# Synchronization Improves Potentiostat Performance

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# Noise in Potentiostat Systems

- Intrinsic Noise
  - Generated by electrochemical cell
  - Electrochemical Noise
- External Pickup
  - Mains frequency and harmonics
    - 50/60 Hz, 100/120 Hz
    - Nearby RF
    - Motors, CRTs, other instrumentation
- Move the lab?
- Shielding
  - Faraday Cage
    - Surround cell and leads with conducting and *earthed* shield, connect to ground of instrument

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# Noise in Potentiostat Systems

- Internal Noise
  - Generated within the Potentiostat system
    - Component noise
      - Operational Amplifiers (Op-Amps)
      - Resistors (Johnson noise)
      - Voltage reference (Internal standard)
    - Power supply
      - Often a major contributor
  - Limits smallest signal that is measurable
    - pA – aA currents, μV voltages
  - Applied Potential Noise
    - Actually applied to the cell
      - Noise can hide natural effects – EIS, ECN
        - » Very low amplitude signals
      - May yield large currents on capacitors (double layer!)

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# Internally Generated Noise

- Power Supply
  - Linear
    - "Good old days"
    - Most Noise & ripple @ mains, 2x, 3x mains
      - Internally radiated
      - Current spikes on ground plane
  - Controlling the noise
    - Filtering
      - Also filters signal !
    - Integrating over a mains cycle
      - Also filters signal !
    - Take data slowly!

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# Internally Generated Noise

- Power Supply
  - Switch-Mode or Switching
    - High efficiency (less heat)
    - Can serve as DC-to-DC converter
    - Noise occurs at switching frequency and harmonics
    - YOU can control the frequency!
      - Above frequencies of interest
  - Controlling the noise
    - Synchronize data acquisition/waveform generation to the switching frequency

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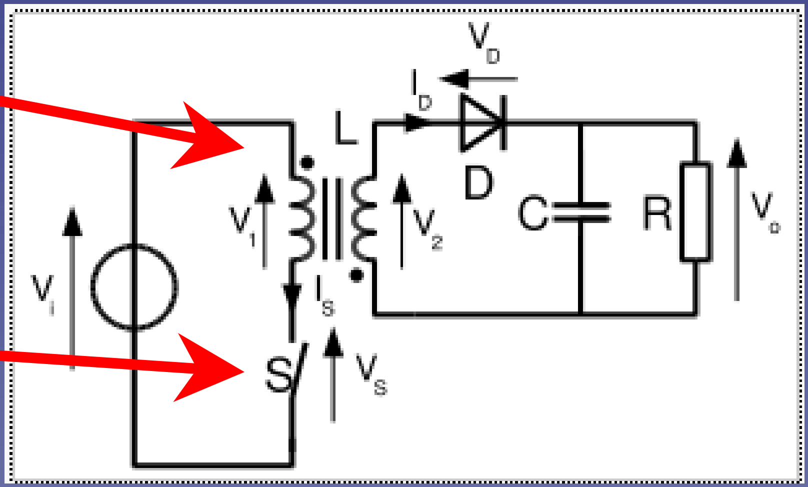
# Switch-Mode Power Supply

