Chapter 5:

Signals & Noise

Signals and Noise

- The analytical measurement

→ is made up of two components (S & N)

- The signal (S)

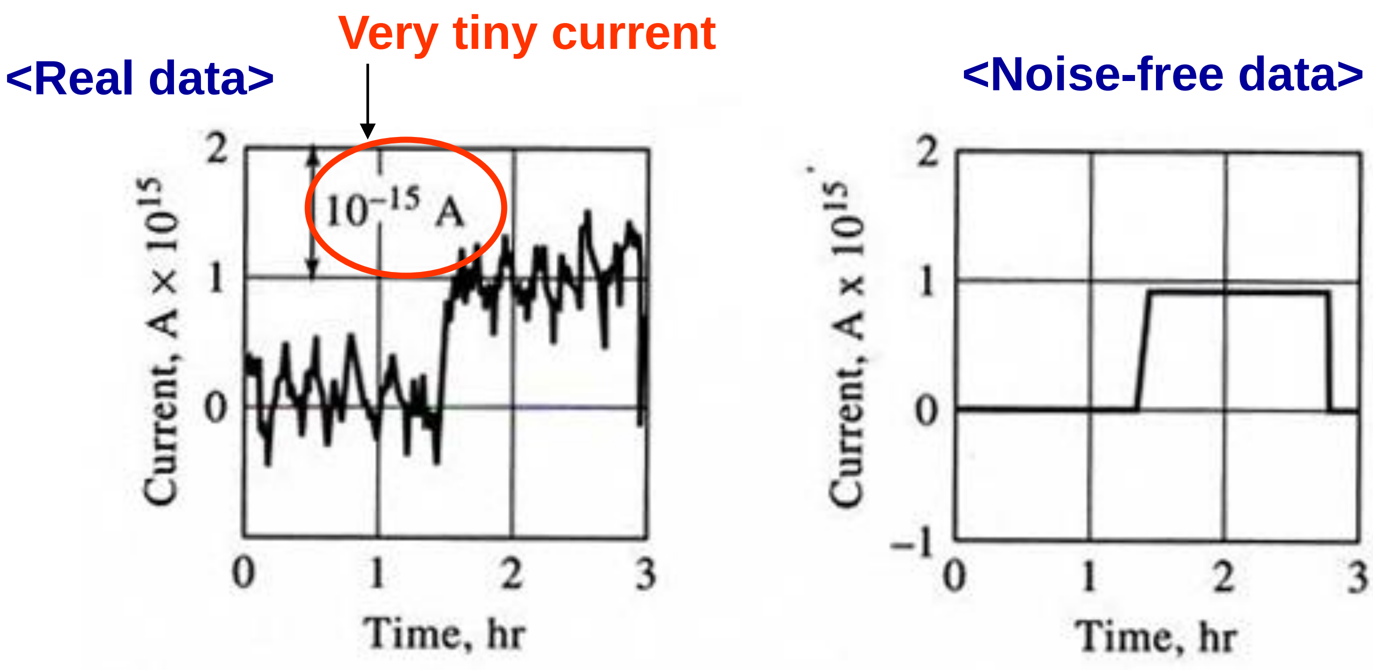
→ Carries information about analyte

- The noise (N)

→ Extraneous information that is unwanted

Noise degrades accuracy and precision (also LOD)

Signals and Noise



(a) (b)

Figure 5-1 Effect of noise on a current measurement: (a) experimental strip-chart recording of a 0.9×10^{-15} A direct current, (b) mean of the fluctuations. *(Adapted from T. Coor,* J. Chem. Educ., *1968,* 45, *A594. With permission.)*

Signal-to-Noise Ratio (S/N)

In most measurements,

- The average strength of the noise is constant and independent of the magnitude of the signal.

- The effect of noise on the relative error of a measurement becomes greater as the quantity being measured decreased in magnitude.

$$\boldsymbol{S/N} = \frac{\text{mean}}{\text{standard deviation}} = \frac{\bar{x}}{\boldsymbol{s}}$$

Rule of thumb :

If **S/N is 10 or greater**	=	direct recording
less than 10	=	need noise filtering
less than 2 or 3	=	impossible to detect

Signals and Noise

S/N = 4.3

S/N = 43
(better precision)

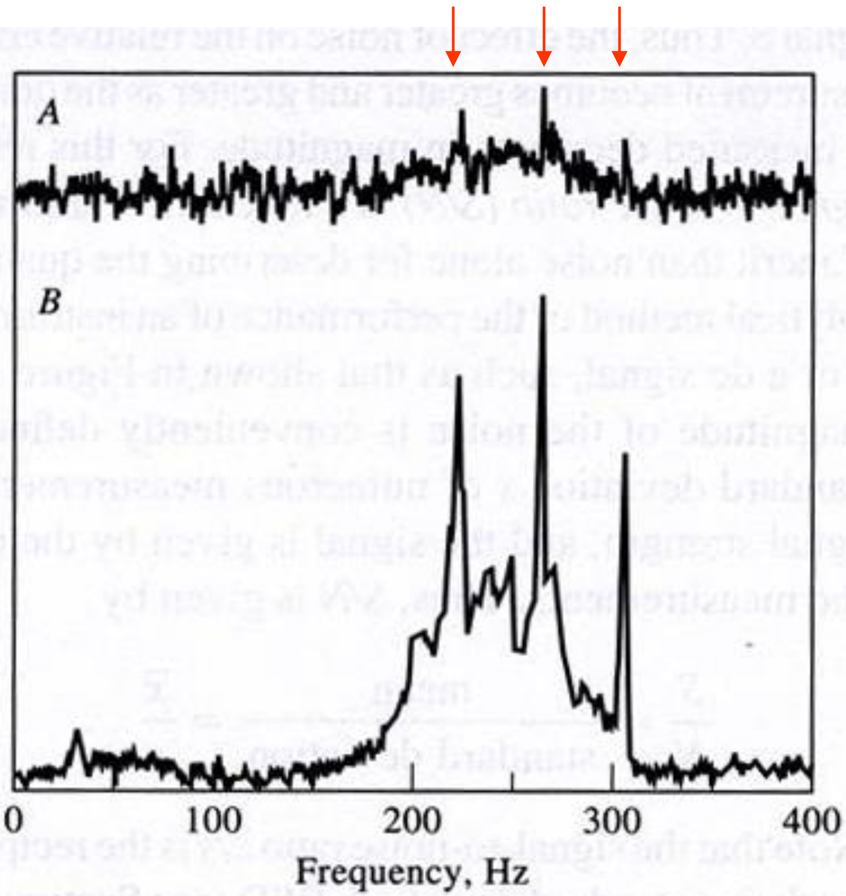


Figure 5-2 Effect of signal-to-noise ratio on the NMR spectrum of progesterone: *A*, *S/N* = 4.3; *B*, *S/N* = 43.
(Adapted from R. R. Ernst and W. A. Anderson, Rev. Sci. Inst., ***1966**, 37, 101. With permission.)*

Sources of Noise in Instrumental Analysis

1) ***Chemical Noise*** : Chemical noise arises from a host of uncontrollable variables that affect the chemistry of the system

- variation in temperature, pressure, or humidity
- changes in vibration, or light intensity

2) ***Instrumental Noise*** :

- Endogenous (within system): recorder, spectrometer, source amplifier, signal processing etc

  <Johnson noise, Shot noise and Flicker noise>

- Exogenous (outside system): environmental noise

  < Antenna effect>

(a) Thermal Noise (Johnson or Nyquist noise)

- This arises because the electrons or charge carriers which carry an electronic current always have a thermal motion.

