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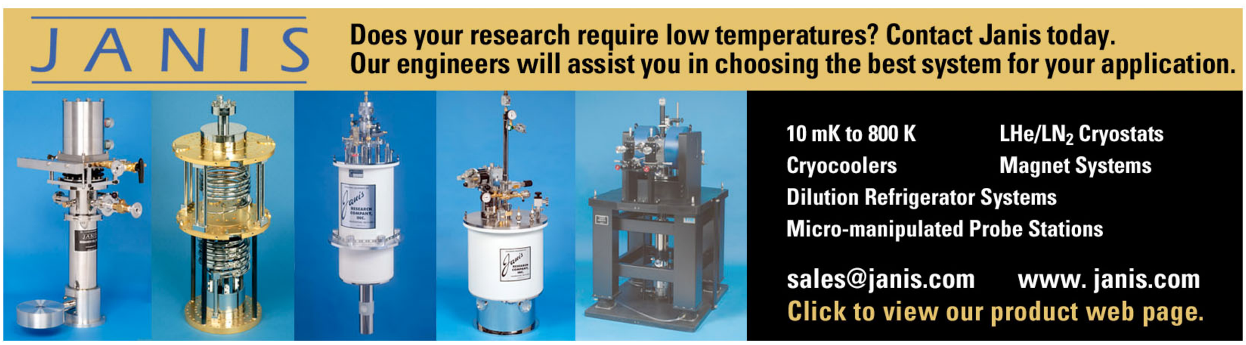

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Reduced electron multiplier dead time in ion counting mass spectrometry

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Detector dead time in electron multiplier ion counting applications has been reduced. A first-in first-out buffer allows a traditional ion counting system to accept pulses 10 ns apart. Lower dead time (10 ns) results from elimination of electrical ringing that trails electron multiplier output pulses. The improved system has been tested on $^{34}S/^{32}S$ isotope ratio measurements.

High gain electron multipliers provide a convenient ion counting method for quantifying mass spectrometer ion signals. These widely used detectors are robust and sensitive. They also have a wide dynamic range which is particularly useful in mass spectrometry. However, the ion counting rates are ultimately limited by detector dead time and by counting electronics. These factors also introduce a slight nonlinearity into the detector response. The nonlinearity is often ignored, but becomes important at high count rates and for high accuracy measurements such as isotope ratios.

Two modifications reduce the effective counting system dead time into the 10 ns range. First, fast emitter-coupled logic electronics capture the pulses, store them in a high speed first-in first-out (FIFO) buffer, and shift them out to the mass spectrometer (CAMECA IMS-3f/4f) counter at a slower transistor-transistor logic (TTL) compatible speed. Second, ringing at the output of the electron multiplier has been largely eliminated.

The IMS-3f/4f uses 17-dynode (Balzers SEV-117) electron multipliers. The electron multiplier first dynode operates at ground potential because the IMS-3f/4f analyzes both positive and negative secondary ions. The output signal passes from the anode through the vacuum wall to the outside where it is capacitively coupled to the counting electronics. The electron multiplier is mounted on an insulated platform. Insulator stand-offs and vacuum feedthroughs produce total signal lead lengths of about 6 cm.

Electron multiplier signals then pass through a preamplifier, a level discriminator, and a circuit to convert the short duration (<10 ns) analog pulses into digital logic with fixed pulse widths. A variety of different amplifiers have been used in the past on the six IMS-3f/4f instruments at Charles Evans & Associates. In most of the existing circuits, a monostable multivibrator controls the overall dead time. An arriving ion triggers the monostable and subsequent ions cannot be counted until it times out. Long monostable times, typically 30–50 ns, allow ringing from the electron multiplier to die down. In the IMS-3f/4f counting system, the output pulses are fed to a 16-bit (0–65, 535) TTL counter operating for a fixed 10 ms counting time.