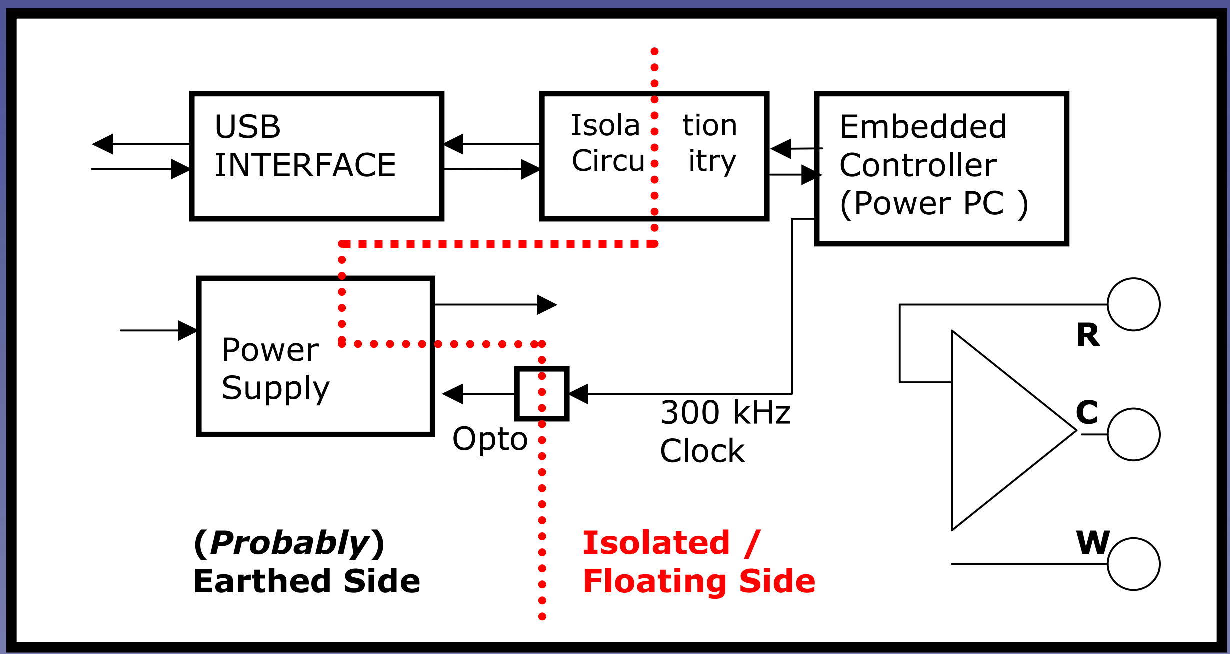
- Input voltage can be DC
  - DC-to-DC converter
- May provide isolation between Input and Output:
  - Special Transformer
  - Control circuitry for Switch S must also be isolated
    - Opto-coupler
- Isolation allows operation with grounded/earthed electrodes!




Switch-Mode Power Supply as used by Gamry

# Overall Schematic

- Isolation of Potentiostat provided by
  - Digital USB isolators (USB may be earthed)
  - Power Supply Transformer
  - Opto-isolator on PS Controller Clock
  - Experiments with **Earthed electrodes** are possible




Isolation in the Reference™ 600

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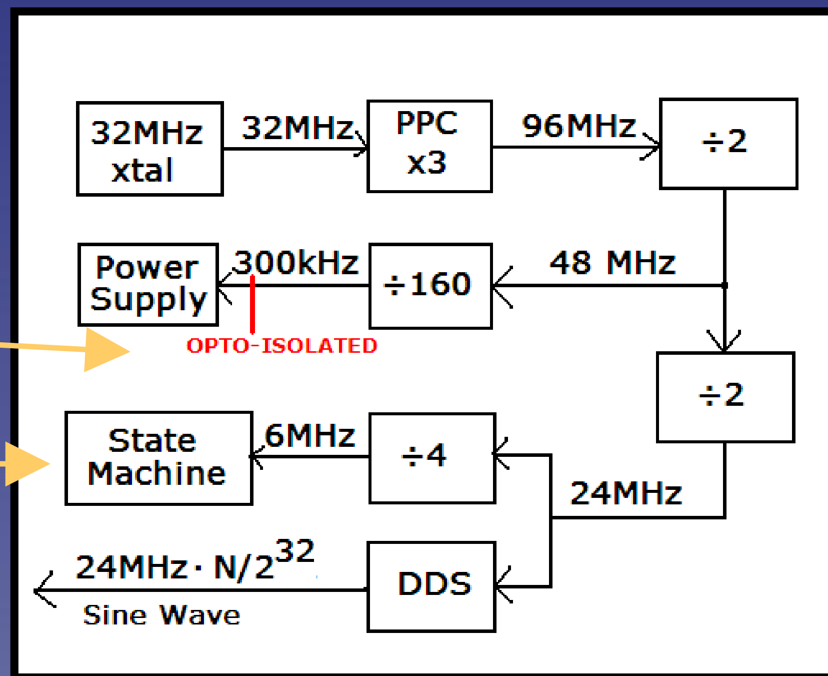
# One Crystal Controls All