- This random motion increases (as temperature increase) → very small fluctuating voltages to appear across any resistance in the electrical circuit

- This noise may be called "**white noise**"

It contains component at all frequency values

Constant across the spectrum

- It is important to note that thermal noise is present even in the absence of current in a resistive element and disappear only at absolute zero

- Lowering thermal noise → cooling (PMT, photodiode)

(b) Shot Noise

- This noise is encountered wherever electrons or other charged particle cross a junction. (pn interface or photocells: evacuated space between the anode and cathode)

- Such event is not entirely smooth and continuous

  : random and quantized → noise

$$i = \sqrt{2 I e \Delta f}$$

For root-mean-square current fluctuation in a frequency, Δf

I : magnitude of the total current

e : charge of electron

Δf : bandwidth of the signal processing circuit

- Shot noise is a significant source of noise in spectrophotometers at low light levels

Flicker Noise (1/f noise)

- The cause of flicker noise are not well understood.
- Flicker noise becomes significant at frequencies lower than about 100 Hz (sometimes 300 Hz)

$$\mathbf{V} \propto \mathbf{1}/\boldsymbol{f}$$

- This causes drift (especially DC).
- Flicker noise can be reduced significantly by using wire-wound or metallic film resistors rather than the more carbon composition
- Frequency dependent

Flicker Noise (1/f noise)

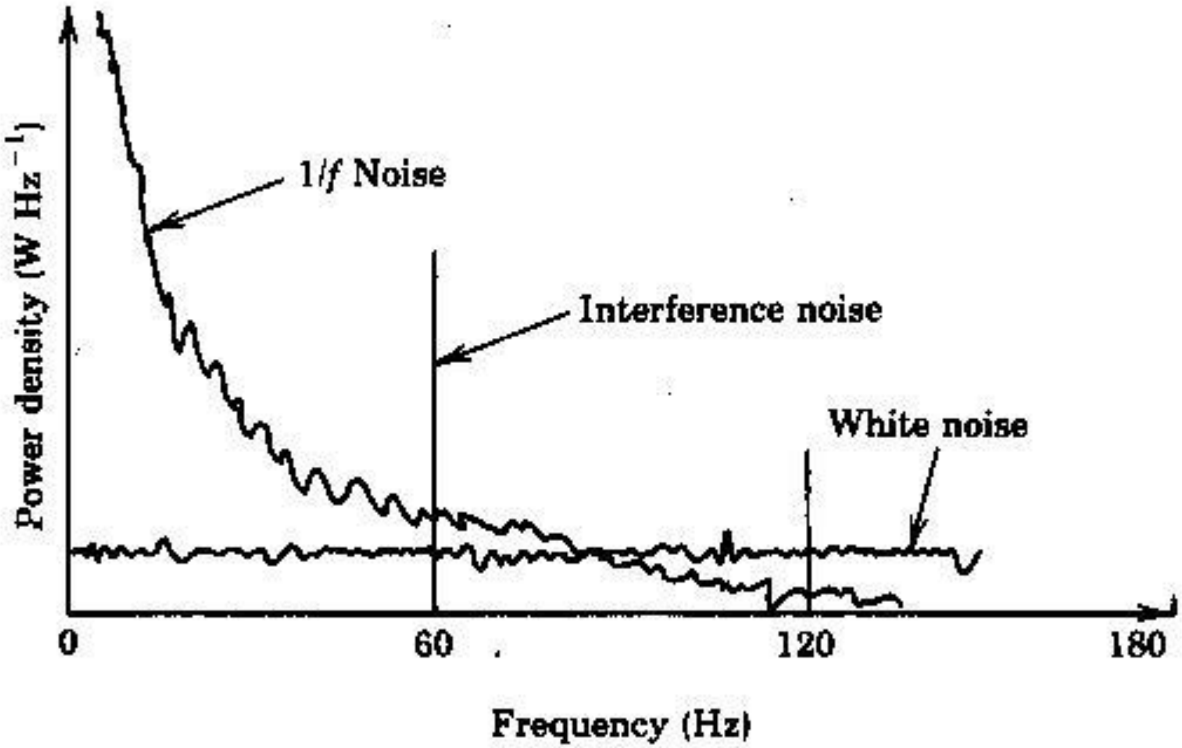


Fig. 12.1 Some representative power density spectra for noise. In most instruments $1/f$ noise predominates at low frequencies and white noise at high ones. Here types of noise are defined by frequency dependence.

(d) Environmental Noise (Interference Noise)

* Environmental noise is composite of noises arising from the surroundings

- Mechanical vibration

- Light from room

* Each conductor in an instrument is potentially an antenna capable of picking up electromagnetic radiation and converting it to an electrical signal

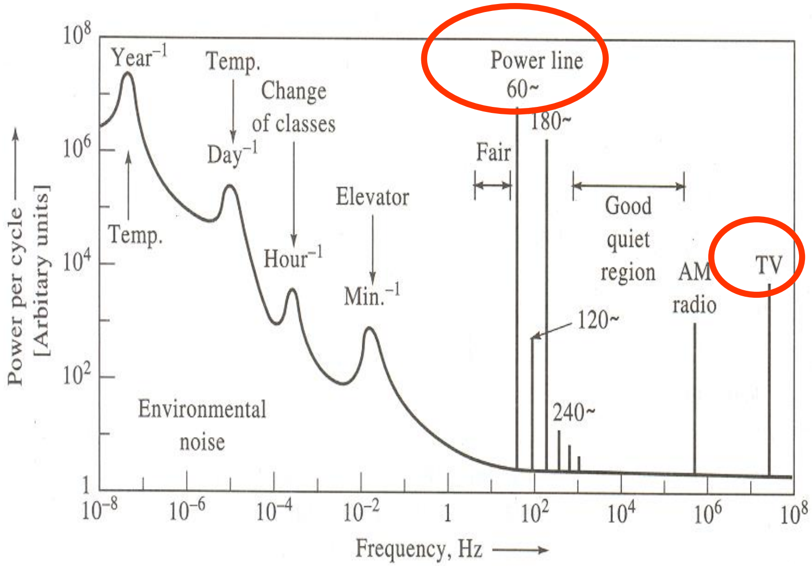


Figure 5-3 Some sources of environmental noise in a university laboratory. Note the frequency dependence and regions where various types of interference occur. *(From T. Coor, J. Chem. Educ., 1968, 45, A540. With permission.)*

S/N Enhancement

Both hardware and software methods are available for improving S/N ratio of a method.

1) **Hardware noise reduction:**

   is accomplished by incorporating into the instrument design components such as filters, choppers, shields, modulators, and synchronous detectors.

2) **Software noise reduction:**

   - are based upon various computer algorithms that permit extraction of signals from noisy data.

