Application Note Mass Spectrometry

Achieving the optimum accuracy and resolution in single-ion-counting

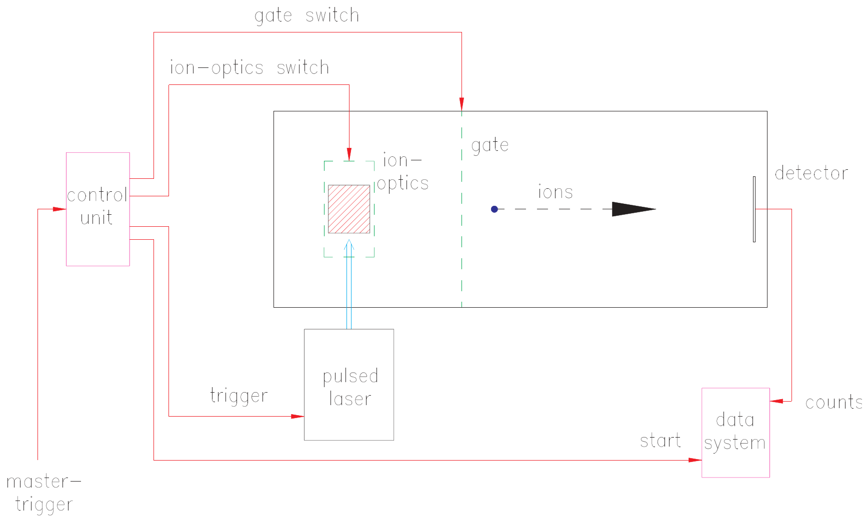
Discussion and comparison

There are different approaches to single-ion counting. We would like to put them into perspective, identify the advantages and disadvantages of each approach and illustrade the advantages of real-time counting approach of the FAST ComTec Model P788X Series multistip single ion counters.

- Comparison of methods: analog transient digitizers versus digital multistop Single Ion Counters
- The road to success with real-time ion counting

Comparison of methods

Lets start with basics by describing how a time-of-flight mass-spectrometry system works and what the timing characteristics of each components are using experi-mental data from our customers.



Typical trigger uncertainties and jitter:

1) triggering the acceleration pulser and firing of the laser: 1 ns best , 7 ns typical

2) firing of the laser and the trigger output: 50 – 100 ps

3) Accuracy (jitter and walk) of the trigger input:

in a transient digitizer:

+/- 250 to +/- 1000 ps typical

in the model P7887 +/- 125 ps

In other application notes we discussed the use of transient recorders and wave form digitizers. The latter are the obvious choice when the ion count rates exceed upper limits as can be seen on the comparison chart of the Signatec PDA 500 v/s the FAST ComTec P7886 on our web page www.fastcomtec.com.
We limit this discussion here to ion rates where the MCP detector still provides discrete pulses. However statements about the timing accuracy also apply to transient recorders which employ real time sampling as in the Signatec Model PDA 1000.

Transient Digitizers

These devices are designed for digitizing analog input currents with high accuracy.In mass-spectrometry applications 8-bit and 12-bit digitizers are predominately used.

At low ion counting rates single ions are buried in the system noise. There have been methods described that claim that this problem can be some extend in which single ions are summed and noise reduced.

There are, however, several dis-advantages using such a method for low ion counting rates:

a) Every time bin in a sweep has to be summed even if just one ion is contained, thus significantly reducing the sweep repetition rate capabilities.

b) Pulse shape and amplitude variation will influence the accuracy of the measurement

c) Intricate mathematics have to be used to separate (deconvolute) adjacent mass lines that have less than one pulse width separation. Pulses from MCP's or PMT's do not have a Gaussian shape but typically have short rise-times and much longer fall-times (tails) and varying amplitudes that will make accurate separation and calculation of the line strength difficult if not impossible

By triggering the transient digitizer directly off the actual laser pulse (via a detector and discriminator) low jitter values are possible. For input currents real time sampling as used on all Signatec transient digitizers results in the

FAST ComTec
GmbH · Grünwalder Weg 28a · D-82041 Oberhaching · Germany
Tel 49-(0)89-66 51 80 50 · FAX 49-(0)89-66 51 80 40 · http://www.fastcomtec.com