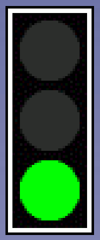
- A single 32 MHz crystal is the master timing for nearly everything!
- Power supply switching frequency
  - Opto-isolated to PS controller
- Data acquisition *via* "State Machine"
  - Synchronize with internally generated noise
  - Always sample at the same instant of internal noise waveform during an experiment




Clock generation in a Reference™ 600

# State Machine

- **Finite state automaton**
  - "state"
    - Has outputs
      - Digital signals to control data acquisition
    - Has inputs
      - Digital signals from the external world, or even its own outputs!
    - Has rules for transitions into another state
- Examples
  - Door: Open or Closed
  - Traffic Signal: Green, Yellow, Red, Yellow-Red



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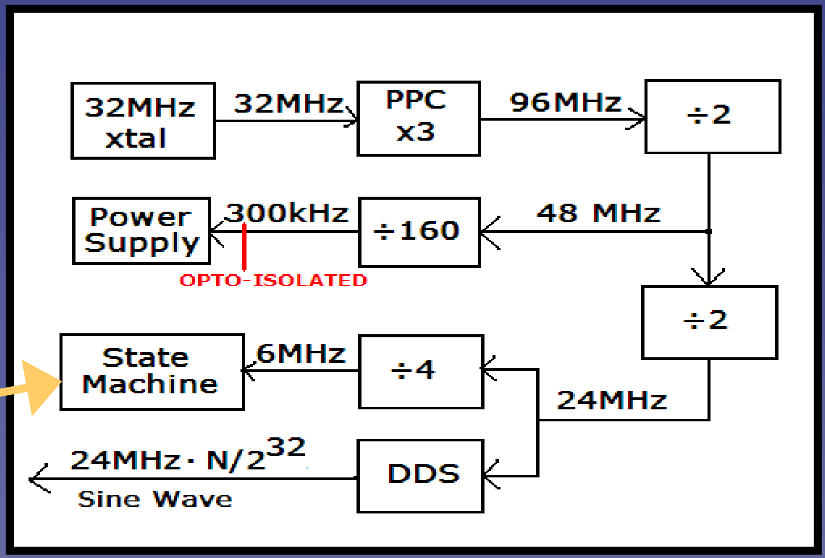
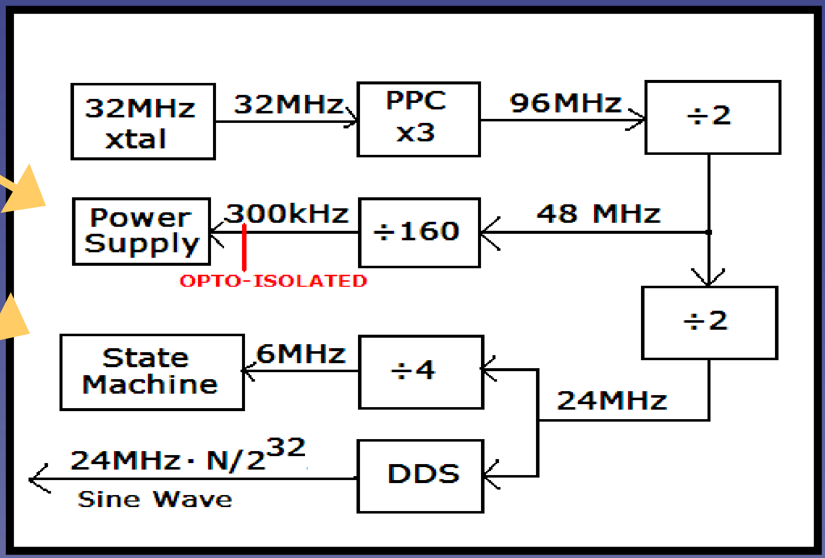
# State Machine

