ORTEC®

AN52

Application Note

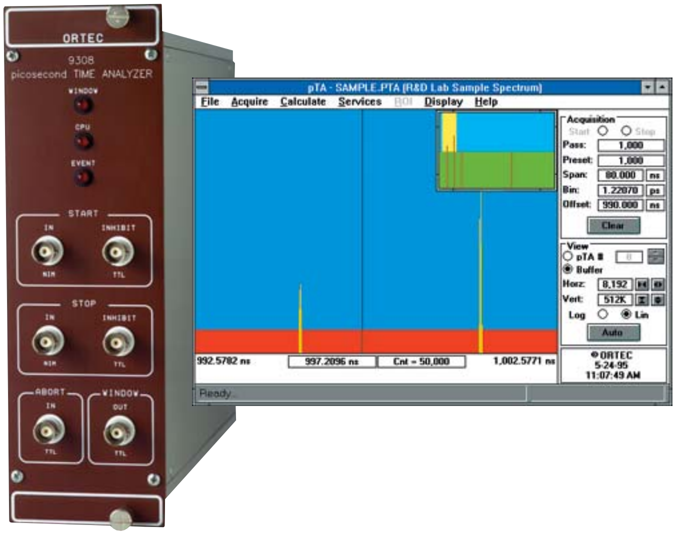
Picosecond Time Analyzer Applications in . . .

- **LIDAR and DIAL**
  - **Time-of-Flight Mass Spectrometry**
    - **Fluorescence/Phosphorescence Lifetime Spectrometry**
      - **Pulse or Signal Jitter Analysis**

CONTENTS of this Note: *Section 1 explains the concepts of Multiple-Stop Time Spectrometry and the capabilities of the ORTEC Picosecond Time Analyzer for this purpose. Section 2 describes use with stochastic input signals: Time-of-Flight Mass Spectrometry (Sec. 2.1), LIDAR/DIAL (Sec. 2.2), and Fluorescence/Phosphorescence Lifetime Spectrometry (Sec. 2.3). Guidelines for optimum data acquisition in those applications are provided in Section 2.4. Use of the Picosecond Time Analyzer in periodic signal analysis is covered in Section 3.*

1. Principles of Multiple-Stop Time Spectrometry

ORTEC's Picosecond Time Analyzer (Model 9308) connects to a personal computer to form a high-resolution, multiple-stop time spectrometer, capable of recording event times in the range of 0 to 325 µs with picosecond precision. Its 16-bit digital resolution is particularly useful for applications in LIDAR, Time-of-Flight Mass Spectrometry, fluorescence- and phosphorescence-lifetime measurements, and pulse or signal jitter analysis.



The instrument can operate in either **Histogramming** Mode or **List** Mode. Normally, the Histogramming Mode is used to record a time spectrum, with repetitive sampling and signal averaging being used to improve the statistical precision in the recorded spectrum. List Mode is useful when the sequence of event arrival times must be preserved for examination. Figure 1 illustrates the sequence of external and internal signals for the Picosecond Time Analyzer (in either mode), when recording of Stop pulses has been enabled, and Start pulse recording has been disabled.

In the Histogramming Mode, each scan or pass through the time range is triggered by a "Start" input, which establishes zero for the time scale. Typically, this Start signal corresponds to the stimulation of a process that will generate "Stop" pulses that are correlated to the Start event. For example, a pulsed

LASER operating at a 100-kHz repetition rate could be used to measure the distance to multiple objects located at distances ranging from 100 to 147 meters. Each LASER pulse starts a pass, and the photons reflected from the various objects generate the Stop pulses that arrive 667 to 980 ns after each LASER pulse. The arrival times of multiple Stop pulses can be recorded during each pass through the selected time range.

Within 1 µs of completing a pass, the instrument is ready to accept a Start trigger for the next pass. By preselecting the desired number of repetitive passes, data from multiple passes can be automatically summed to form a histogram representing the number of Stop pulses accepted vs. the respective Start-to-Stop time interval. In the LASER ranging example above, the histogram shows the probability of LASER reflections from the various objects vs. the distance to each object.

