TIME RESOLVED XAS DATA COLLECTION WITH AN XIA DXP-4T SPECTROMETER

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Time resolved XAS Research Opportunities

From a research point of view, time resolved experiments can be divided into two categories: single shot experiments and cyclically repetitive experiments. The former can only be carried out once per sample, the experiment typically either destroys the sample or transforms it into a new state from which it is difficult to return to the original. Chemical reactions often fall into this category. Cyclically repetitive experiments, on the other hand, are carried out on materials can be returned to their starting state, allowing the experiment to be repeated as often as necessary to collect data of interest. Many mechanical, electrical, and phase equilibrium experiments fall into this category. Biological systems may fall into either category.

Repetitive experiments, in turn, have two subcategories: continuously cycling experiments and pump-probe experiments. In the former case, the state of the system moves more or less continuously between a sequence of physical states as some driving parameter, such as temperature, pressure or voltage, is continuously cycled. In pump-probe experiments, the driving parameter is applied discontinuously, as using a laser pulse, and the system responds by making an abrupt transition to a new state from which it more slowly decays to its starting state.

The DXP-4T, a recently introduced, modified version of the DXP-4C Digital X-ray Spectrometer, can be applied to XAS studies of either class of cyclically repetitive experiment.

Functional Design of the DXP-4C

The front panel of the DXP-4T, which is shown in Figure 1 is identical to that of the DXP-4C with the addition of a “Sync” input, which is used to control its timing functions as discussed below. Figure 2 sketches out the high level functional design of a single channel of the DXP-4T, which is identical to that of the DXP-4C. The input is from a preamplifier, which is conditioned using analog electronics and then digitized using a 10 bit 20 MSA ADC. The primary spectroscopy functions are implemented in the FiPPI using digital combinatorial logic. These functions include pulse detection, pileup inspection, pulse filtering, peak capture, and input count rate counting. Captured peak values are passed to a digital signal processor (DSP) which corrects them to achieve good energy resolution and then bins them to generate spectra. The DSP also handles the interface to the outside control computer, accepting operating parameters and sending back spectra.

Figure 3 shows the FiPPI’s internal operation in further detail. It operates by using a fast triangular filter (with an adjustable peaking time typically set at 300 ns) to detect pulses using threshold crossing detection. The times between successive pulses in counted with the system clock to determine whether they are sufficiently isolated to avoid piling up in the slow channel filter. The amplitudes of non-piled-up pulses are captured at a sampling interval following their detection and sent to the DSP for further processing. The FiPPI processes new data values continuously, while the DSP only works with the captured values., a division of labor which allows the DXP-4C to achieve very high throughput in a high density package at low cost.

The DXP-4T Modification

Figure 4 shows how the FiPPI is modified in the DXP-4T. Basically, only two changes are required. The first is a Phase Counter, with a RESET input which is attached to the front panel SYNC input. The second is that the buffer is enlarged to capture the output of the Phase Counter at the same time a good peak is detected by the Pile-up Checker (i.e. its "arrival time"). The exact structure of the Phase Counter is different, depending upon whether the DXP-4T is being used in a pulse-probe experiment or in continuously cycling experiment. Because the FiPPI is realized in a field programmable gate array (FPGA) the appropriate design is downloaded prior to starting the experiment.

The two Phase Counter designs are not radically different. In the pulse-probe case the system clock is the counter CLOCK, divided it to achieve appropriate time resolution. It counts to a preset maximum value, corresponding to the total time interval to be measured, and then stops. The SYNC pulse RESETS the counter again each time the experimental system is pumped.

In the continuously cycling case, the GATE signal is used as the Phase Counter CLOCK, while the Sync pulse is used to RESET it again each time the experimental system passes through the "first" state.

In both cases, as in the DXP-4C as well, counts are collected only when the Gate signal is high. This is the standard operating mode and is intended to provide a means by which multiple detectors can accurately count for equal periods.

Time Resolved Application # 1: Phase Locked Spectra

The concept of Phase Locked spectrometry is an extension of other sorts of phase locked measurements: spectra are collected in phase with a continuously cycling phenomenon. The studied phenomenon may either be naturally cyclical or, as is probably the more common case, cycled on purpose as a noise reduction strategy - in the same way phase locked amplifiers are used.