   - data should be converted to digital forms from analog forms

Hardware Methods: Grounding and Shielding

- Environmental noise generated by electromagnetic radiation can be reduced by grounding and shielding

(also by minimizing the lengths of conductors within the instrumental system)

- The optimum configuration is often found only after trial and error: more art than science

- Shielding becomes particularly important when the output of a high-resistance transducer, such as the glass electrode, is being amplified

Faraday Cage (Shield)

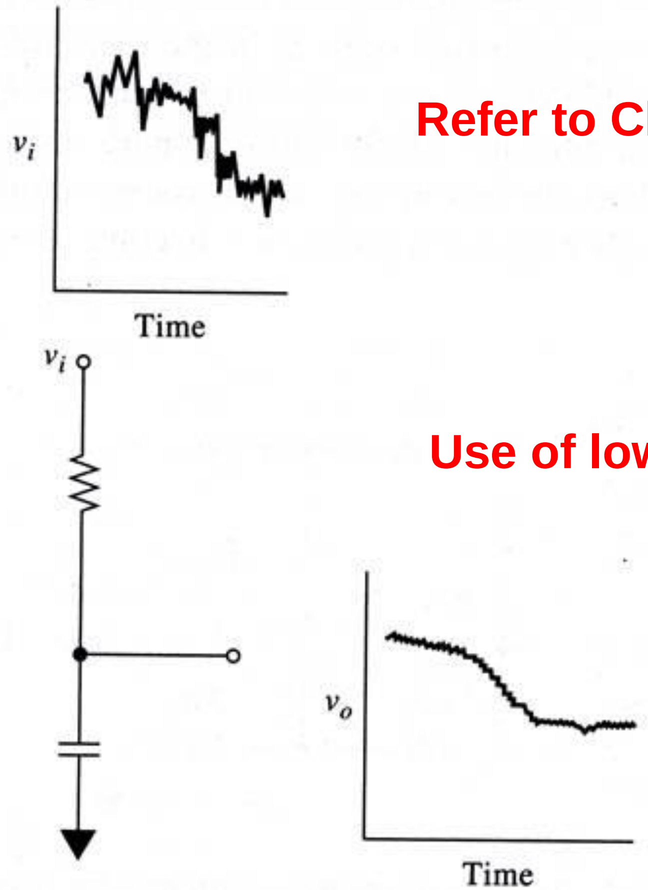
Faraday cage is grounded to dissipate any electric currents generated from the external electromagnetic fields and thus block a large amount of the electromagnetic interference

Hardware Methods: Analog Filtering

-Environmental noise can be eliminated by proper frequency selection

- High pass filter - effect of drift and other flicker noise
  (can be used when the analytical signal is at high frequency)
- Low pass filter - high frequency components including thermal and shot noise (white noise)
- Narrow band filter - attenuate noise outside an expected band of signal frequency

Hardware Methods: Analog Filtering

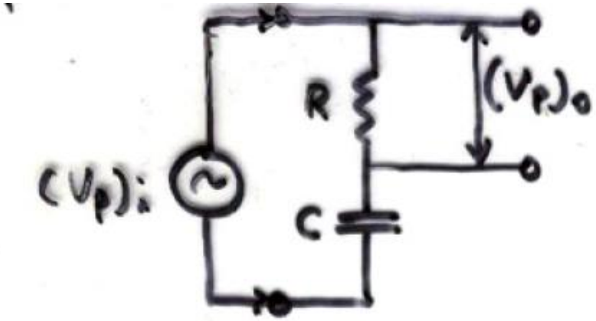


Refer to Chapter 2.

Use of low-pass filter

Figure 5-5 Use of a low-pass filter with a large time constant to remove noise from a slowly changing dc voltage.

High pass filter (with RC circuit)



High freq → pass

low freq → removed

High-pass : remove low-frequency noise (1/f noise)

$$i_p = \frac{(V_p)_i}{Z} = \frac{(V_p)_i}{\sqrt{R^2 + \left(\frac{1}{2\pi f C}\right)^2}} \quad \text{— (1)}$$

peak current

R ↑ resistance

$\frac{1}{2\pi f C}$ ↑ capacitive reactance

C : capacitance $\left(C = \frac{Q}{V} \right)$

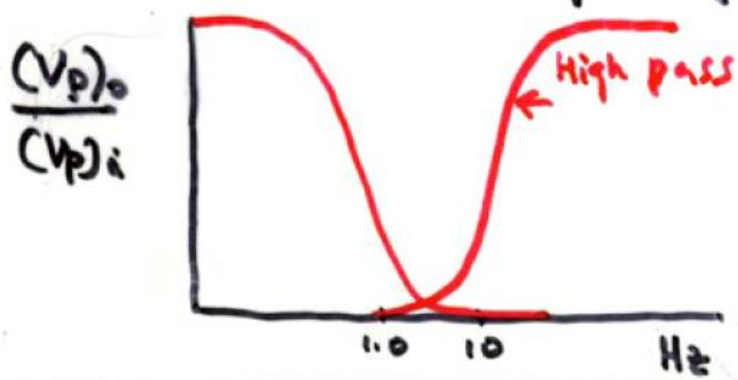
$$\boxed{(V_p)_o = i_p \times R}$$

$$\hookrightarrow i_p = \frac{(V_p)_o}{R} \quad \text{— (2)}$$

$(V_p)_o$: out-put peak voltage

High pass filter (with RC circuit)

$$\frac{(V_p)_o}{(V_p)_i} = \frac{R}{\sqrt{R^2 + \left(\frac{1}{2\pi f C}\right)^2}} = \frac{R}{Z} \quad \text{—(3)}$$



High frequency

$$\frac{(V_p)_o}{(V_p)_i} = \text{high}$$

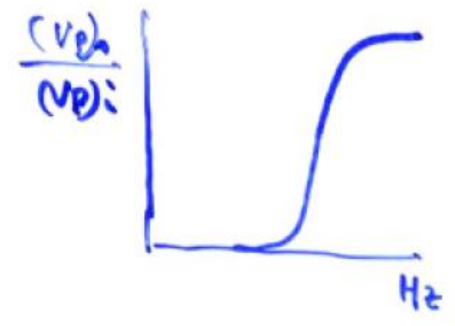
low freq → low

High pass filter (with RC circuit)

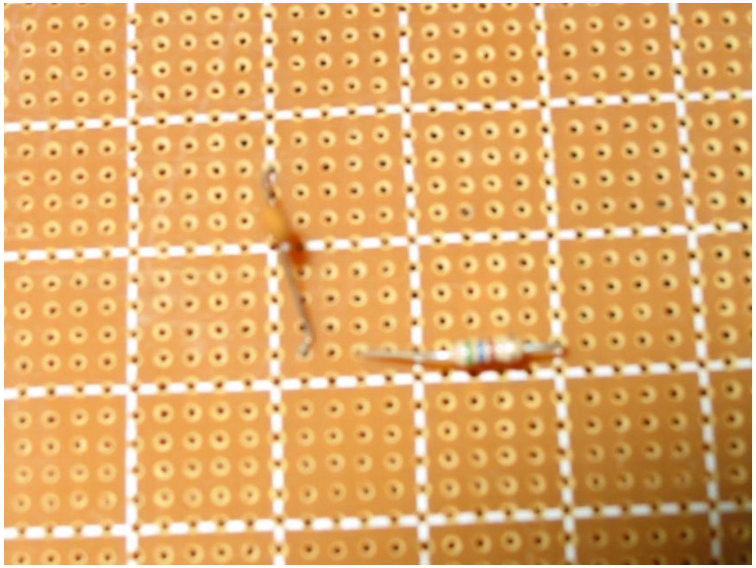
High-pass filter

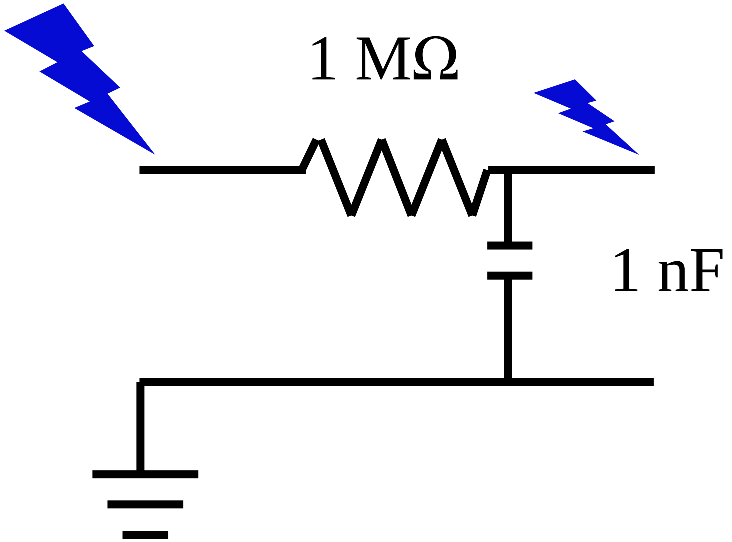
$R = 5.0 \times 10^5 \, \Omega \qquad C = 10^{-12} \, F$