The Time Span for the histogram is recorded with 16-bit resolution. On the shortest span this provides an 80-ns data acquisition window spread over 65,536 equal time bins — with a digital resolution of **1.221 ps/bin**. This window can be delayed relative to the Start trigger by 0 to 325 µs of digital Time Offset to examine any portion of the time spectrum with picosecond precision. In addition, the window can be expanded by factors of two to measure Time Spans up to 163.84 µs with 16-bit resolution.

The number of stop pulses that can be recorded in each pass through the time span is limited only by the 50-ns pulse-pair resolving time. Continuous rates up to 2 MHz and burst rates to 20 MHz can be accommodated. Compared to the competing technique of a time-to-amplitude converter coupled to an ADC, the multiple-stop capability and the low dead time in the Model 9308 permit much higher data rates, particularly on the longer time ranges.

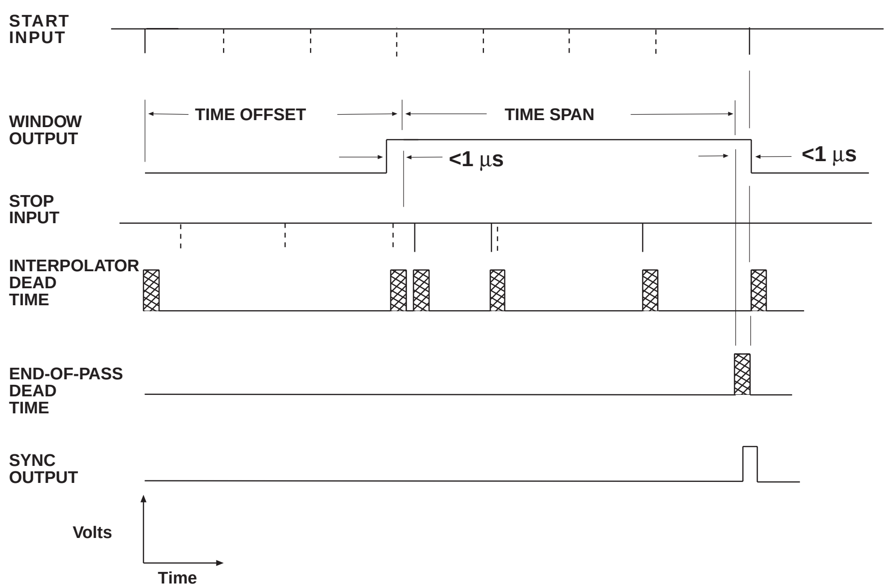


Fig. 1. Timing Diagram for the Model 9308 Picosecond Time Analyzer.
(Dashed lines represent Start and Stop pulses that are rejected by the instrument.)

2. Applications Involving Stochastic Events

2.1. Application to Time-of-Flight Mass Spectrometry

Figure 2 illustrates the typical application of the Model 9308 with a Time-of-Flight Mass Spectrometer (TOF-MS). The sample is maintained at a positive voltage, which serves as the accelerating voltage. A variety of pulsed sources can be used to break molecules loose from the sample surface and to ionize these molecules. The pulsed desorption and ionization source also triggers the start of a pass in the Model 9308.

Once ionized, the molecules are accelerated by the voltage applied to the sample, with lighter molecules reaching higher velocities than heavier molecules. The flight time of these ionized molecules through the field-free drift tube to the detector is proportional to the square root of their mass/charge ratio.

The microchannel plate detector produces an analog pulse of subnanosecond duration as each molecule strikes the detector. This analog pulse is amplified by the VT120A Preamplifier, and the Model 9307 pico-TIMING™ Discriminator precisely extracts the arrival time from the signal.* A timing logic pulse from the Model 9307 drives the Stop Input of the Model 9308 Picosecond Time Analyzer.

Multiple arrival times, corresponding to different mass/charge ratios, are recorded by the Model 9308 for each desorption pulse. A spectrum of improved statistical precision can be acquired by repeating the process for a large number of desorption pulses, while automatically adding the results of each pass to the sum of the previous passes. The result is a spectrum of the number of ions detected vs. flight time. Using the calibration feature of the Model 9308, the horizontal axis of the spectrum can be labeled to read directly in units of atomic mass or Daltons.