The first example of the latter use was a situation where the experimenters wished to determine if a subtle change occurred in the environment of Cu atoms in a high TC superconductor when it went through the superconducting transition. Standard EXAFS measurements had been made on the samples, but these had proven inconclusive since day-to-day drifts in the data, arising from environmental effects, had been larger than the effect to be measured. That is, the measurements were essentially confounded by laboratory 1/f noise. Therefore an attempt was made to measure the phenomenon in phase locked mode, collecting data into one or the other of two spectra depending on the conductivity state of the sample. Here we describe how the DXP-4T was used in this technique. The results will be reported elsewhere in this conference by Bridges.

The sample was a thin film of high TC superconductor deposited on a low thermal mass heater and mounted in a cryostat. The heater was then programmed to oscillate the sample between the normal and superconducting states at about 2.5 Hz. Figure 5 shows both the output of T sensor measuring the sample resistivity and the output signal of digital logic which generated both Gate and Sync pulses from this signal. As may be seen, the Gate signal is high whenever valid data can be collected and low during transitions when the sample is not in a well defined conductivity state. The Sync signal goes high briefly each time the sample goes normal, and thus assures that spectrum #0 corresponds to the normal state.

Figure 6 shows how this technique is extended to the general case (illustrated by three phases) again using the two digital signals: a Gate and Sync. The former drives the Phase Counter, the latter resets it after every three (in this case) counts. Thus the counter counts 0 to 2 and resets, which defines 3 collection periods. Each time an x-ray count is detected and sent to the DXP for binning, it is "tagged" with the counter's current value. The DXP can then bin it into the appropriate spectrum according to its tag value. As noted above, the circuit is slightly more complex than shown, with counting suppressed when the Gate is logically low, so that data are only collected when the system is in a well defined experimental configuration, as per Figure 5. Depending on the amount of DXP-4C memory, 16 or more spectra can be binned during a cycle, thus allowing even fairly complex cycles to be characterized. Moreover, since the basic DXP clock operates at 20 MHz, cycle rates of over 100 kHz could be studied.

Time Resolved Application # 2: Time Resolved Spectra

Figure 7 shows the DXP-4C used in a pulse-probe experiment: time resolved EXAFS, where the fluorescent yield is to be measured as a function of time after a trigger. The study of structural relaxation in a light sensitive protein following a laser pulse. is an example. Here the division ratio of the system clock sets the time granularity of the study and the SYNC pulse is used to RESET for each laser pulse. If a relatively large number of time values are desired, memory limitations will reduce the number of energy bins in the spectra that are collected. In Figure 7 only a single energy bin is used (e.g. single channel analysis is performed). Detected x-rays are again time tagged but now the DXP bins them by their arrival time only if they fall into the set SCA window. Figure 8 is a cartoon of the time resolved SCA output from Figure 7, showing number of fluorescent counts collected vs time after the strobe. Because the system clock is 20 MHz, experiments of this class could readily be carried out with sub-microsecond time resolutions, possibly to 50 ns.

Generalizations

The time resolved collection process can be generalized in several ways. First, , time can be used to represent some other parameter, such as location in scanning instruments. Thus the DXP-4T can be used to produce spectra as a function of location or other variable. Secondly, given adequate memory, the distinction between phase locked and time resolved modes of operation can be arbitrarily blurred. While the time resolved discussion only presented time resolved single channel analysis, working with a single channel is not a requirement of the method. Each x-ray is identified by both its energy and arrival time. How the two dimension array of energies and time is binned is only limited by available memory. If, for example, the DXP-4T were specified with its 32K memory option and only 32 time point were needed, then spectra of 500 bins (2 words/bin) could be collected at each time point. As the number of time bins expands or contracts, the number of energy bins can be adjusted accordingly.

Acknowledgment:

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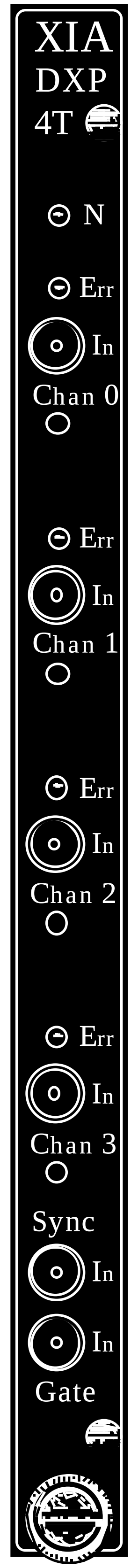

Figure 1: New XIA 4-channel DXP-4T X-ray Spectrometer, showing front panel timing input connections.

