faraday cup can be directly connected to any ground referenced picoammeter.
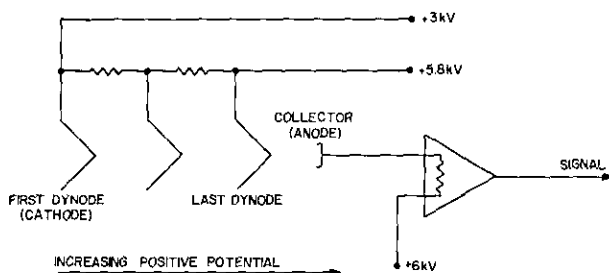

FIGURE 1.

Figure 1 shows that for an electron multiplier looking at negative ions, the collector is not only a high impedance source but is also at a high voltage with respect to ground. Most pulse and current preamplifiers are not manufactured to accept such large common mode potentials at their inputs and decoupling the signal from the dc voltage powering the electron multiplication process is a major concern in negative ion detection. This remains a problem even if the first dynode is reduced to a few hundred volts, for the collector will still be at a potential in excess of 2500 V. The methods used in decoupling are dependent on the signal handling techniques and before making circuit designs the user must have chosen either pulse counting or analog current as the preferred detection method for his work. With that primary decision made, the simple schematics shown in Figures 2 and 4 below will provide the necessary decoupling. The choice of the component values depends on the details of the circuit operation and the following explanation, while not electronically complete, allows the calculation to be made.

Pulse Counting

Figure 2 illustrates the basic schematic for pulse counting with an electron multiplier. The +6 kV power supply is connected to the multiplier resistor chain via R_1, the numerical value of which is determined by the current drawn through the resistor string and the potential difference desired between last dynode and collector. Typically, R_1 is 1 Mohm, causing a potential drop of approximately 170 V. The +3 kV voltage noted for the first dynode can be established either by a power supply or by using a high ohm resistor R_3 to
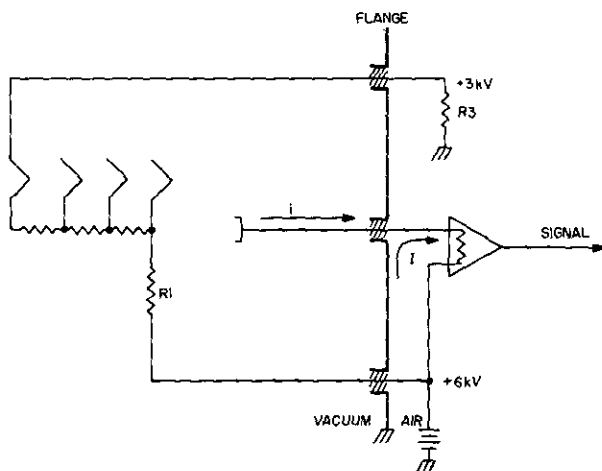

FIGURE 2.

ground. Usually a resistor is used and its value is made equal to the total resistance of the string across the multiplier including R_1.

The determination of the values of R_2 and C depends on a knowledge of some fundamental properties of transmission lines. First, let us consider the value of C. Any pulse signal cable between the multiplier collector and the pulse preamplifier needs protection from hum and "glitch" pickup that might be translated into pulses by the preamplifier. The common method is to use coaxial shielded cable to transfer the pulse train from the vacuum system to the preamplifier. Coaxial cables have a specification called the characteristics impedence which is typically 50 ohms for cable used in scientific instruments. That is, any length of coaxial cable viewed from one end and terminated at the other between central conductor and shield with a 50 ohm resistor looks like a 50 ohm resistor. This is approximately true no matter what frequency the cable is required to carry.

It is important therefore, to select a value of C that has a low impedence compared with 50 ohms at the frequency of operation because that impedance will act as a series resistor to the pulse train and reduce its voltage amplitude as seen by the preamplifier. But what is meant by the frequency of operation for a pulse counting circuit? It is not the number of pulses per second but rather that infrequency capability necessary to preserve the shape/voltage characteristic of the typical pulse to the preamplifier without excessive distortion. The theory is inappropriate for this text but one can arrive at a rule of thumb, that the required frequency capability is 10 times the maximum pulse counting rate to which the multiplier and preamplifier can respond.

