

# Application Note Mass Spectrometry

## Basics (section 1)

- Basics (this section)
- Discussion and comparison (section 2)

### # K \$ Time-of-Flight Mass Spectrometry

The main principle of a time-of-flight mass spectrometer is shown in Fig. below

A continuous ion beam (1) is flying without deviation through the inactive ionoptics (all electrodes have ground potential). The electrodes in the reflector and detector are ready with fixed continuous voltages to transmit and guide ions. Apertures (2) help to cut and localize the beam.

representing a mass value. Saving these incoming time-values, we have finished one cycle of capturing data. We repeat this cycle to get a good signal to noise ratio and to improve the dynamic range. The sequence of taking data on a time-of-flight mass spectrometer will be described in the topic [Experimental Sequence of taking data](#).

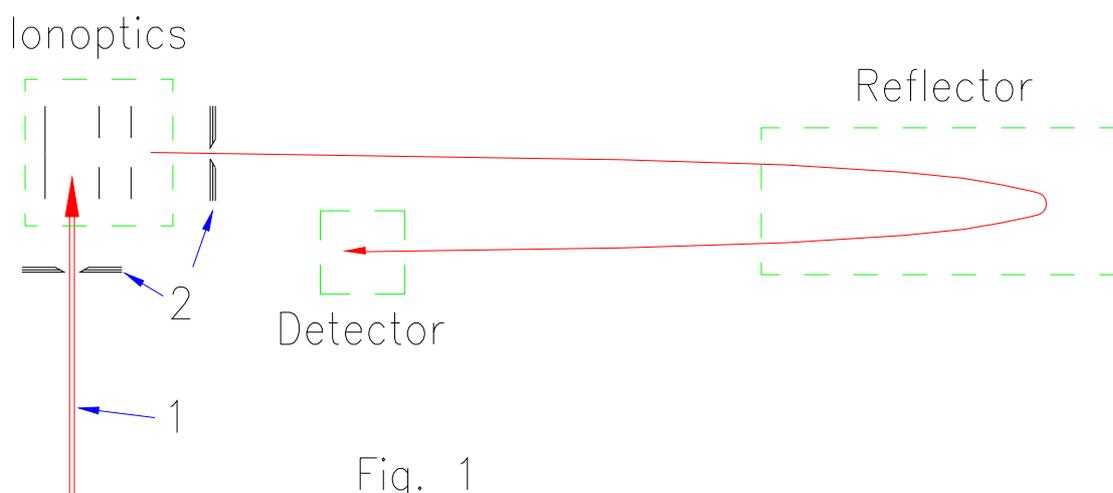


Fig. 1

At a fixed time (the start-time of time of flight) the ionoptics-electrodes are switched to their active-potentials and extract a bunch of ions. Depending on their mass-variation the ions reach the detector successively in a time-window corresponding to their respective masses. First the small masses arrive at the detector, then come the heavier ions. On the detector the ions produce a small negative pulse upon arrival.

It is the task of the electronics to resolve the incoming signals into fine steps of time, each time-increment

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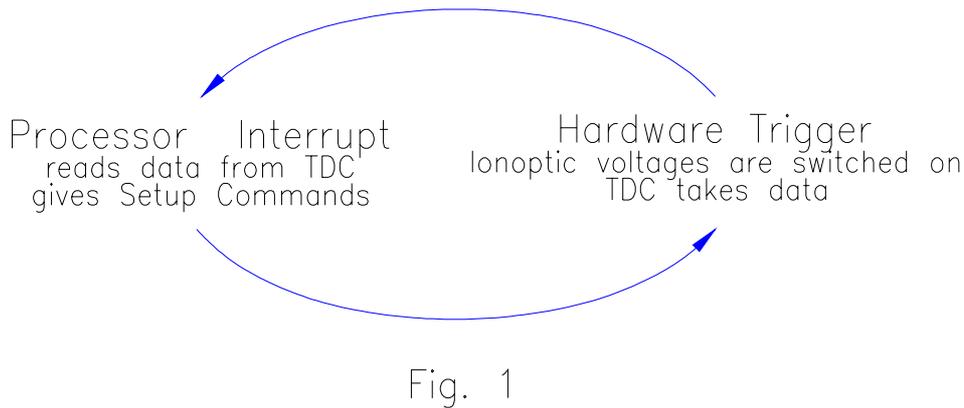
K ToF; ToF, theory

\$ Time-of-Flight Mass Spectrometry

### # K \$ Experimental-Sequence of taking data (Time-of-Flight Mass Spectrometry)

This topic will deal with the basic process of taking data on a mass spectrometer, i.e. starting one bunch of ions and registering their time of flight. How the measured times of flight are correlated to the respective ion masses will be dealt with in [Generation of a Mass Spectrum](#).