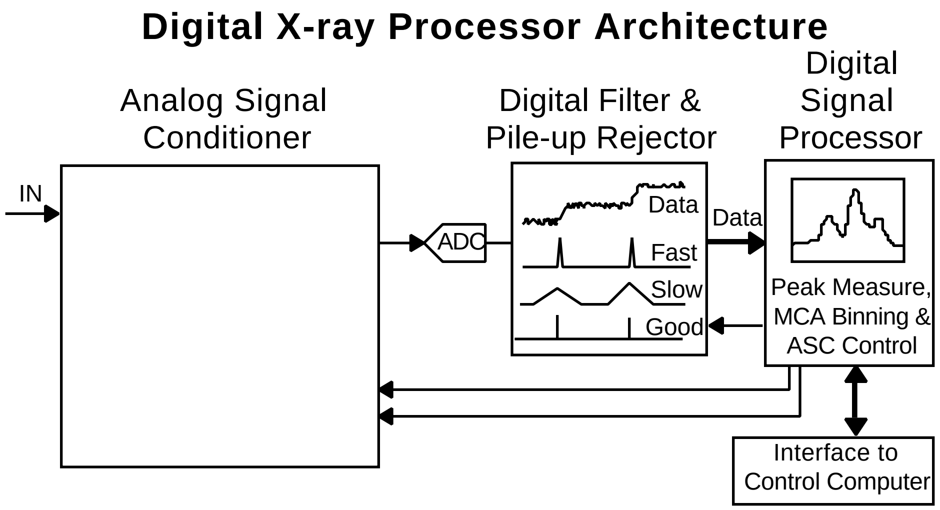

Figure 2: DXP-4T block diagram showing major functions

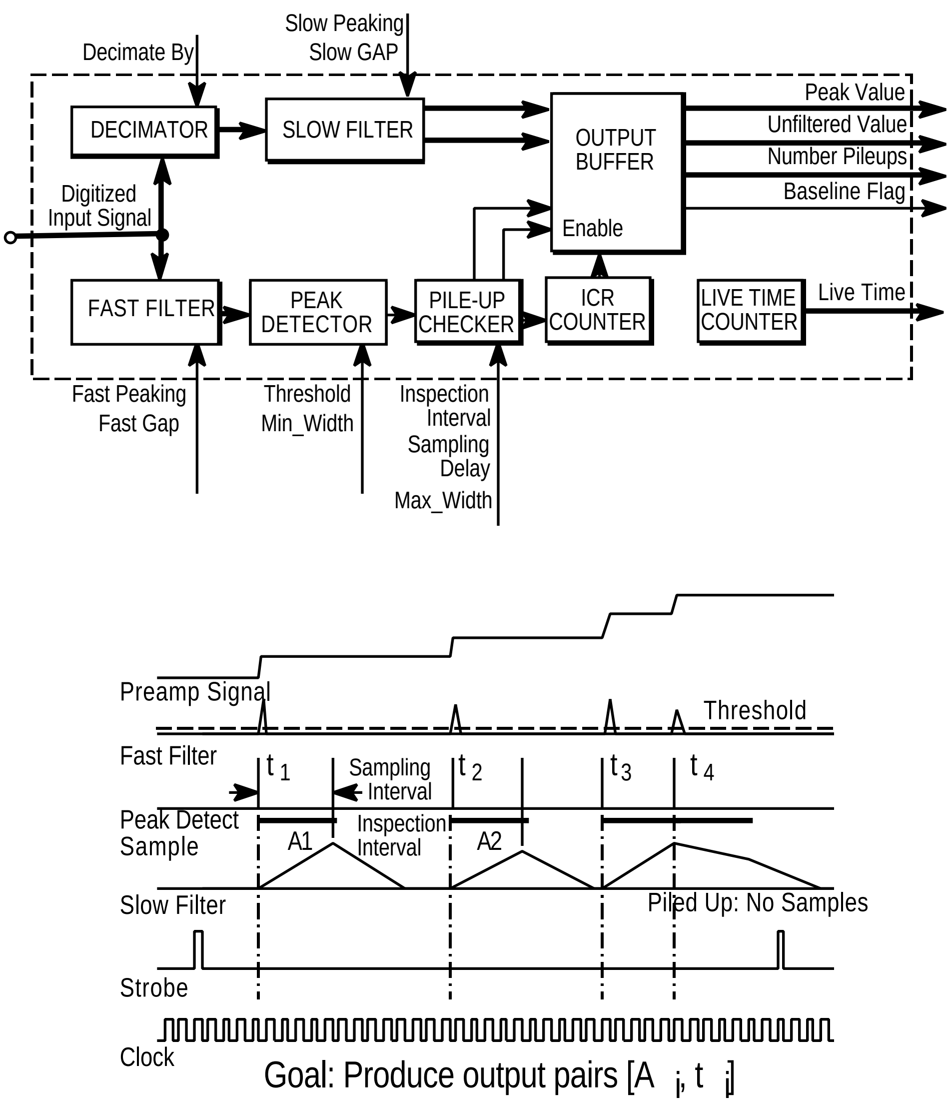

Figure 3: Structure of the DXP_4C's digital filter and pileup inspection block (FiPPI)