- Implemented as an integrated circuit
- A CLOCK synchronizes all transitions
  - Prevents ambiguities during transitions
  - Controls time between transitions/decisions
- Controls data acquisition timing
  - Within a point
    - Current interrupt
    - When to take data
  - Time between points



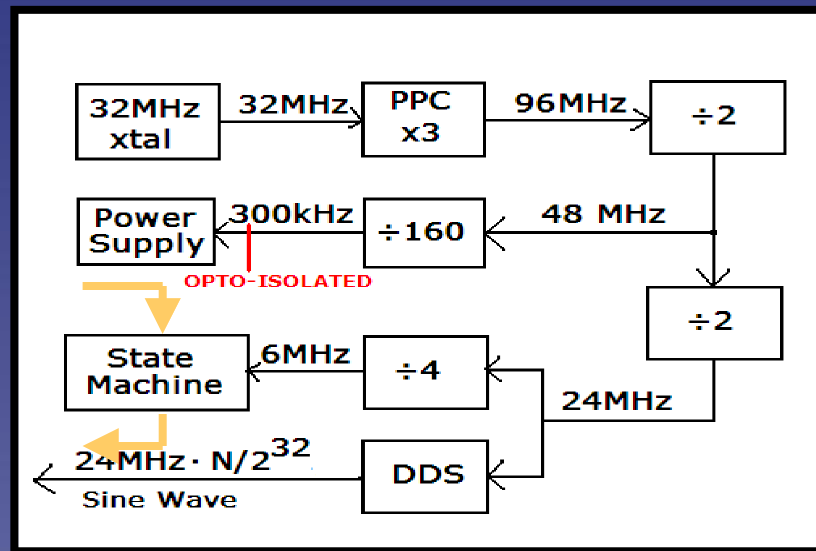
# State Machine

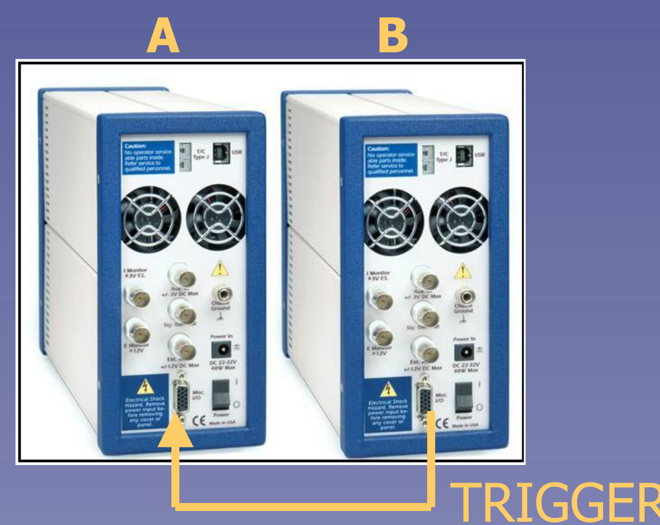
- Because power supply noise frequency (300 kHz) and data acquisition are derived from same clock, they can be made synchronous
- Data acquisition
  - 3,333 µs or a multiple!
- Always measure data at the same point on (possible) noise waveform



# Noise Measurements

- Reference™ 600 has two "synchronization" digital signals
  - Input pulse to start data acquisition
  - Pulse out when data acquisition starts
- Effect of Non-synchronized?
  - Two experiments, same data point timing
  - (1) Normal clocking - use **A** only
  - (2) **A** is triggered by pulse from another Reference 600 ( **B** )