For this application the Model 9308 is typically operated with a Time Span of 81.92 µs, which yields a digital resolution of 1.25 ns/bin over the 65,536 bins covering the entire spectrum. Because the uncertainties in flight times are normally 10 to 20 ns, this digital resolution offers 8 to 16 data points across the FWHM (full width at half maximum height) of the peaks in the spectrum. If the shape of a particular peak must be examined in greater detail, the Time Offset and Time Span can be adjusted to spread more bins across that peak.

The Picosecond Time Analyzer achieves high resolution by precisely measuring each arrival time. The vernier interpolator in the instrument requires approximately 50 ns to perform this task. To avoid spectrum distortions caused by dead-time losses, the desorption and ionization source intensity should be selected so that the probability of additional ionized molecules arriving within the 50-ns interpolator dead time is less than 1%. This limit can be relaxed to 10% when the dead-time correction feature is applied.

*A Model 9327 1-GHz Amplifier and Timing Discriminator is a more compact alternative to the VT120/9307 combination.

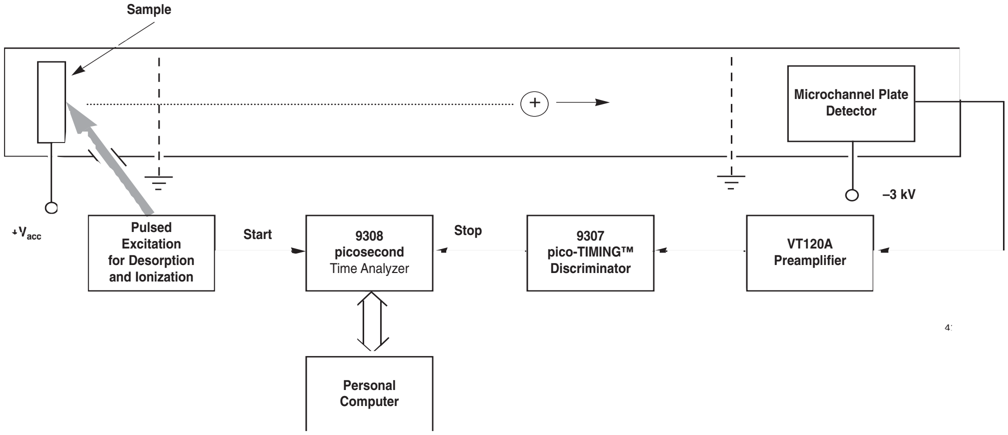


Fig. 2. Simplified Diagram of a Time-of-Flight Mass Spectrometer Using the Model 9308 Picosecond Time Analyzer as a Multiple-Stop Time Spectrometer.

The high data rates permitted by the low end-of-pass dead time and the multiple-stop capability of the Picosecond Time Analyzer, together with the 65,536:1 time resolution, make the Model 9308 a particularly productive tool for time-of-flight mass spectrometry.

2.2. LIDAR Applications

Figure 3 shows the application of the Model 9308 to LIDAR measurements. A pulsed LASER triggers the start of a pass on the Model 9308 at the same time that it sends a light pulse towards a distant object. The light reflected by the object is detected by a photomultiplier tube and amplified by the Model VT120A Preamplifier. The Model 9307 pico-TIMING* Discriminator extracts the arrival time from this analog pulse and sends a corresponding timing logic pulse to the Model 9308. In the Model 9308 the arrival time of the Stop pulse is measured relative to the “zero time” defined by the Start pulse.

If the LASER pulse illuminates multiple objects at different distances the reflected light pulses from the various objects will be recorded at their respective positions in the time spectrum. The Model 9308 can automatically sum the responses from many repetitions of the LASER pulse to achieve improved statistical precision in the time spectrum. Based on the speed of light, the horizontal axis of the spectrum is calibrated in terms of distance to the object, rather than the photon flight time. The picosecond precision of the Model 9308 over time intervals as long as 325 µs permits position determination with a resolution of <9 mm up to distances of 48 km. Longer distances can be accommodated by inserting an additional digital delay between the LASER trigger and the Model 9308 Start Input. Digital delays are available from *PerkinElmer Instruments Signal Recovery* as well as other manufacturers.