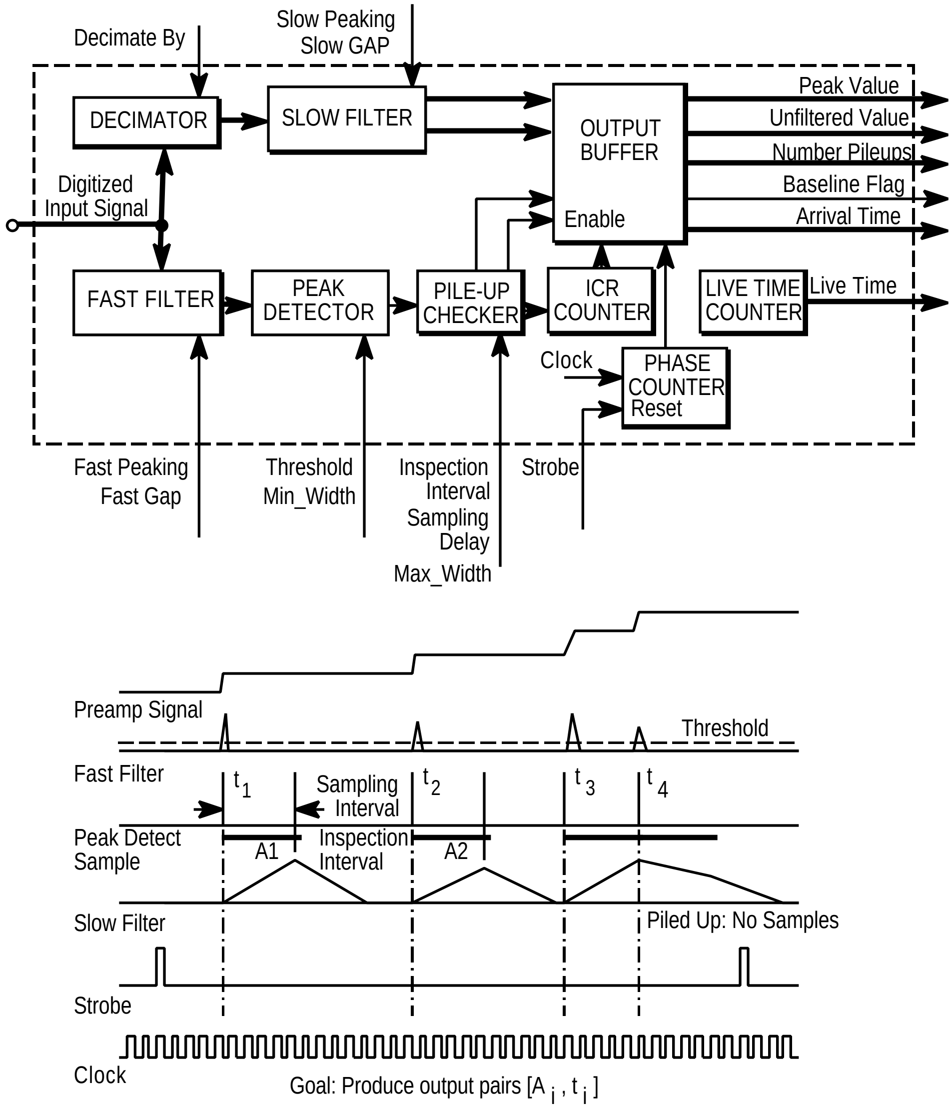

Figure 4: Structure of the DXP_4T's digital filter and pileup inspection block (FiPPI)