# Noise Measurements

- Measured V across 2000 ohm resistor @ 0V with potentiostat **A**
  - Faraday Cage!
  - Same potentiostat, but trigger came from A or B
- 2000 data points averaged

| Point Timing/µs | Internal Trigger (A) (synchronized) | | External Trigger (B) (un-synchronized) | |
|---|---|---|---|---|
| | Average/µV | Std Dev/µV | Average/µV | Std Dev/µV |
| 10,00 | 35,1 | 69,6 | -43,6 | 124,1 |
| " | 50,9 | 68,8 | 0,9 | 123,7 |
| 3,33 | 426 | 80,9 | -131 | 370 |
| " | 348 | 80,3 | -168 | 383 |
| 3,33 * | 262 | 47,6 | 528 | 92,2 |
| " * | 261 | 47,1 | 449 | 96.8 |

* 200 kHz filter applied

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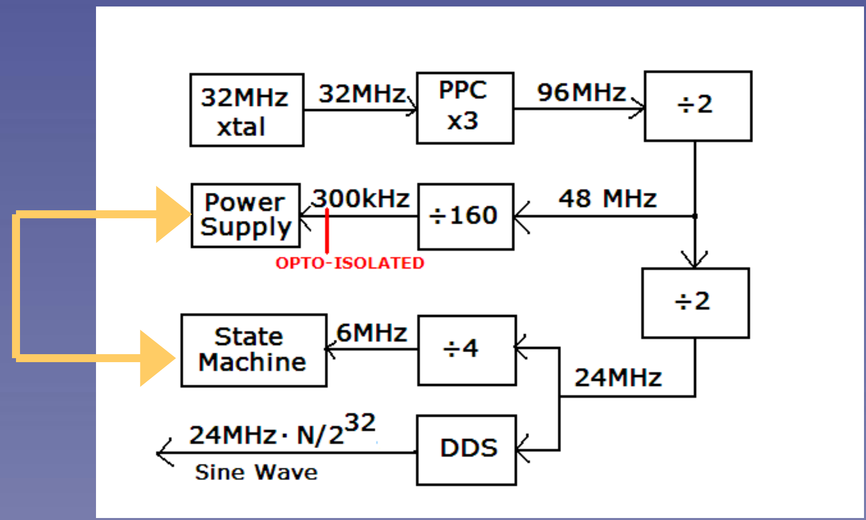
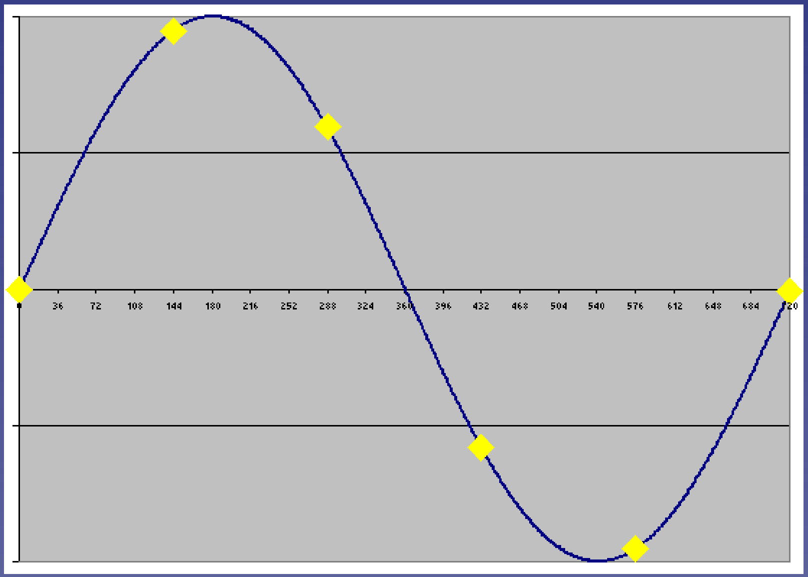
# Synchronization

- Synchronization of power supply and data acquisition improves measured noise by a factor of 2 or more
- 200 kHz filter did not entirely remove noise with external trigger
  - Noise >200kHz is attenuated, reduces noise bandwidth
  - Synchronization does not help component noise
  - Possibly noise was introduced post-filter