In addition to measuring the distance on the horizontal scale of the histogram, the vertical scale measures the probability of photon scattering from the distant object. That information can be used to measure the concentration of specific molecules in the atmosphere at precisely defined locations. In that case, one must correct the photon counting rate for absorption in the intervening atmosphere. That correction can be achieved by using a parallel LIDAR system operating at a wavelength that suffers similar absorption in the atmosphere, but which is not absorbed by the molecule of interest. This technique is called **DIAL (Differential Absorption LIDAR)**. It can be used to measure the concentration of ozone in the atmosphere or the concentration of pollutants in smokestack effluents. Such applications incorporate optical telescopes to limit and align the fields of view for the two LASER wavelengths, and to separate the echo pulses according to wavelength. Those details have been omitted from Figure 3 to simplify illustration of the signal-processing electronics.

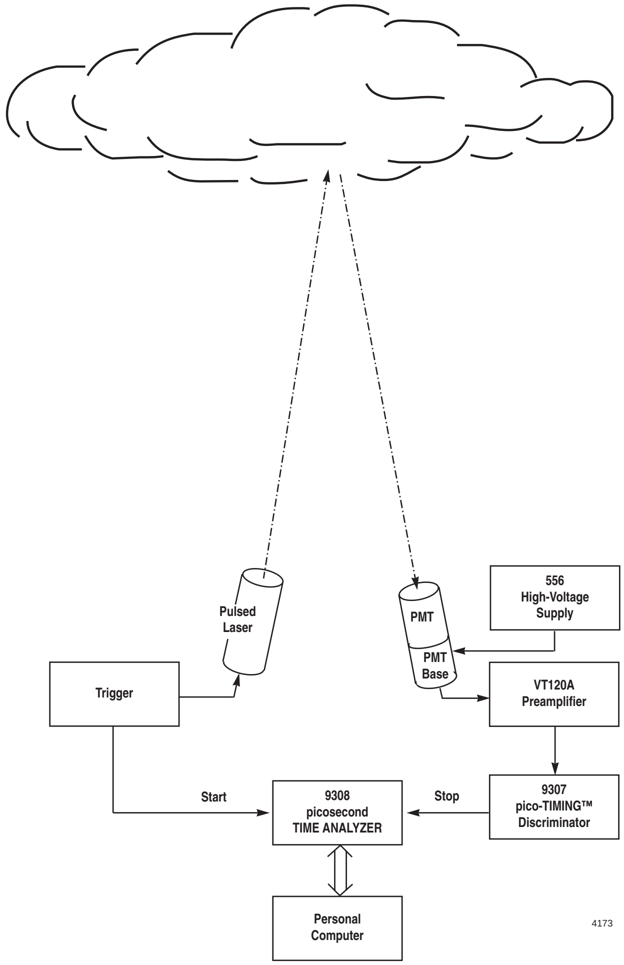


Fig. 3. A Simplified Diagram of the Model 9308 Picosecond Time Analyzer Applied to Atmospheric Measurements by LIDAR.

*The Model 9327 is a more compact and convenient alternative to the VT120/9307 combination.

2.3. Fluorescence/Phosphorescence Lifetime Spectrometry

Figure 4 outlines a system that is capable of measuring fluorescence lifetimes in the picosecond to nanosecond range, or phosphorescence lifetimes in the microsecond range. This system can be used to study molecular structure and molecular interactions. It can also be used to identify the presence of specific molecular species, or to measure concentrations of ions which quench the fluorescence decay.

A cavity-dumped LASER is used to illuminate the sample with periodic, picosecond flashes of light. The cavity dump is selected so that the light pulses are separated by a time much greater than the lifetime to be measured.

A beam splitter passes a large fraction of the LASER light pulse to a photodiode to signal the Start time for the Model 9308. The pulse from the photodiode is amplified by the preamplifier and passed to the Model 9307 pico-TIMING Discriminator.* The Model 9307 marks the arrival time of the analog pulse by sending a timing logic pulse to the Start Input of the Picosecond Time Analyzer.

A much smaller fraction of the light from the beam splitter strikes the sample, where the light pulse drives molecules into an excited state. Shortly after this stimulation, the molecules decay to the ground state by emitting a photon. The probability of decay vs. time is an exponential function with a decay time constant that is characteristic of the molecule and its environment.