Ideally, the entire electron multiplier pulse height distribution can be counted and any minor ringing can be blocked by the discriminator. This ideal situation has not been previously required for IMS-3f/4f instruments because the TTL based counting system cannot accept pulses separated by 10 ns. The new FIFO buffer captures 100 MHz instantaneous count rates (pulse pairs separated by 10 ns) as long as the average count rate is much lower. The IMS-3f/4f counting system uses TTL technology driven by long cables. To ensure compatibility with all models and vintages of IMS-3f/4f, we limit the output rate of the FIFO to 10 MHz. A 16-count FIFO easily covers the situation in which a steady signal produces a 10 MHz average count rate and two pulses arrive by chance 10 ns apart. The mass spectrometer counting system further limits the average rate because the 0–65, 535 counter running for 10 ms can only reach 6.5535 MHz. However, it is desirable to keep the FIFO output frequency as high as possible because imaging applications produce ion intensities that change significantly within a 10 ms counting cycle.

This FIFO concept provides the impetus to reduce the electron multiplier dead time. Figure 1(a) shows the wave form of a typical electron multiplier output pulse. Notice that the first two or three ringing cycles are as high as 15% of the original pulse. The ringing has a period of 8–12 ns and amplitude proportional to the original pulse amplitude. The entire pulse height distribution could be detected by setting the discriminator threshold low. However with 10 ns dead times, the ringing cycles from the large pulse are counted. Setting the discriminator threshold low to accept the entire pulse height distribution leads to overestimation of signal intensity (double pulsing). Setting the threshold high to avoid double pulsing eliminates some of the distribution. Although the double pulsing tends to cancel the lost counts, isotope ratio measurement reliability suffers. The measured mass bias (or mass fractionation) factor depends strongly on discriminator threshold, but there is no naturally reproducible way of setting the threshold. In addition, the fraction of ion arrivals that produce double pulsing is count rate dependent. At high count rates, subthreshold ringing cycles from two closely timed ion arrivals add constructively to reach threshold. This produces higher double pulsing (and the illusion of negative dead time) at high count rates.

If ringing were purged from the electron multiplier, high discriminator thresholds or artificially lengthened (30–50 ns) dead times would no longer be necessary. A circuit with 10 ns dead time requires the intensity of *all* ringing cycles to be less than the entire pulse height distribution. Ringing in the Balzers electron multipliers has been essentially eliminated with the components shown in Fig. 2. A 0.001 μF capacitor bypasses the last dynode. The anode (output) is ac source terminated by a 50 Ω resistor in series with a 0.001 μF capacitor. It is very important to

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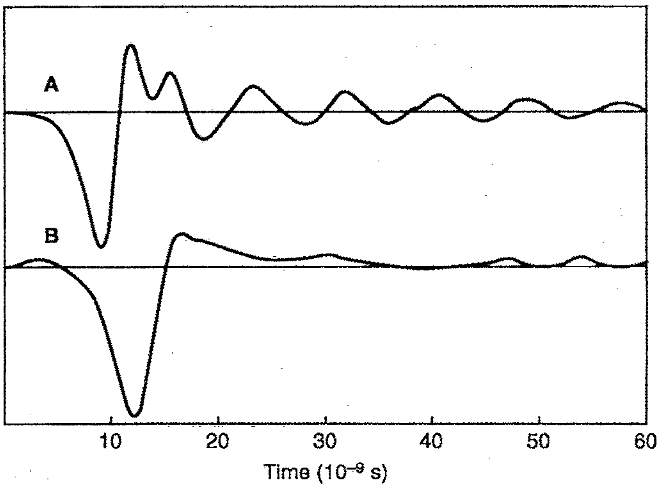

FIG. 1. (a) Typical electron multiplier output pulse before circuit modification. (b) After modification.

attach all components directly to the electron multiplier inside the vacuum with *minimal lead length*. The same components outside the vacuum provide no improvement.

The preamplifier input must be low impedance and purely resistive. A conventional inverting operational amplifier configuration does not work well as a transimpedance amplifier because low input impedance, achieved by negative feedback, only occurs at low frequency, where the amplifier's loop gain is high. At high frequency, the amplifier loop gain decreases and the output has an extra phase shift. The input impedance becomes complex and its value increases. In our experiments, the best results are achieved with the output of the electron multiplier driving into a 40 Ω resistor. Voltage developed across the resistor is then amplified by a high input impedance low noise operational amplifier (CLC401). The amplifier circuit is a conventional noninverting configuration. The main point is to avoid interaction between the electron multiplier and the amplifier. Figure 1(b) shows a typical output pulse after the above modifications.