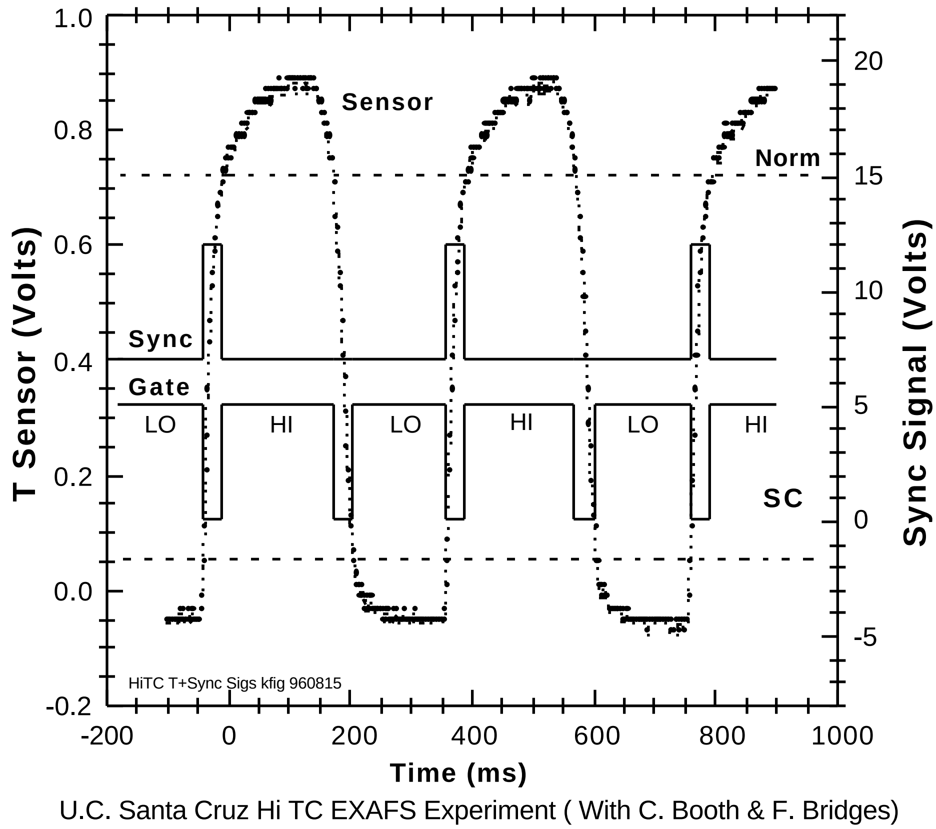

Figure 5: Generating GATE and SYNC signals from a cycling temperature signal

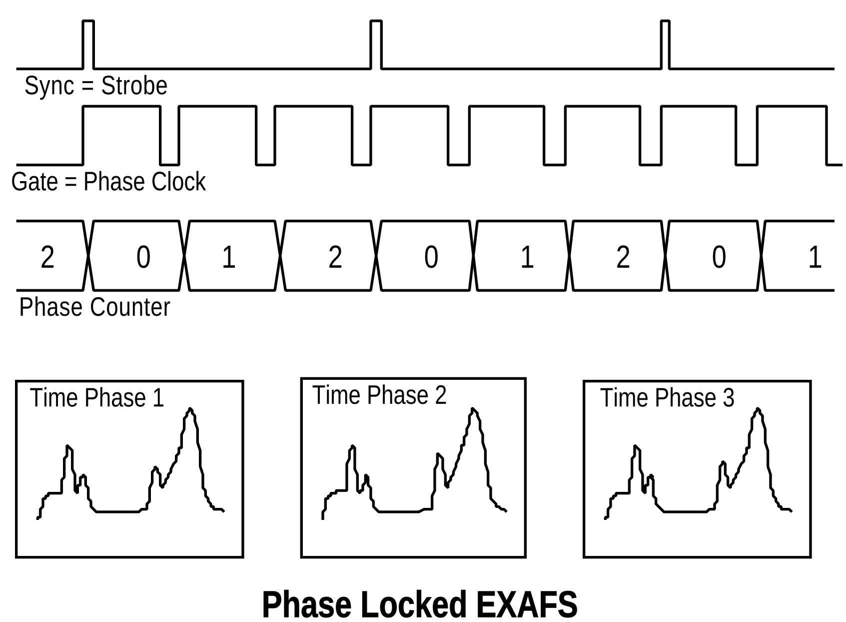

Figure 6: Generating phase labels for X-ray pulses in the DXP-4T's FiPPI