The intensity of light received from the sample is restricted so that individual photons from the decay can be detected at the microchannel plate photomultiplier tube (µCP-PMT). The resulting output pulse from the µCP-PMT is amplified by the Model 9306 Preamplifier. The arrival time of this analog pulse is defined by the Model 9307 pico-TIMING Discriminator* in the form of a logic pulse sent to the Stop input of the Model 9308. The Model 425A is incorporated to delay the Stop signals sufficiently that they arrive at the 9308 after the 50-ns interpolation dead time from the Start pulse.

Figure 5 demonstrates typical spectra acquired for fluorescence lifetime measurements. The Model 9308 Picosecond Time Analyzer is a productive solution for fluorescence and phosphorescence lifetime spectrometry, because this one instrument can measure the sub-nanosecond lifetimes from fluorescence decay as efficiently as it can record microsecond decays from phosphorescence. Furthermore, it can accomplish these measurements with low dead time and exceptionally high data throughput. Due to its crystal-controlled clock, the horizontal time scale of the 9308 is pre-calibrated with a 100 ppm absolute accuracy. Compared to a Time-to-Amplitude Converter (which requires calibration), the 9308 is a factor of 50 times more stable against temperature changes, and delivers orders of magnitude higher data rates in Phosphorescence lifetime spectrometry.

Additional information on fluorescence lifetime spectrometry is available in Application Note AN50.

*The Model 9327 is a more compact and convenient alternative to the 9306/9307 combination.

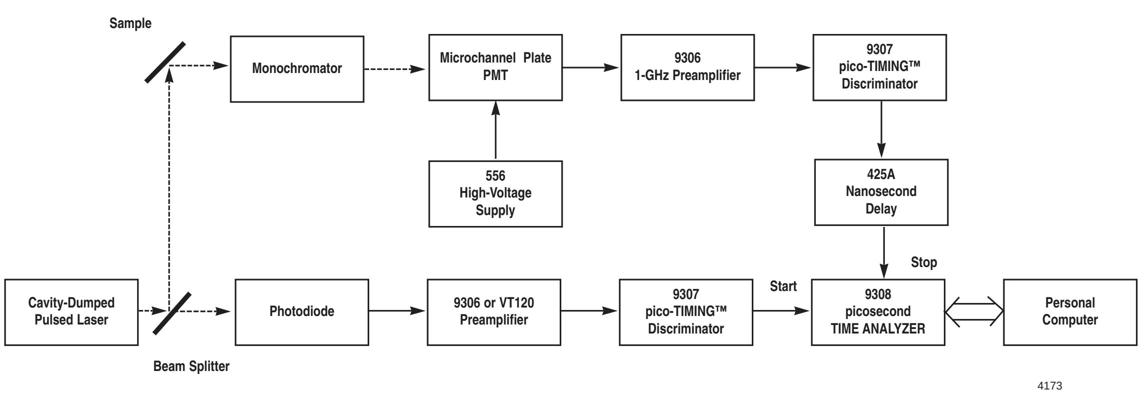


Fig. 4. The Conventional Start/Stop Arrangement for Fluorescence/Phosphorescence Lifetime Spectrometry.

2.4. Factors Controlling Accuracy and Throughput

2.4.1. Limiting Spectrum Distortion

The Model 9308 Picosecond Time Analyzer can accommodate continuous data rates up to 2 MHz, and burst rates up to 20 MHz. These maximum rates imply some loss of data during the interpolator dead time if the arrival time of the Stop pulses is random rather than periodic. If high data rates are absolutely essential, one can use the known interpolator dead time to compute a correction to the acquired spectrum, thus overcoming any distortion caused by the dead-time losses. More common practice is to restrict the event rates so that the spectrum distortion is negligible, e.g., less than 1%. For the conventional Start/Stop arrangement, the general guideline is:

The counting rate in any 50-ns section of the time spectrum must be less than 1% of the accepted Start pulse rate, in order to limit dead-time losses to less than 1% in the vicinity of that section of the spectrum.