The new electron multiplier modifications, preamplifier circuit, and FIFO counting system have been tested together by measuring the $^{34}S/^{32}S$ isotope ratio in Canyon

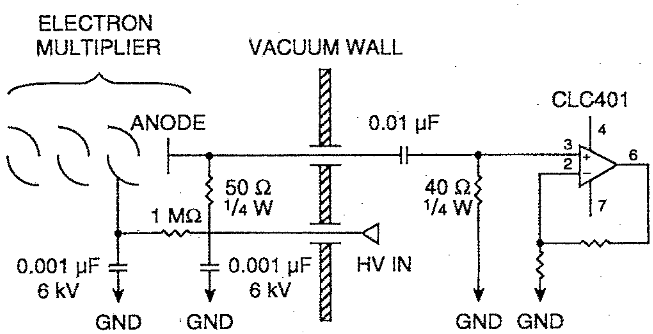

FIG. 2. Circuit modifications for reduced electron multiplier ringing.

Diablo troilite (a sulfur isotope standard with $^{34}S/^{32}S$ equal to 0.045 00). For these measurements, we worked at a precision of about 0.03% which requires at least 10^7 counts of the minor isotope. In a reasonable experiment, the ^{32}S count rate is 1 MHz, the ^{34}S count rate is ~45 kHz, and the time required to collect 10^7 counts of ^{34}S is ~220 s. The dead time corrections follow either the paralyzable or nonparalyzable model,[1] or some combination of both types.[2] For modest corrections (up to 4%), we find that the two models produce equivalent results. However, whatever model is used to measure dead time should also be used for subsequent corrections.

Equation (1) is the general form of the paralyzable dead time correction where M and A are measured and actual count rates, respectively, and τ is dead time. Equation (2), derived from Eq. (1), provides a format for measuring dead time in isotope ratio experiments. In Eq. (2), R_M is the $^{34}S/^{32}S$ ratio measured at different count rates and $^{32}S_A$ and $^{34}S_A$ are the actual count rates during the isotope ratio measurements. The slope is dead time (τ) and R_A is the isotope ratio with no dead time contribution. Comparison of R_A with the known Canyon Diablo troilite $^{34}S/^{32}S$ value provides a good estimate for the mass bias in the measurement. At modest count rates, the measured values ($^{32}S_M$ and $^{34}S_M$) serve as adequate estimates of actual count rates.

$$M = A \exp(-\tau A), \quad (1)$$

$$\ln(R_M) = \ln(R_A) + \tau(^{32}S_A - ^{34}S_A). \quad (2)$$

A series of $^{34}S/^{32}S$ measurements were made on Canyon Diablo troilite at different ion arrival rates. The secondary ion intensity was changed by varying the entrance slit. All other instrumental conditions were identical during the measurements. Fitting the measured isotope ratios and ion arrival rates to Eq. (2) provides a detector dead time estimate of 9.24 ns. A dead time free $^{34}S/^{32}S$ isotope ratio measurement (0.044 35) comes from the intercept, $\ln(R_A)$ (−3.1156). Comparison of the measured isotope ratio with the known value for Canyon Diablo troilite indicates a mass bias factor of −0.737% per unit mass number. Note that the dead time correction required for a 1 MHz ion arrival rate is 0.928%. Both dead time and mass bias corrections are much larger than the 0.03% Poisson precision of the isotope ratio measurements. The ion intensity measurements demonstrate extremely linear electron multiplier response (except for dead time considerations) over a range from the lowest count rate of ^{34}S (0.039 MHz) to the highest count rate of ^{32}S (3.9 MHz). Measurements over a range of ion arrival rates show that all of the components work well together.

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[1] G. F. Knoll, *Radiation Detection and Measurement* (Wiley, New York, 1979), pp. 96–99.
[2] M. Lampton and J. Bixler, Rev. Sci. Instrum. 56, 164 (1985).

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