Taking [Time-of-Flight Mass Spectrometry](#) in the most simple minded way, taking data with a time-of-flight mass spectrometer can be described with Fig. 1 on the next page: Alternatingly the processor of the server computer gets an interrupt causing it to read data that the TDC (Time-Digital-Converter) has taken previously and then



The circuit that alternately creates a processor interrupt and a hardware trigger is shown in Fig.2. Counter A is driven by a 4Mhz crystal clock, its divider number being loaded from the computer. The output of counter A drives the input of counter B whose divider number can also be loaded from the computer. The output of counter B then generates the interrupt to the processor on the server computer. The divider

giving to all hardware modules their setup commands so that they can receive another trigger. When the hardware modules receive a trigger, they fire, causing the ion optics to switch on, the ion gate to open, and the TDC to start registering ions that hit the detector of the mass spectrometer.

numbers to these two counters are derived from the entries into the Minimum Rep-Rate(Hz) edit control on the Trigger Setting dialog window and the Repetition Rate(Hz) edit control in the Slowly Varying Parameters dialog window.

The output of counter B also gives a gate signal to counter C who receives its clock input from the output of counter A. Thus counter C can generate a hardware trigger at some fixed time after counter B has generated a processor interrupt. This time delay will leave the processor enough time to read out the previously registered data from the TDC and give the necessary setup commands to the different hardware modules (e.g. delay generators) in the server computer.

How the delay generators and the TDC interconnected is shown in Fig. 3. All the delay generators are synchronously triggered by the hardware trigger generated from counter C in Fig. 2. The two delay generators shown thus have a total of 6 outputs which have a fixed time relation to each other. These delay times can be controlled by the server computer.

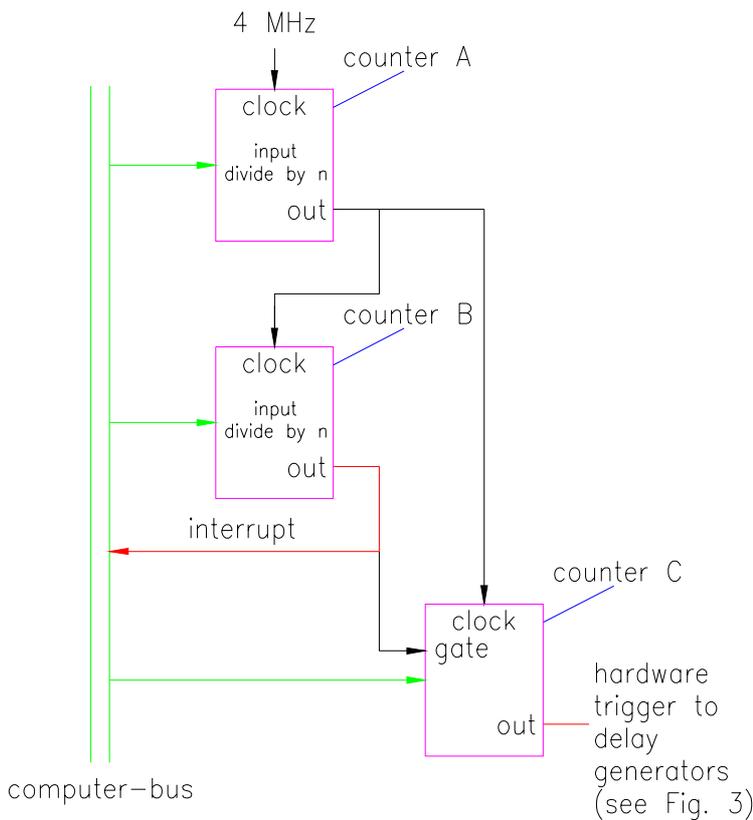


Fig. 2

# time\_sequence\_taking\_data  
K ToF; ToF, experimental sequence  
\$ Experimental Sequence of taking data

– The T0 output from delay generator 1 is used as a start signal to the TDC. After receiving this start signal the TDC starts counting time, registering the incoming stop signals (arrival times of ions on the detector) from the photomultiplier tube. Thus the arrival of ions at the detector viz. the time of the incoming signals at the TDC are a definite measure of the pertaining ion masses. After due time, i.e. after all ion masses of interest have been registered by the TDC, the server computer will deactivate the TDC and read all the registered stop signals from it.