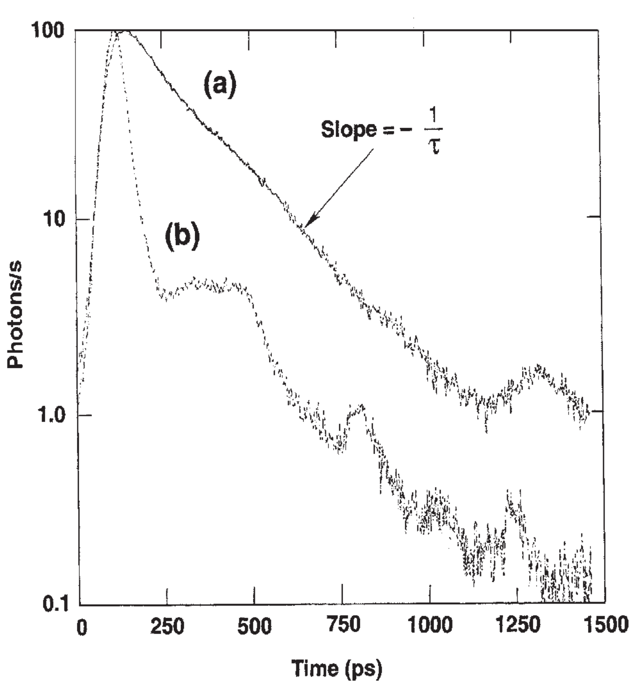


Fig. 5. (a) The Fluorescence Decay of Diphenylbutadiene in Butanol (τ = 128 ps). (b) The Instrument Response Function for τ = 0. (Courtesy of Dr. John Kauffman, University of Missouri-Columbia.)

The easiest way to test for this criterion is to acquire a spectrum for a known number of passes, **n**. Examine the spectrum, and find the region that has the highest number of recorded events. Span the highest count section of that region with a 50-ns wide region-of-interest. Read the total counts, **P**, in this region-of-interest. The above criterion is met if **P/n** is less than 0.01.

The above limit can be relaxed to a factor of 10 higher value if the spectrum is corrected for dead-time losses at the end of data acquisition. The 9308 software provides that option.

2.4.2. Using the Reversed Start/Stop Mode

When using the 80-ns Time Span in fluorescence lifetime spectrometry, the dead time contribution of vacant passes can be significant if the criterion in Section 2.4.1 is met. Each LASER pulse starts a pass in Figure 4, but less than 1% of the passes will record a Stop pulse. This can lead to excessive dead time at high LASER repetition rates.

A productive solution is to reverse the Start and Stop inputs to the Model 9308 (Fig. 6). With that modification the passes are started by the fluoresced photon pulses from the microchannel plate PMT. The LASER trigger pulses are delayed by an amount equal to the desired Time Span plus 50 ns, and fed to the Stop input of the Model 9308. Consequently, the rate of generating passes drops by a factor of at least 100, and every pass is guaranteed to contain a Stop event. This solution eliminates the "vacant pass" dead time and permits higher throughput of data to memory.

Of course, one must ensure that the spacing between LASER pulses is greater than the desired Time Span. Furthermore, the time spectrum will be reversed, with time increasing to the left in the display. The calibration feature in the Model 9308 software can be used to label the time axis in the reverse direction.

2.4.3. Counting Statistics Control Precision

When the criterion in Section 2.4.1 is met, the acquisition of data in the histogram follows the laws of Poisson Statistics. The most important consequence is the dependence of the precision of the data on the number of events counted. Normally, the conditions generating the recorded events remain stable over the duration of the measurement. Hence, the following rule applies:

If the number of events counted in any one bin, or over any number of bins of the histogram