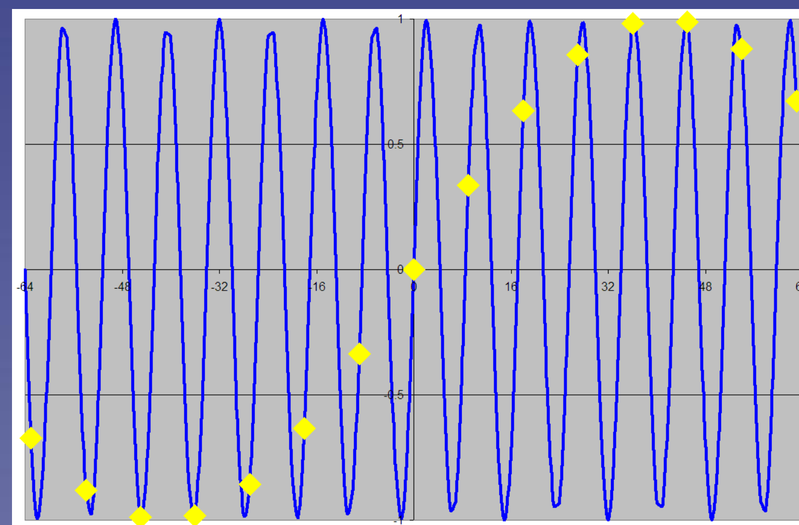
# Synchronization and EIS

- Conventional Wisdom
  - You **MUST** sample many times/cycle
  - You **MUST** use an “anti-Aliasing” filter to eliminate all frequencies above the “Nyquist” Frequency
    - Nyquist Frequency = $f_{Acquisition}/2$
- If you wish to measure EIS @ 1 MHz, you must take data every 500 ns or **faster**!
- Expensive: € € € € €



# EIS by Sub-Harmonic Sampling

- Conventional Wisdom
  - Assumes you know **nothing** about the signal
- EIS
  - Apply a signal of **known** frequency
  - Measure E, I at **that frequency**
- Break the "rules"
- Can use aliasing to your advantage!
  - Only if data acquisition is synchronized with waveform generation!




One data point every ~1,05 cycles of **sine wave**

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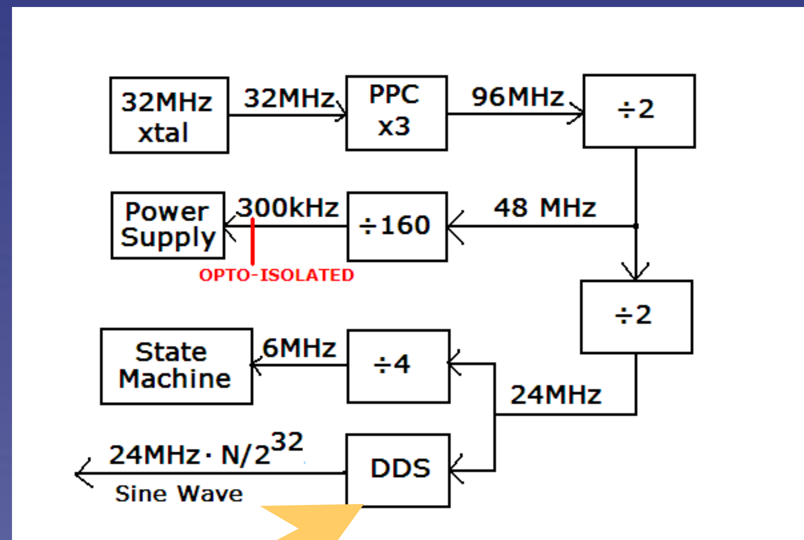
# EIS by Sub-Harmonic Sampling