– Outputs A and B from delay generator 2 switch the ion optics voltages on and off respectively.

Outputs A and B from delay generator 1 open and close the ion gate.

# K \$ **Generation of a Mass Spectrum (Experimental Sequence of taking data)**

Consider now the time sequence:  
 The just mentioned smallest unit of time is in our case defined by the Time-digital-converter (TDC), whose smallest time increment is 0.5 nanoseconds. One cycle which lasts from 5 to 2000us is divided into these units and only the arrival times of the ions are stored in a FIFO-(FirstInFirstOut)register of the TDC. After a bunch of ions has hit the detector, their arrival times are read by the computer and summed into a mass spectrum.

This means that the TDC only needs as many storage places as ions can arrive after a single switching on of the ion optics voltages. The server computer has a large data field which is initially zeroed before the experiment. Each element in this data field corresponds to one time element whose time range is defined in the nsec per point edit control on the Recording Parameters dialog window.

The time of the first sample is defined by the Start edit control, the time of the last sample is defined by the Stop edit control on the Recording Parameters dialog window. Actually you have two measures to use, when entering these limits: mass units(amu) or microseconds.

If you enter the limits of the recording in mass units, then

of course there must be an equation relating the actual time to the mass values that you entered. From the equation relating the energy of a particle to its velocity

$$\frac{1}{2}mv^2 = eU$$

it can be inferred that the time-of-flight of a particle from the ion optics to the detector will be proportional to the square root of its mass, i.e.

$$\sqrt{m} \approx t$$

or

$$m \approx t^2$$

Actual calibration must take into account some more effects. The most basic effect is an uncertainty of the starting time of the ion. This effect can be caused by finite time delays in cables or in electronic switches etc.. Putting this into a calibration formula would look like

$$m \approx (t + t_0)^2$$

this equation already resembling the detailed equations you can find under the topic Mass Calibration Formulas. Further details of the calibration equations and how a calibration is performed will be discussed there.

Like in the Recording Parameters dialog window, when you enter the limits for a mass plot in the X-Axis(Mass Plot) dialog window, you can decide whether you want to enter the limits in mass units (amu) or in microseconds.