$(V_p)_o/(V_p)_i$	f (Hz)
0.01	1.6×10^1
0.10	1.6×10^2
0.20	3.2×10^2
0.40	7.0×10^2
0.60	1.2×10^3
0.80	↓ 2.1×10^3
0.90	High 3.3×10^3
0.99	frequency 1.1×10^4



High pass filter (with RC circuit)



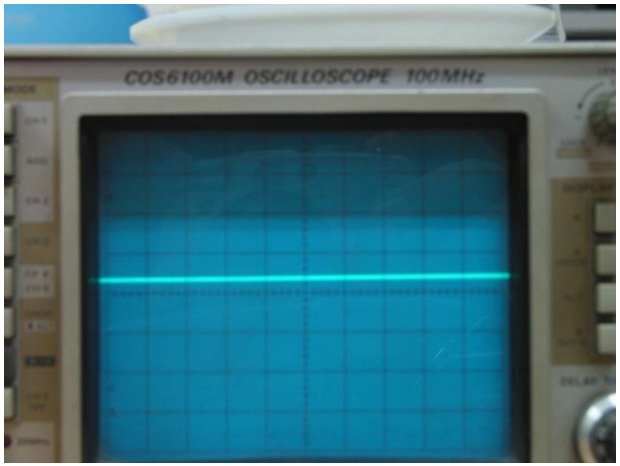


τ = RC (time constant,180 μsec)

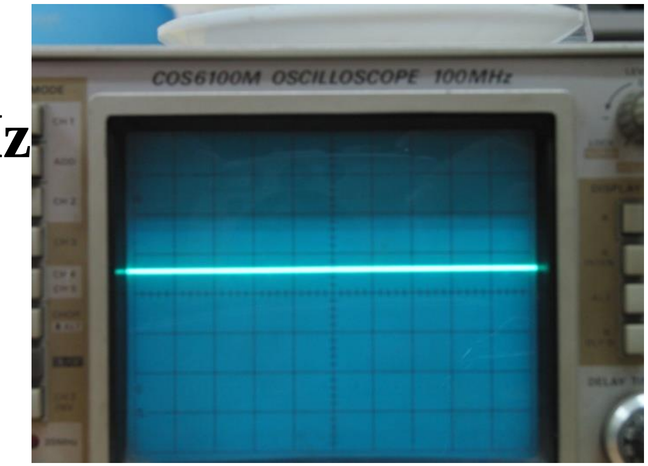
f = 1/2$\pi\tau$ (turnover frequency)

Signal Attenuation (1)

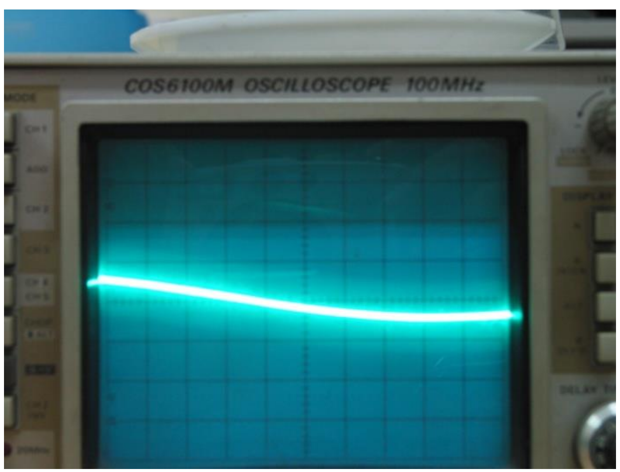
10 Hz



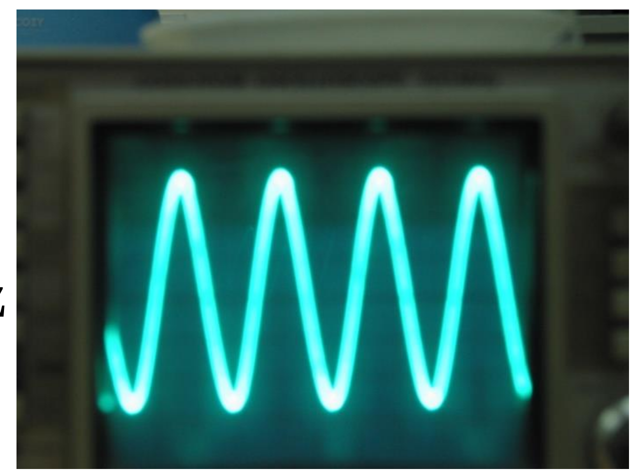
100 Hz



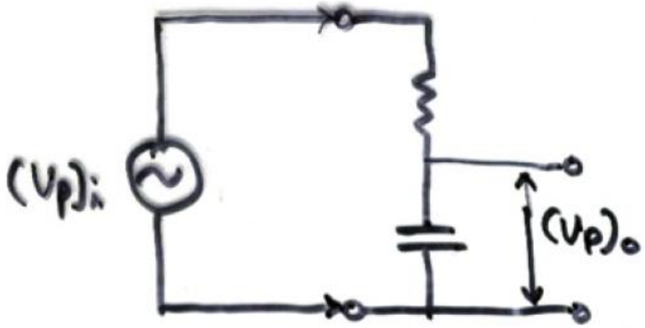
1 kHz



10 kHz



Low pass filter (with RC circuit)



High frequency 영역의 noise 제

: shot noise

thermal noise.

$$(V_p)_o = i_p X_c$$

X_c : Capacitive Reactance

– a property of a capacitor

: analogous to the resistance of a resistor

$V = i R$: resistor

$V_p = i_p X_c$: capacitor

Low pass filter (with RC circuit)

$$\frac{(V_p)_o}{(V_p)_i} = \frac{\frac{1}{2\pi f C}}{\sqrt{R^2 + \left(\frac{1}{2\pi f C}\right)^2}} = \frac{X_C}{Z}$$

~~Low~~ High frequency : removed

Low pass filter (with RC circuit)