- Traditional waveform circuits are unsuitable
  - Accuracy controlled by R, C, L values
  - Inaccurate
  - Frequency can drift
- DDS – Direct Digital Synthesis
  - Produces a low distortion analog sine wave
  - Programmable frequency
    - 24MHz * N / $2^{32}$
  - Used in TV, radio, cell phones

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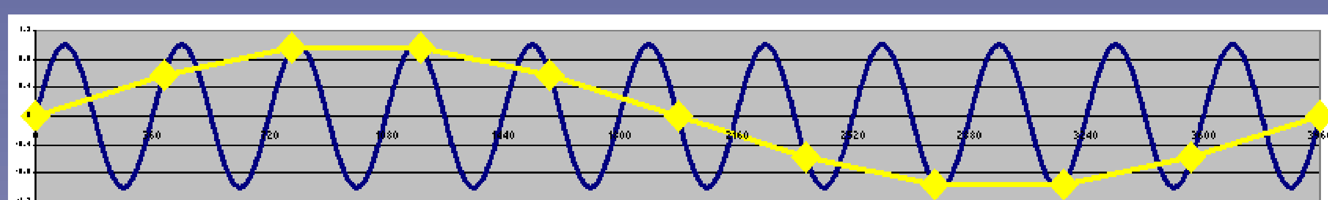
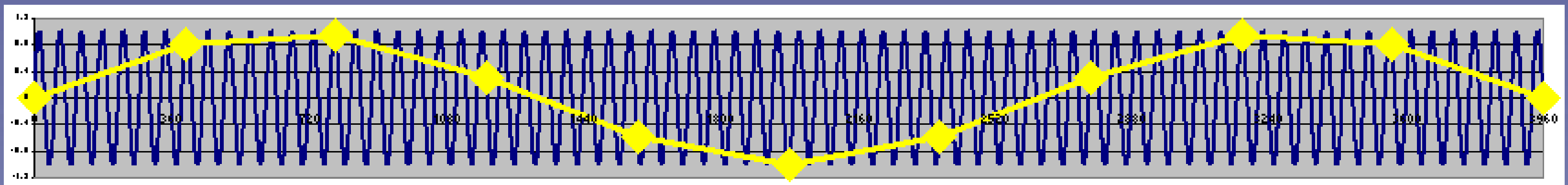
# What is Sub-Harmonic Sampling?

- Requires a repetitive signal
  - Box-Car Averaging
  - Down-mixing
  - Heterodyne
- Example: f= 2 777,777… Hz; period = 1/f = 360 µs
- Take a data point every 396 µs ( f / 1,1 )
  - < 1 point per cycle
  - $f_{ACQUISITION}$ > Nyquist frequency
  - Point 1 396° (36°); point 2 792° (72°) ; point 3 1188° (108°) ; … point 10 3960° (360° or 0°)
- After 3960 µs we have 10 points, evenly spaced every 36°



# Sub-Harmonic Sampling

- At higher frequencies, many cycles may be skipped
  - Start skipping cycles above ~10 kHz
  - @ 1 MHz, skip 166 cycles (of 1 MHz) between readings
- Only possible if DDS and data acquisition clock are locked together
  - @ 1MHz: 10ns → 3,6°
- Stringent requirements on Sampling ADC as well
  - ADC input should have 1 MHz bandwidth!
    - Not often specified!
  - Sample-and-Hold "Aperture" jitter is an important specification
    - 5 ps rms typical (Reference™ 600)



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# Is Internal Clock Necessary?