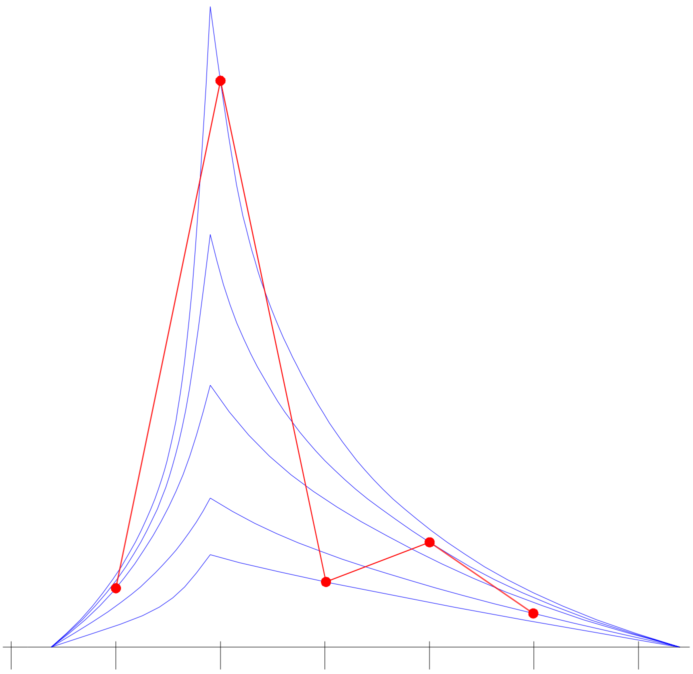


Fig. 2

optimum time resolution. Therefore using a transient-recorder for single ion counting at low rates is not recommended.

For more information see the data sheet of the model PDA1000

ETS (Equivalent Time Sampling) Transient Digitizers

Low cost transient digitizers using this method are still available today. The more expensive ones are capable of accepting an external start signal, which allows using standard delay generators accepting an external master trigger as a control unit. The lower priced ETS transient digitizers cannot accept an external start signal, but must be used to trigger the external devices. This makes it necessary to use a control unit which perfectly synchronizes the outgoing delays with the incoming master trigger. (standard delay generators only make a perfect timing relationship between the outgoing delays. The jitter between the master pulse and the outgoing delays may be as large as 100nsec.)

The second problem occurring with ETS transient digitizers has to do with the statistical pulse hights that occur on MCP or PMT detectors at low count rates, i.e. when one wants to do single ion counting. In Fig.2 you see five ion signals at statistical amplitudes. The red line then shows the result after four sweeps of the ETS. Of course, as a thorough statistical analysis can show, adding up many of these individual ion signals will then again result in a curve of sensible shape, but that certainly is not the rationale of single ion counting.

To achieve the same statistical accuracy as transient digitizers ETS devices have to perform two, four or eight times the number of sweeps than standard transient digitizers
Thus an ETS transient digitizer only makes sense for very high ion signals, not for detecting a few ions at high sensitivity - in addition they also have all the disadvantages listed in the transient digitizer section.