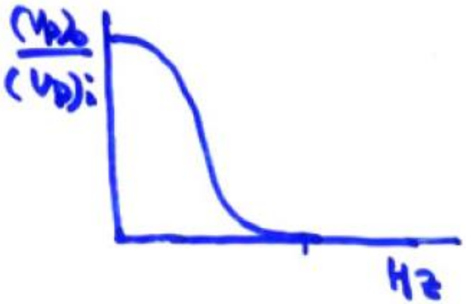
low-pass RC filter

$R = 2.5 \times 10^3\ \Omega$

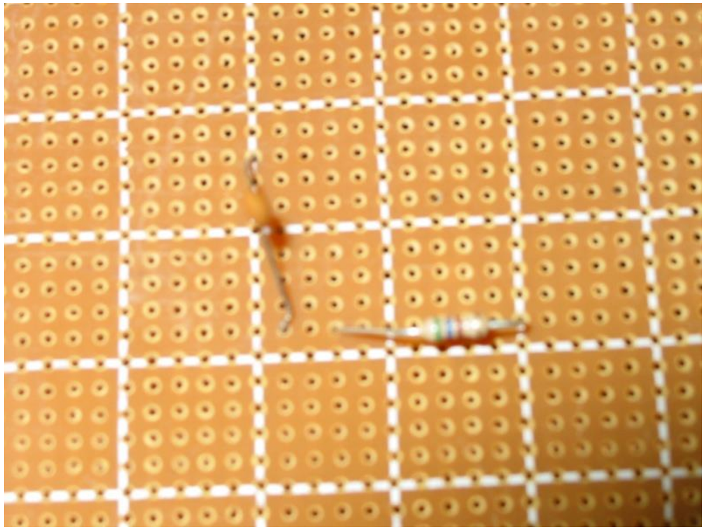
$C = 0.015\ \mu F$

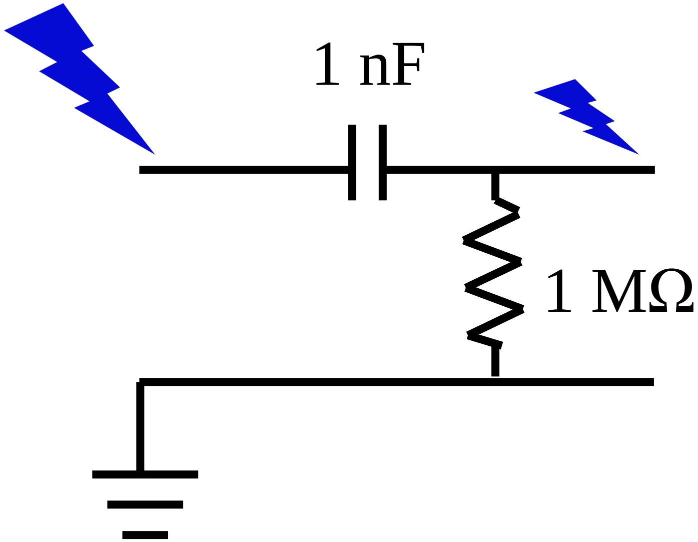
$(V_p)_o/(V_p)_i$	f (Hz)
0.01	4.2×10^3
0.10	4.2×10^2
0.20	2.1×10^2
0.40	97
0.60	57
0.80	32
0.90	21
0.99	6.1

↓ low frequency



Low pass filter (with RC circuit)



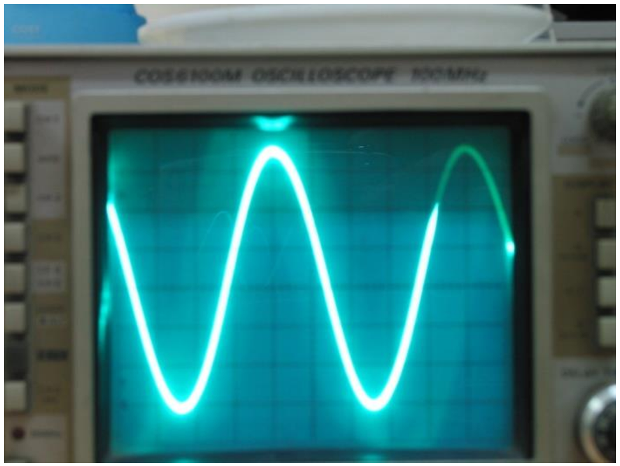


τ = RC (time constant,180 μsec)

f = 1/2$\pi\tau$ (turnover frequency)

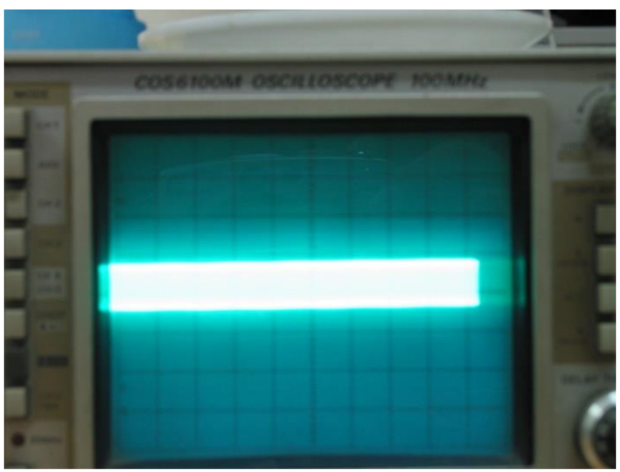
Signal Attenuation (2)

10 Hz

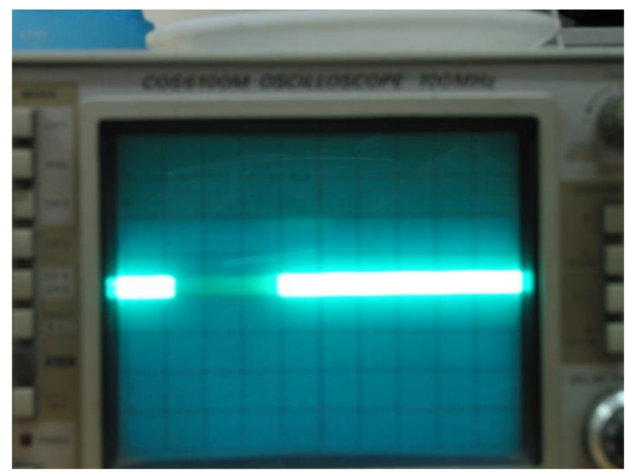


100 Hz

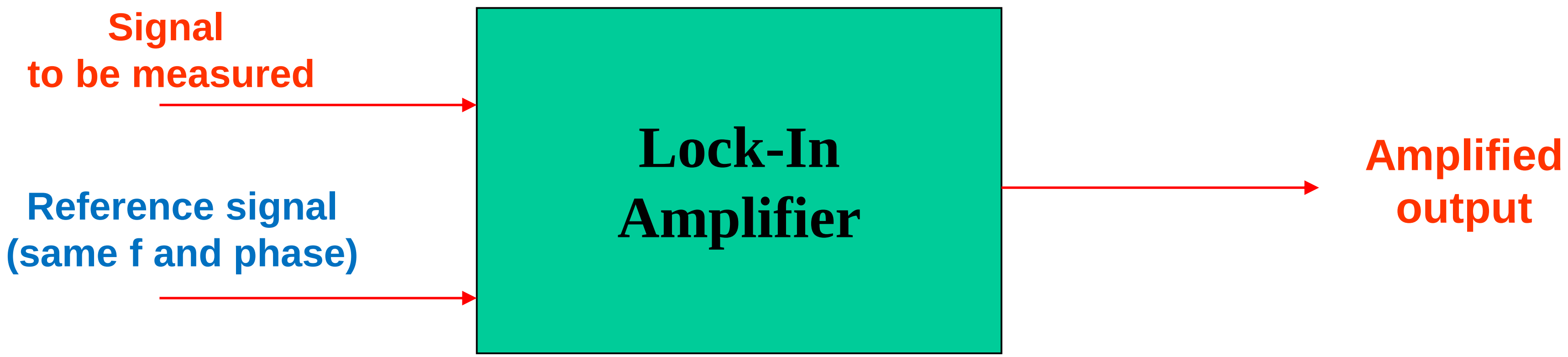
1 kHz



10 kHz



Hardware Methods: Lock-in Amplifiers



- A lock-in-amplifier is generally relatively free of noise, because only those signals that are "lock-in" to the reference signal are amplified. All other frequencies are rejected by the system

- Lock-in amplifiers permit the recovery of signals even when the S/N is unity or less

- A reference signal that has the same *f* and phase as signal.