Most multipliers used in mass spectrometers have a maximum counting rate of 1 MHz; the calculations of the value of C for 10 MHz as the required frequency capability, can be made using the equation

$$X_c = 1/2\pi f C$$

If one assumes that $X_c = 2$ ohms is sufficiently low to give tolerable losses, this equation gives $C = 0.003 \mu F$.

But why not make C very large and so reduce X_c to a still smaller value? This is not done because any relatively harmless discharge that may occur between the multiplier collector and ground will cause the energy stored in C to be rapidly dumped into the input of the preamplifier. This event can easily destroy the input circuit components of the pulse preamplifier. The larger the capacitance, the larger is the stored energy. So C

should have the smallest acceptable value and that quoted above is adequate for most circumstances.

One final consideration about this capacitance is its position. Does it have to be inside the vacuum system as shown? In general, the answer is yes. Leakage "pulses" in the insulator, particularly on days of high humidity are difficult to identify as spurious. It is safer to build a high voltage, low outgassing capacitor inside the vacuum envelope.

The value selected for R_2 depends partly on C but as a primary concern, it must be regarded as a parallel resistor to the signal load. If R_2 is chosen as 50 ohms clearly it would approximately halve the current spike of the pulse supplied to the input of C. Thus R_2 should be large. However, if it is very large, then the dc time constant determined by R_2 times C will be long. This time constant does not affect the pulse transfer characteristics significantly, but its effect on the electron flow through R_2 would be to reduce the positive potential of the collector as the signal electrons continued to arrive. At some high electron arrival rate at the collector, its potential would be insufficient to attract further electrons and the pulse amplitude would decline until it fell below the discriminator level in the preamplifier. The signal would then disappear.

It is a common fault to make R_2 infinite, that is, to forget about it altogether. Clearly in this case the charge accumulating on the collector does not dissipate at all except for accidental leakage resistances. Even if pulses are seen initially they quickly disappear as the instrument operates and C charges. At best the performance will be very erratic. The latitude these considerations allow for the value of R_2 is large, however, and it is typically chosen from the range 10^3 and 10^6 ohms. An important proviso to this choice of resistance arises if the output end of the coaxial cable is not terminated in 50 ohms in the pulse preamplifier. If neither end of the cable is terminated in 50 ohms a considerable number of spurious pulses can arise from wave reflections (ringing) along the cable.

Current Measurement

Figure 3 shows the circuitry that is commonly but incorrectly applied to negative ion detection using analog or current measurements. On ignoring for the present problems associated with preamplifiers referenced to 6 kV, the error in this circuit is illustrated by an arrow showing the leakage current I between ground and the signal lead. If the signal lead is fed through the vacuum
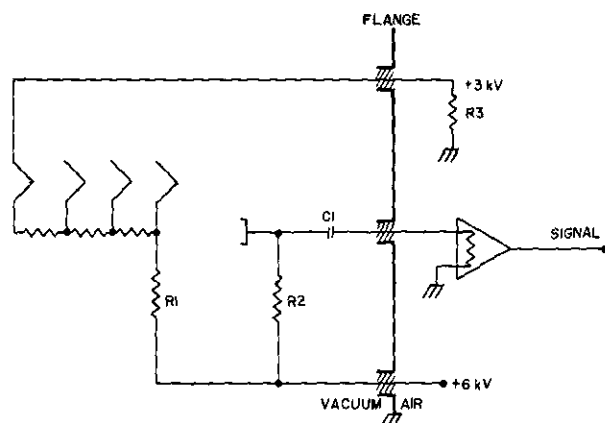

FIGURE 3.

wall using the normal single insulated feedthrough, 6 kV is imposed across the resistance of the insulator. On making the assumption that the effective resistance of this insulator is 10^{10} ohms, the leakage current is 6×10^{-7} A.