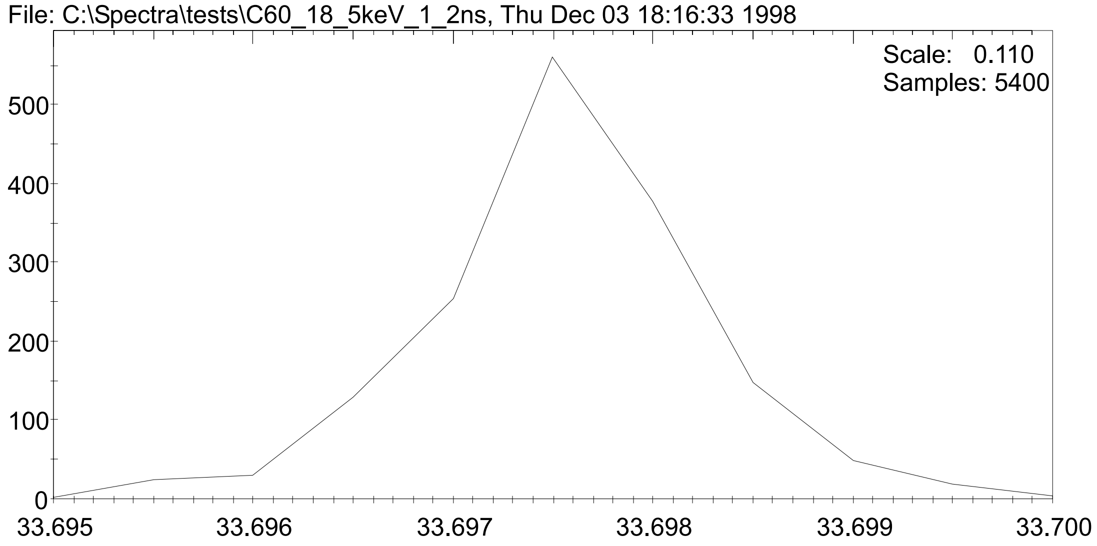
Multistop Single ion counters

These are devices like the FAST ComTec Model P7887
A problem common to all analog voltage digitizers is that the spectrum one gets at low ion counting rates is not really the probability of an ion reaching the detector but only some more or less garbled function of that information. You see rise and fall times of your electronics, you will see tailing and ringing on electrical decay curves, and out of all that one has to pick what is presumed to be ions.

Since you will only achieve a gain in dynamic range for summing up less than 100 shots, and even that gain is not so significant, it makes a lot of sense to eliminate the above electronic artifacts by only registering a digital yes or no answer as to whether an ion has arrived.

Since a leading edge discriminator can be used, for example, to give this yes/no-answer if an ion has arrived, your mass lines stay very close to what is actually happening physically can be seen on page 4.
What is shown there is the arrival probability of C60 ions from the detector.
As only the leading edge is being used to determine the time information pulse shapes, amplitudes width etc. are of no consideration.
Averaging sweeps at low ion rates is very efficient because just the actual stop pulses need to be summed while empty time bins are ignored.
It is therefore possible to achieve very high sweep repetition rates that other system can NOT match.
A further advantage is the virtually unlimited number of time bins that can be selected. This will by far exceed the mass-range that are used in mass-spectrometry.
In fact a P7887 could cover 2^37 time bins with 250 ps time resolution. Burst count rates of up to 4 GHz can be achieved with the P7887.
A recent option is an oven stabilized PLL oscillator that offers an incredible temperature stability. This option is called Model 788xOV and a datasheet can be downloaded from our web-site. The 788xOV provides the ultimate in time stability - the ideal match for spectrometers offering high mass resolution and an exceptionally large mass-range.

FAST ComTec has developed and manufactured ultra fast multistop digital time digitizers for 19 years. FAST ComTec also represents the transientrecorders and DSP



line of Signatec in Germany, Austria and Switzerland.

There are a variety of different instruments on the market that are based on other methods. They usually offer excellent time resolution but very limited multistop capabilities and mass-range because the analog circuitry used causes significant dead time after every stop and is limited in dynamic range. To record higher mass numbers these devices require a change in their time resolution to one or several nano seconds.

Most applications do normally not allow a choice between either approach - the ionisation method used dictates which system should be used for optimum results - see the comparison P7886/Signatec PDA500.

Summary

In general a **Multistop Single Ion Counter - i.e a Model P7887** is the choice where each sweep sees fewer than one ion per time bin down to one ion per several sweeps (the number of individual ionic species detected per sweep should in any case be smaller than one single particle to choose counting techniques). The P7887 will process recorded ions only and has therefore a very high sweep repetition rate. Noise is suppressed by setting the threshold of the discriminator used above the noise level. The discriminator generates norm pulses that sum into a single time bin relative to the arrival time of the ion, no matter how wide an input pulse the detector generates.

A **Transient Digitizer** is the one and only choice when laser ionisation is used. The large number of ions generated by the laser cause MCP detectors to output a current proportional to the numbers of ions detected. High peak amplitude resolution is 12 bit at 5 ns time resolution (up to 200 MHz sampling rate) and 8 bit at 1 ns time resolution (1000 MHz sampling rate)

Using a transient recorders where few ions are detected is not recommended because the system would mainly sum noise and as the actual pulse form is digitized, wide pulses tend to broaden the summed peaks.