- Two Reference™ 600 Potentiostats
  - Normal connection
    - Internal DDS of **A**
  - External DDS
    - Same DDS type
    - Same crystal type
    - Signal Out from **B** → External Signal In **A**
  - Measured EIS 65 Hz-357 Hz
  - Applied Vac quite similar for both experiments

**A** **B**

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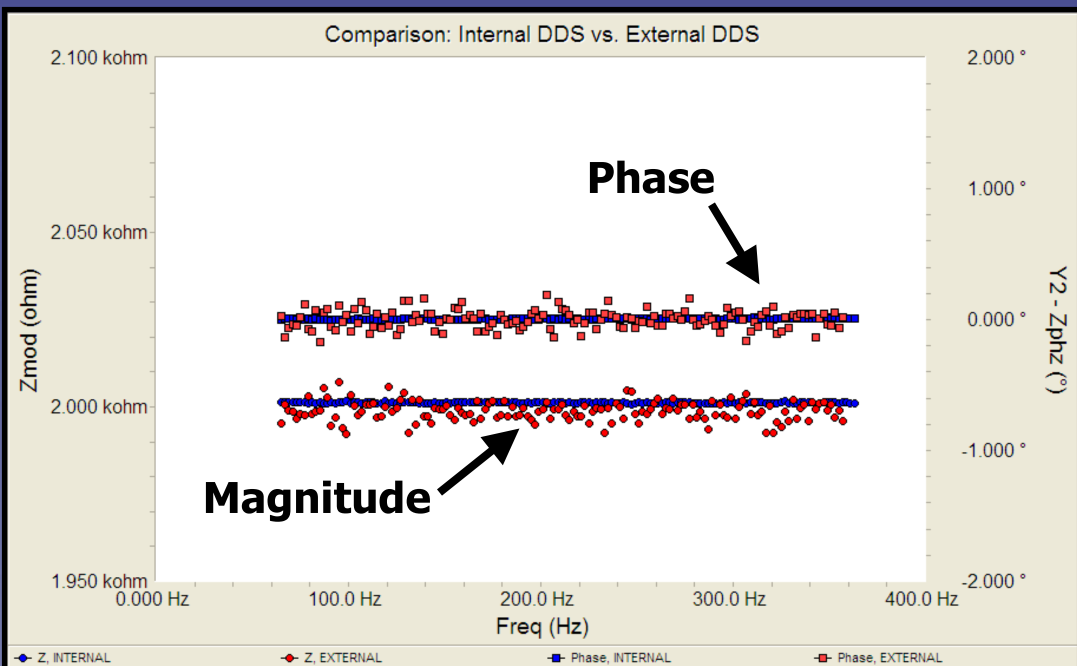
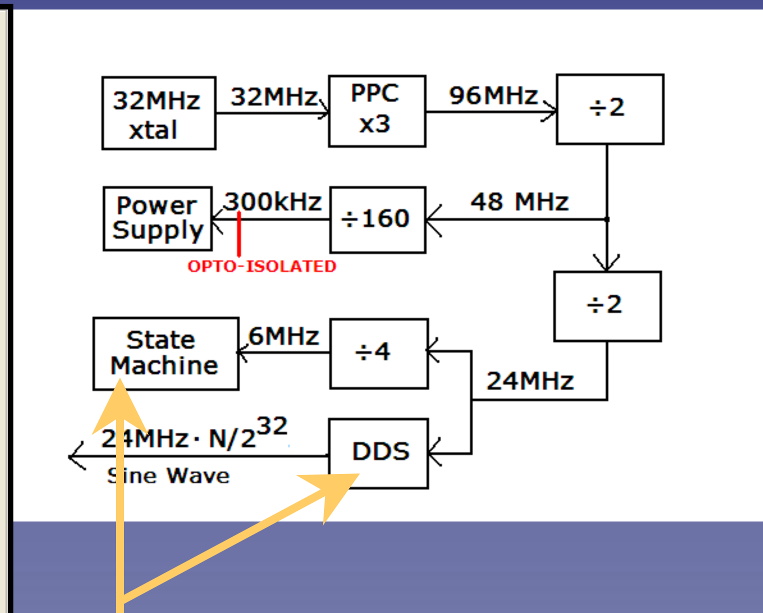
# Is Internal Clock Necessary?

| | ♦(\|Z\|) | ♦( ♐ ) |
|---|---|---|
| **Internal** | 0,007% | 0,004° |
| **External** | 0,14 % | 0,072° |




**YES!**

# Acknowledgments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- You, the audience
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