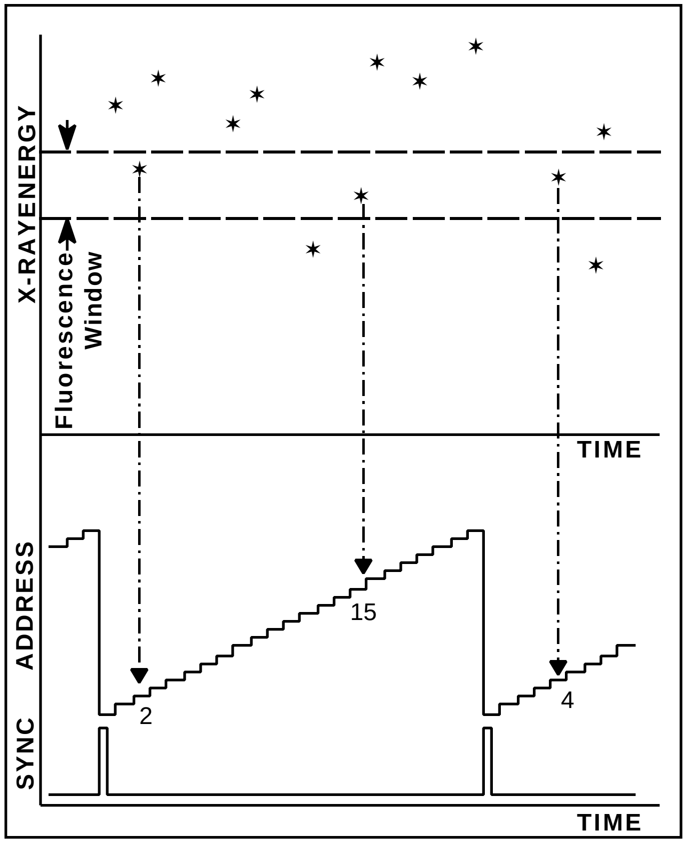

Figure 7: Time binning X-rays within an SCA window in a pulse-probe experiment.

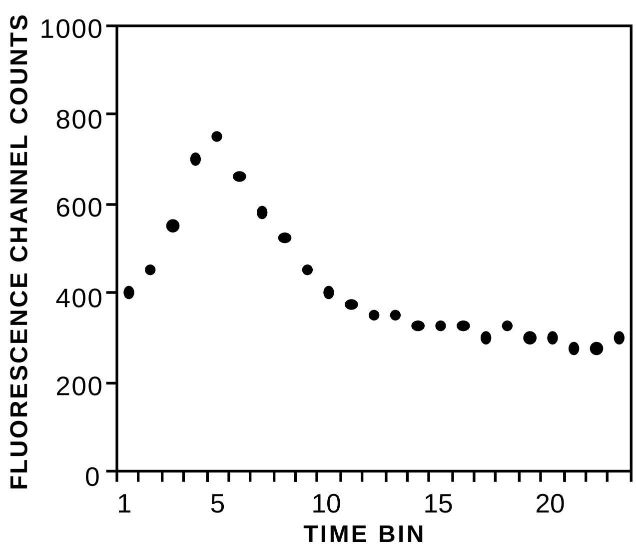

Figure 8: Cartoon of data output from the time resolved SCA experiment shown in Figure 7.