Hardware Methods: Lock-in Amplifiers

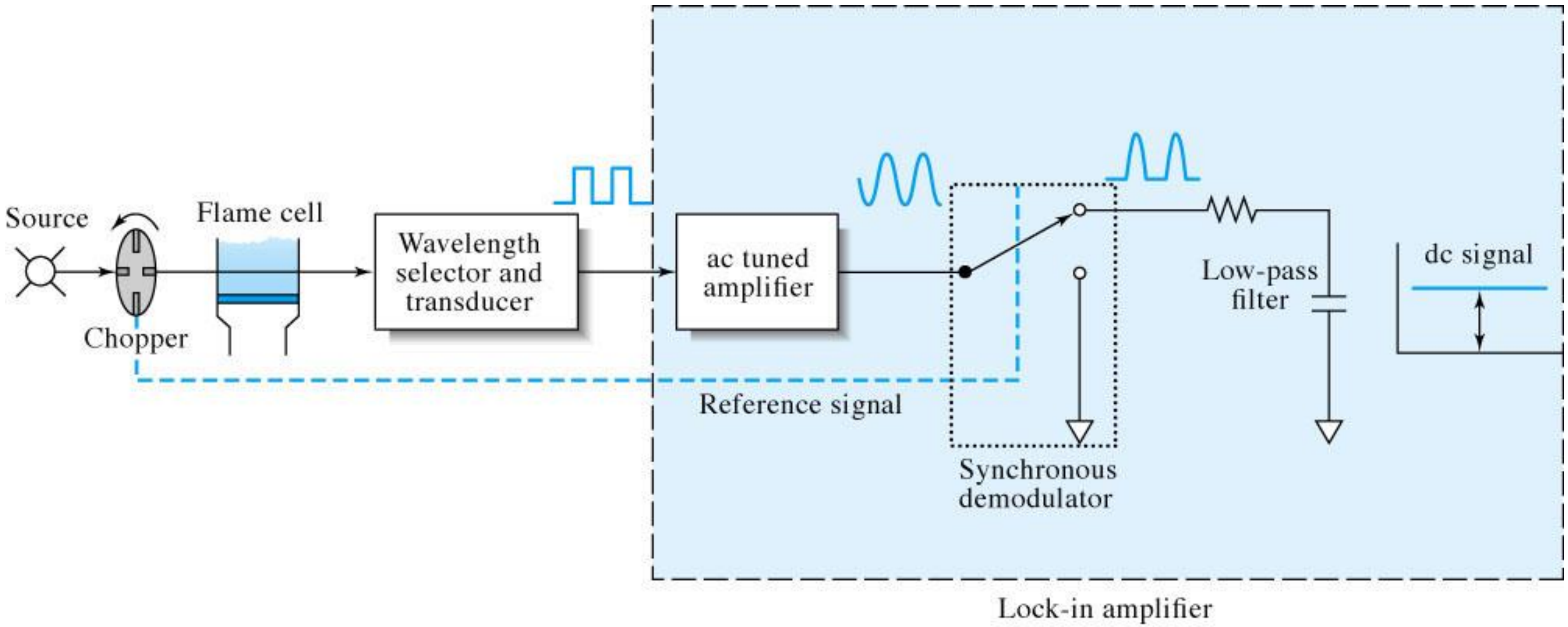


Fig. 5-8: Locl-in amplifier in AAS

Hardware Methods: Lock-in Amplifiers

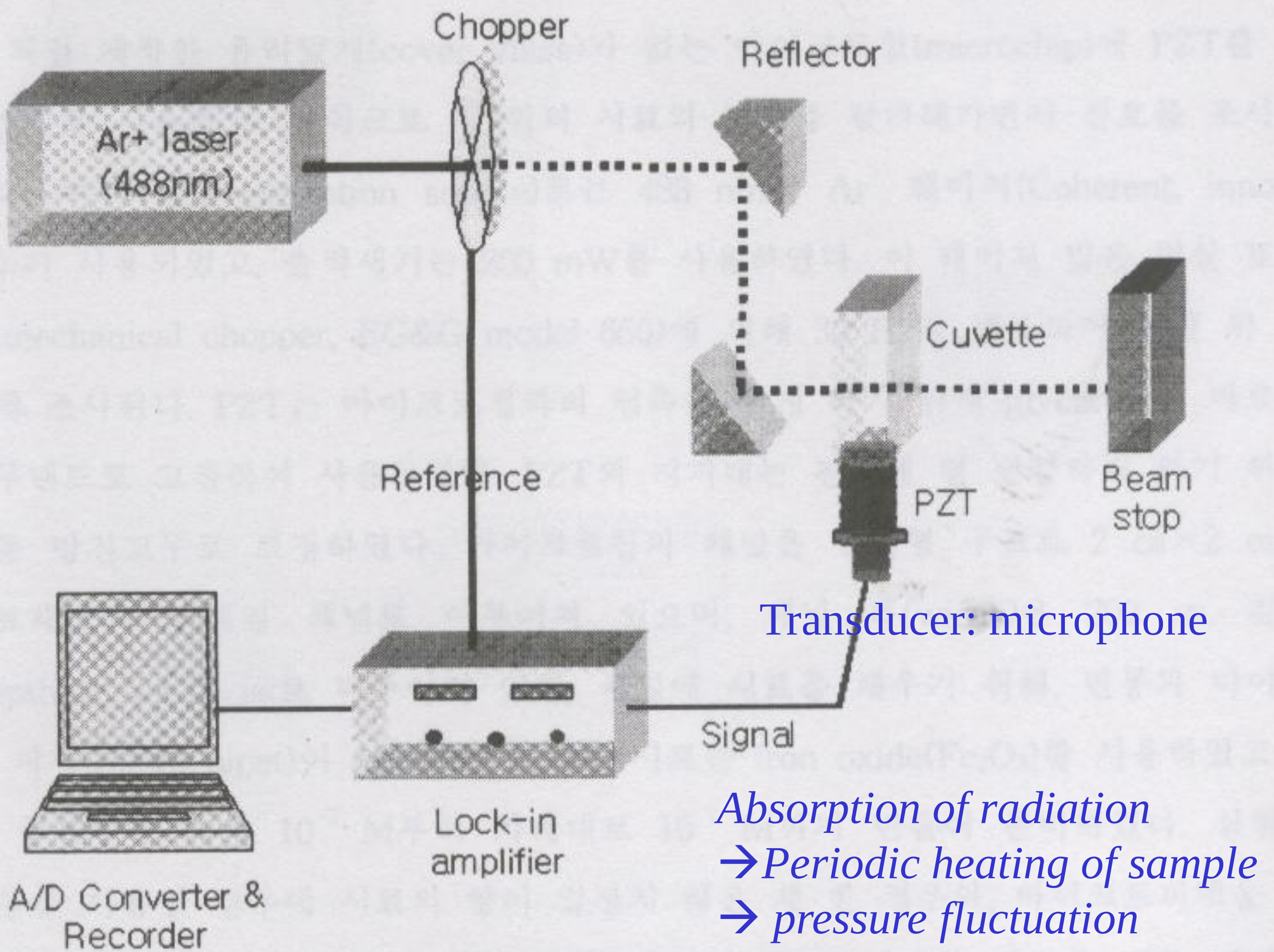


Figure 7. Schematic diagram of the PAS system in the cuvette

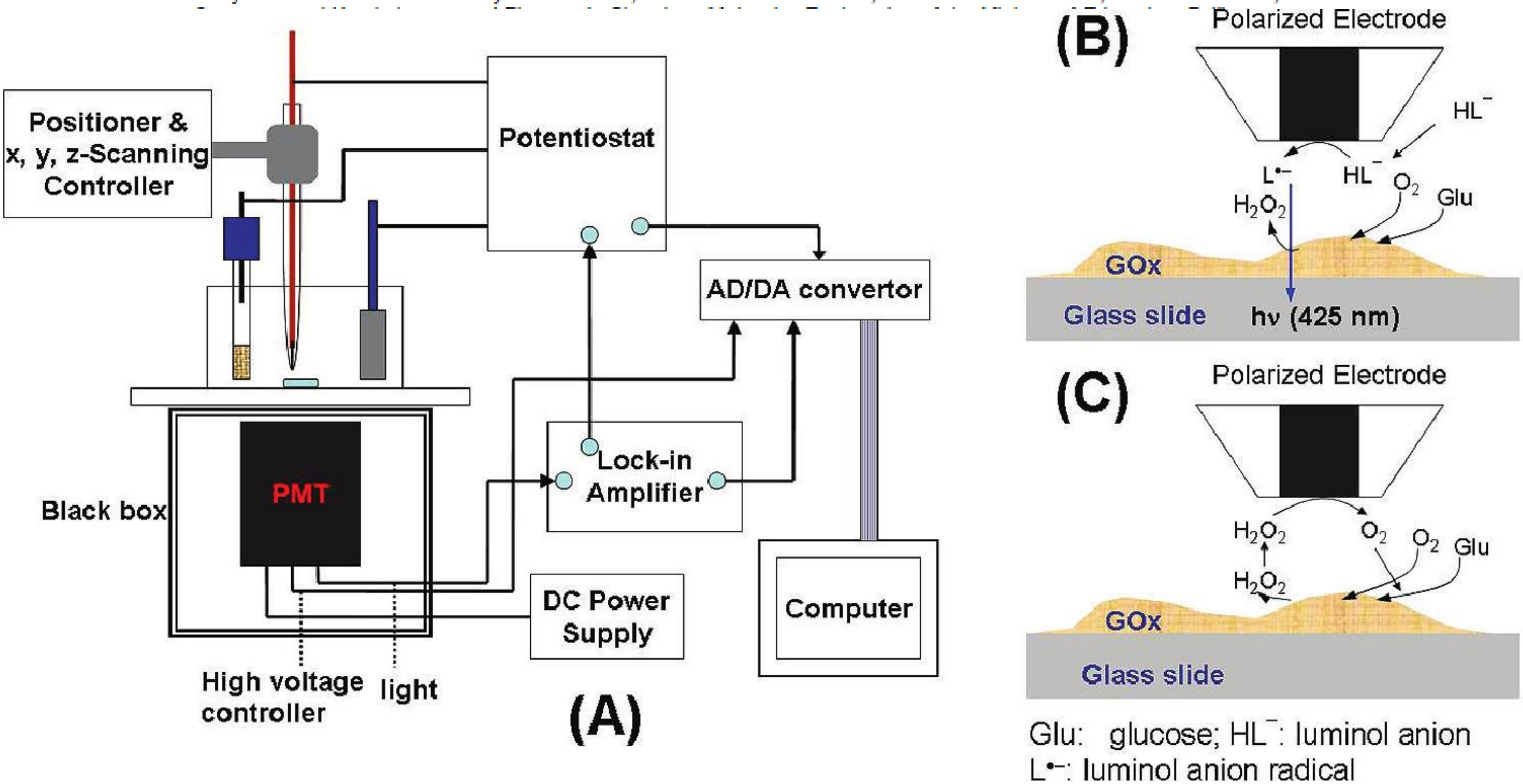