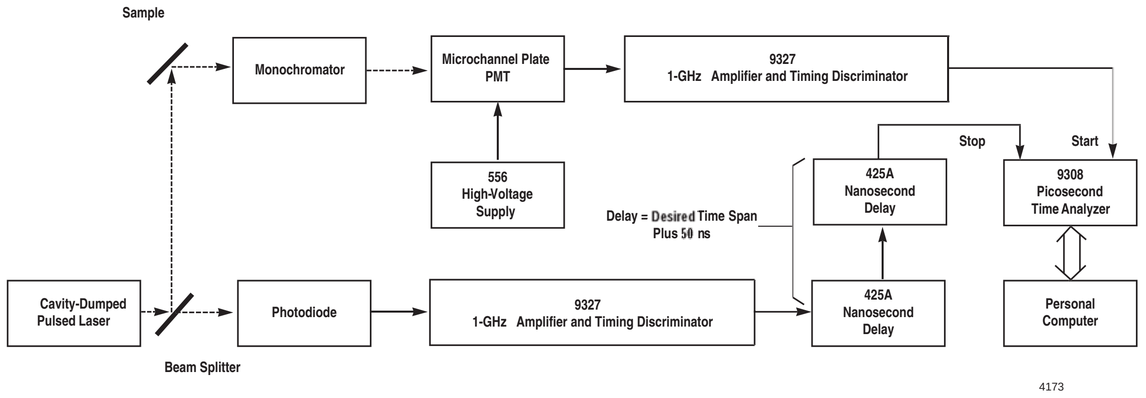


Fig. 6. The Reversed Start/Stop Arrangement for Fluorescence Lifetime Spectrometry.

is *N*, then the predicted standard deviation in that number of events is

$$\sigma = \sqrt{N}$$

A more revealing way to examine this issue is to compute the percent standard deviation, σ%, i.e., the standard deviation in *N* expressed as a percentage of *N*.

$$\sigma\% = \frac{\sigma}{N} \times 100\% = \frac{100\%}{\sqrt{N}}$$

The following table lists several significant values for σ% as a function of *N*.

Number of Events Counted, *N*	Percent Standard Deviation, σ%
1	100.0%
100	10.0%
10,000	1.0%
1,000,000	0.1%

Clearly, the precision improves as the number of counts increases, and the improvement is proportional to the square root of *N.* This is why increasing the number of repetitive passes improves the statistical precision in the definition of the spectrum.

Poisson Statistics also governs the precision of the net peak counts after background subtraction, and ultimately controls detection limits. For more information on this subject consult Chapters 4, 5, and 11 of the book, *Quantitative X-Ray Spectrometry*, by Ron Jenkins, R.W. Gould, and Dale Gedcke (Marcel Dekker, New York, 1981 and 1995).

3. Jitter and Period Analysis with Periodic Waveforms

Figure 7 shows a configuration for measuring the jitter in a pulse train of TTL logic pulses. The logic pulses are driven by an oscillator, and the goal is to measure the variations in the periods between pulses. For applications having a single source of signals, recording of Stop pulses is disabled in the Model 9308, and recording of Start pulses is enabled. The arrival time of each Start pulse is measured relative to the previous Start pulse, and each Start pulse initiates a new pass. The end-of-pass dead time becomes the 50-ns interpolator dead time for measuring each Start pulse.

The LeCroy Model 688AL converts the TTL logic levels to the fast negative NIM logic levels which can be accepted at the Start Input of the Model 9308. If the duty cycle of the pulse train is stable, the TTL to NIM convertor could be simply replaced by a large capacitor. The ac-coupling would produce the required level shifting.

Operation in the Histogramming Mode will generate a peak in the spectrum, whose centroid represents the average period between pulses. The profile of the peak measures the variation of the individual periods from the average. The Histogramming Mode is useful when studying the statistics of jitter and/or modulation.

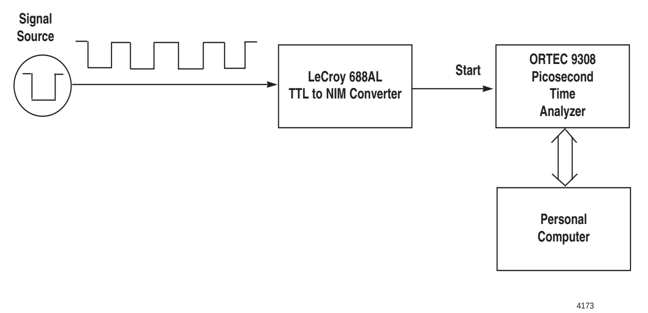


Fig. 7. Jitter Analysis on a Pulse Train of TTL Logic Pulses.

The List Mode documents the change in pulse-to-pulse spacing as a function of time. Consequently, the List Mode is useful when measuring the tuning time of a phase-locked-loop oscillator.

For periods as long as 325 µs, the Model 9308 is able to measure period variations as short as 25 ps.

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