On tracing the circuit it can be seen that the source of this current is the power supply and that, despite being called leakage, to the preamplifier it is indistinguishable from the signal current i. If the best possible feedthrough insulators are used, the leakage current may still exceed the signal current by several orders of magnitude, leaving the old problem of measuring a small difference between large numbers to extract the true signal current. The final consequence of choosing this circuit is illustrated by assuming that the leakage current is bucked-out in the preamplifier. The inherent noise of the current flow cannot be bucked out, however, and the signal current as measured contains this extreme noise component together with any drift components that may occur in both leakage or buckout current sources.
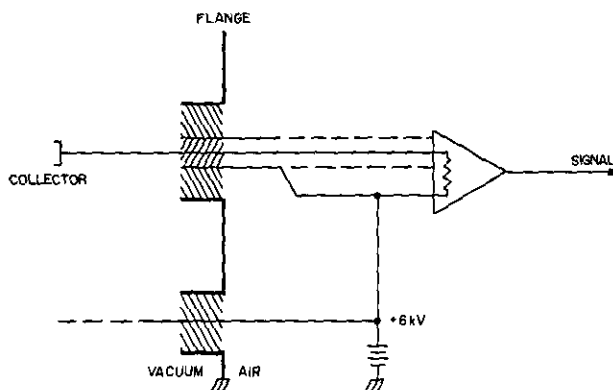
The correct circuitry is shown in Figure 4,

FIGURE 4.

where the triaxial connector has a guard potential on the shield both through the vacuum wall and on the coaxial cable to the preamplifier. Elimination of the potential difference between signal lead and shield ensures transfer of the signal to the preamplifier without appreciable leakage. Of course, leakage currents driven by the power supply still occur between the shield and ground of the triaxial feedthrough. But now they do not enter the signal current circuit to cause spurious signals.

In tackling the problem of an analog preamplifier referenced to a high potential, one must note that there is nothing intrinsically wrong with this arrangement. FET input, operational amplifiers used in signal preamplifiers can be so connected. The difficulties arise when the output signal needs to be further handled by ground referenced equipment as in the cases of a display meter, chart recorder or computer. The output signal from the operational amplifier is still referenced at high potential with respect to ground. A number of solutions are available to decouple the signal from this potential. For example, one commercial instrument used the high voltage referenced signal to modulate an rf carrier wave also generated in the high voltage environment. This modulated rf signal was inductively coupled through a ferrite rod from a transmitting coil at high voltage end to the receiving coil at the ground referenced end. The dc insulation between the two coils provided the necessary isolation and the signal was demodulated and smoothed to remove the carrier. The output was a signal referenced to ground potential that could be interfaced immediately with other instruments. More recent versions of this arrangement use optical isolators as the decoupling devices. Their frequency response and dynamic range is somewhat better than the original "radio" method.

Other Methods of Detecting Negative Ions

The techniques and circuitry described above are well established, proven, reliable in operation, and commercially available. However, they depend on an electron multiplier having its sensitive dynode surfaces exposed to the dirty vacuum system of the mass spectrometer and the important first dynode suffering ion impact damage. Because the nature of these surfaces changes with time in most vacuum environments, some experimentors seek to avoid, partially or totally, surface phenomena. Partial avoidance is achieved with the Daly Doorknob detector. In this method, ions are accelerated toward a metallic but passive surface where secondary electrons are produced. These electrons are then accelerated to very high energies and made to strike a scintillator producing light which is detected by a photomultiplier housed in its own vacuum envelope. The effects of optical radiation from the initial ion impact are minimized by coating the scintillator with a thin metallic film through which the energetic electrons pass but which is opaque to light. The advantage of this approach is that the multiplier dynodes are not subject to ion impact or deterioration as they are maintained in the exceedingly clean vacuum of the photomultiplier enclosure.

Complete avoidance of the interaction between negative ions and sensitive surfaces may be accomplished by using photodetachment. In this case an intense light beam strikes a negative ion, and the electron is liberated by an interacting photon. The electron is then detected by conventional means. This approach has the advantage that it is a purely gas phase phenomenon insofar as the negative ion is involved. The advent of lasers, whose light intensity is sufficiently high to photo detach the electron from virtually all negative ions that cross its beam, makes this approach very attractive where surface effects must be avoided.

Other gas-phase methods that may have specialized applicability consist of crossing a negative ion beam with a molecular beam or passing the negative ions through a cloud of gas. Collisional detachment and charge transfer can produce either free electrons or negative ions of one single species independent of the nature of the original ion. In general however, gas-phase detectors impose additional vacuum system requirements that are unattractive for simple negative ion detection methods.

One final example is, in itself, facetious but perhaps illustrates that the detection of negative ions may not be limited to physical phenomena. It was reported in 1972 that mice colonies breathing air with a negative ion concentration of 3×10^5 ions/cm^3 and zero positive ions were significantly more resistant to death from influenza virus than colonies breathing positive ion-laden or ion-depleted air.