Absorption of radiation
→*Periodic heating of sample*
→ *pressure fluctuation*
→ *acoustic wave*

Anal. Chem. **2009**, *81*, 5070–5074

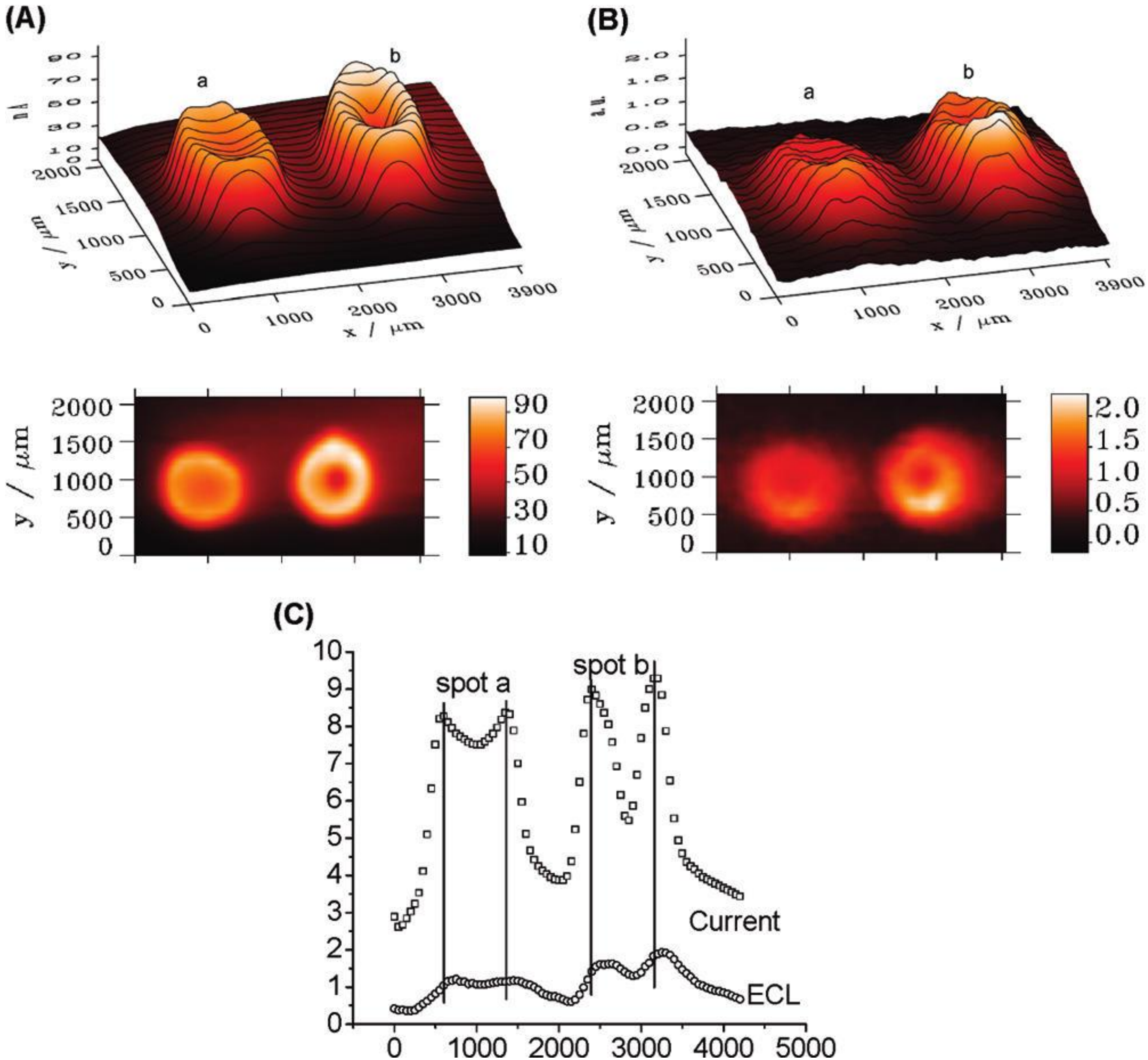
Imaging Biocatalytic Activity of Enzyme−Polymer Spots by Means of Combined Scanning Electrochemical Microscopy/Electrogenerated Chemiluminescence