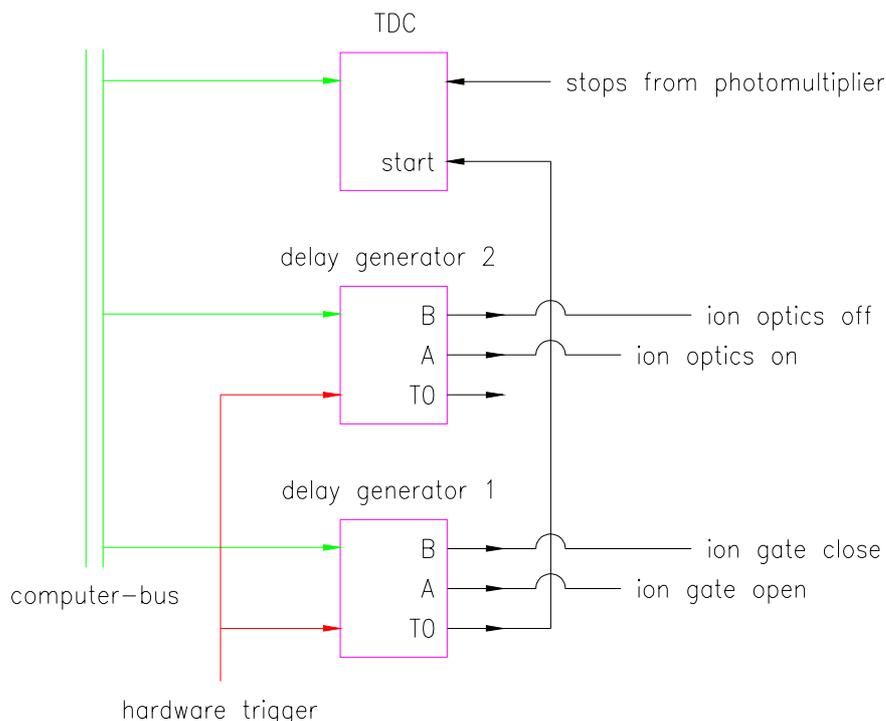


Fig. 3

# generation\_mass\_spectrum  
 K ToF; ToF, mass spectra  
 \$ Generation of a Mass Spectrum

Specifying the times of the events occurring is done more precisely in Fig. 4, where the time-zero point of the time axis and the times of all events listed is of course arbitrarily chosen:

- |   |                     |   |
|---|---------------------|---|
| a | $0\mu\text{sec}$    | delay generators receive hardware trigger   |
| b | $1\mu\text{sec}$    | ion optics voltages are switched on<br>TDC receives start signal  |
| c | $12\mu\text{sec}$   | ion gate opens  |
| d | $12,2\mu\text{sec}$ | ion gate closes   |
| e | $85\mu\text{sec}$   | Ion optics voltages are switched off  |
| f | $350\mu\text{sec}$  | TDC stops taking data   |
| g | $500\mu\text{sec}$  | interrupt is generated on the server computer   |
| h | $550\mu\text{sec}$  | after interrupt latency server computer starts interrupt service routine,<br>reading data from the TDC and giving setup commands to the delay<br>generators |
| i | viz. a              | everything starts over again  |

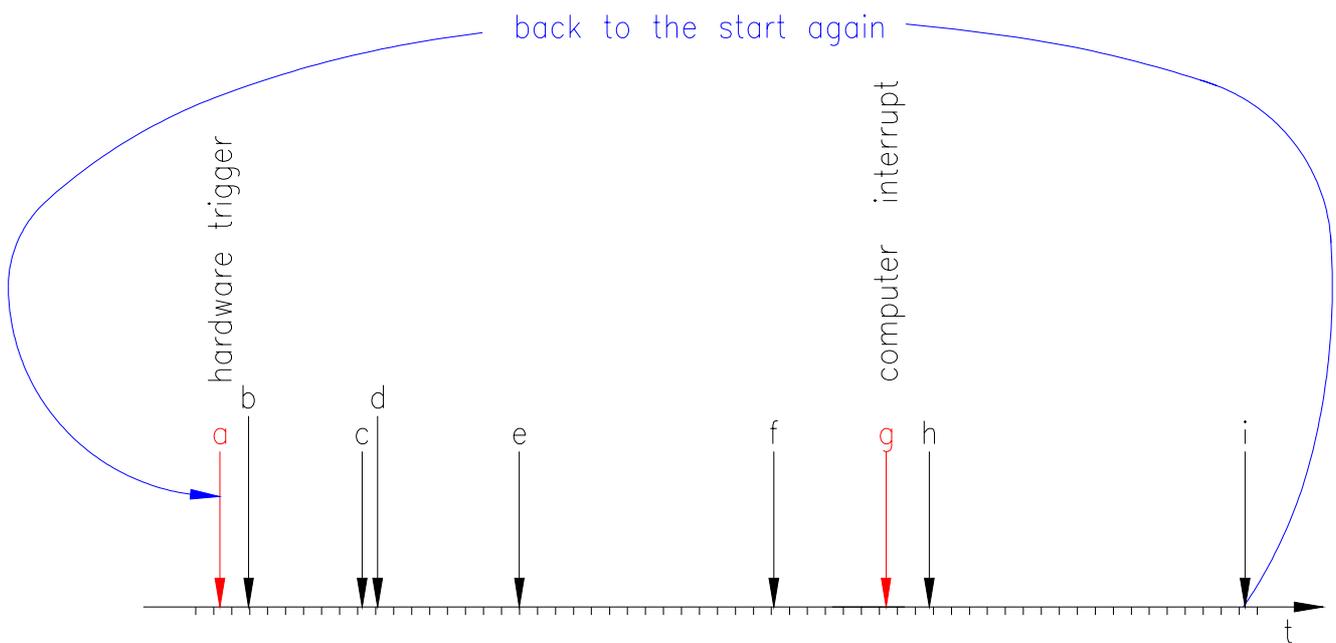


Fig. 4