New developments in ultra fast DSPs such as the **Signatec Model PMP8A** are capable of summing sweeps at data rates of up to 500 megabyte/s

On the following page we show you a diagram which is an example of sampling fast pulses in a Transient Digitizers with a sampling rate of 2 GHz - shown as a red line. The blue line shows the same phenomenon but single ion counting techniques are used.

In order to minimize the effects of ringing, amplitude variations and other electronic effects, we used very clean pulses which varied in time by approx. 4 ns and the line intensity had about a 10 : 1 ratio.

It is interesting to see the results. Using pulses from typical mass spectrometers with the typical distortions one experiences in such applications would result in a slight broadening of the foot base of the peaks in the blue line while the red line would require many more scans to obtain decent results.

As the P7887 is a fully digital design no software corrections are required.

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Max-Planck-Institut für Festkörperforschung,
Heisenbergstr. 1, D-70569 Stuttgart

T. Bergmann, BME Bergmann Messgeräte Entwicklung
Bahnhofstr. 14, 82418 Murnau

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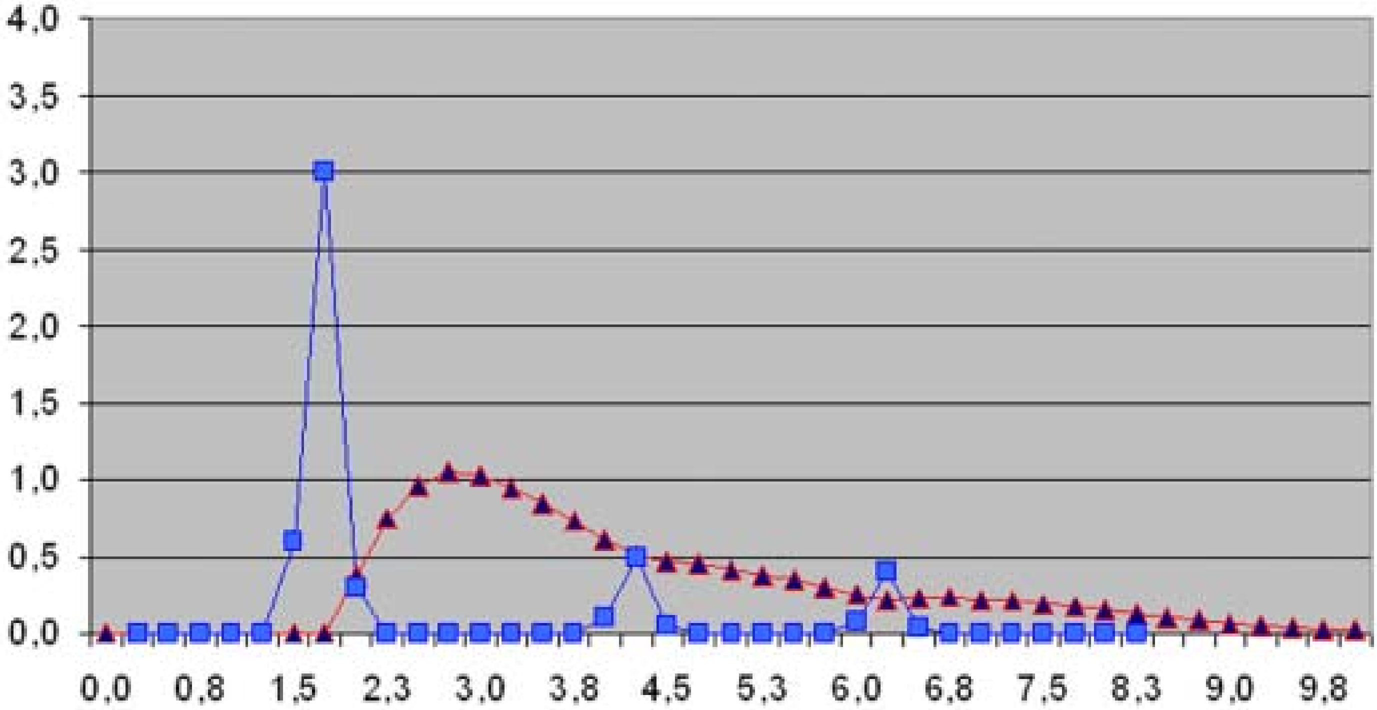
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