Rong Lei,[†,‡] Lutz Stratmann,[†] Dominik Schäfer,[†] Thomas Erichsen,[†] Sebastian Neugebauer,[†] Na Li,[*,‡] and Wolfgang Schuhmann[*,†]

Analytische Chemie−Elektroanalytik & Sensorik, Ruhr-Unversität Bochum, Universitätsstrasse 150, D-44780 Bochum,



Here, we describe a combination of SECM and scanning ECL (SECL) for sequential amperometric and electrochemiluminescent visualization of immobilized enzyme activity on surfaces. A SECM setup was modified by integrating a photomultiplier tube (PMT) underneath the electrochemical cell to collect generated light from the scanned microelectrode tip. A similar SECM/ECL setup with a 1.5 mm diameter hemispherical Au electrode was reported by Miao et al. using approach curves to elucidate the ECL mechanism.[28] Here, a lock-in amplifier was used to amplify the PMT signal. Through a sinusoidal modulation of the potential applied to the SECM tip, the lock-in amplifier can recover signals by selective amplification at the modulation frequency even in presence of a big background noise and thus provide measurements with improved sensitivity and high signal-to-noise ratio.



(A)
(B)
(C)
a
b
x / μm
y / μm
nA
a.u.
spot a
spot b
Current
ECL

Software Methods: Ensemble Averaging

This process is some times called co-addition

- **The results of n repeated sets of measurements of the same phenomena are added and the resultant sum is divided by n to obtain an averaging scan**
- **The data will sum coherently, while the random noise should average zero**
- **S/N improve as square-root of n (number of data collected to determine the ensemble averaging)**

Software Methods: Ensemble Averaging

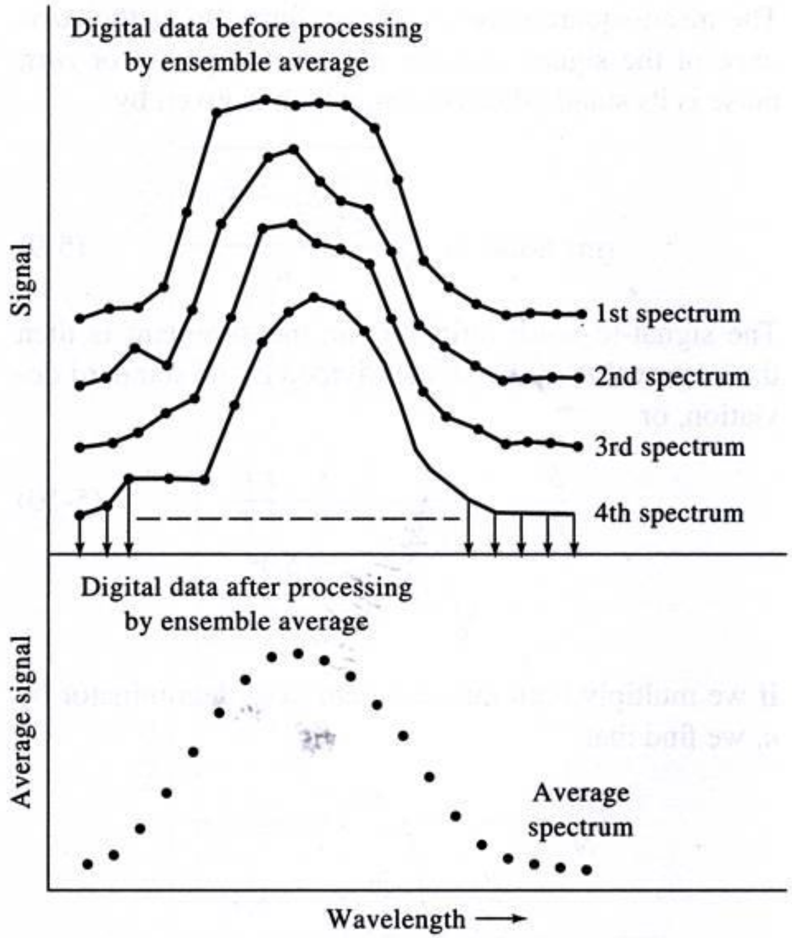


Figure 5-9 Ensemble averaging of a spectrum. *(From D. Binkley and R. Dessy,* J. Chem. Educ., *1979, 6, 150. With permission.)*

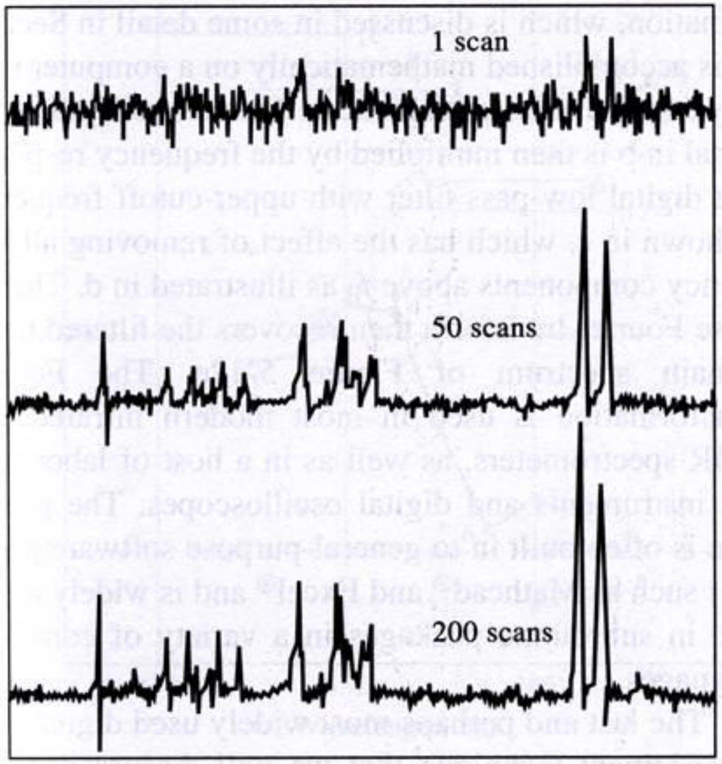


Figure 5-10 Effect of signal averaging. Note that the vertical scale is smaller as the number of scans increases. The signal-to-noise ratio is proportional to $\sqrt{n}$. Random fluctuations in the noise tend to cancel as the number of scans increases, but the signal accumulates; thus, *S/N* increases.

Anal. Chem. **1999,** *71,* 1196−1203

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 3. Effect of Signal Averaging on Limit of Detection

Andrew F. Slaterbeck, Thomas H. Ridgway,* Carl J. Seliskar,* and William R. Heineman*

Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, Ohio 45221-0172

The effect of ensemble averaging on the response of a new spectroelectrochemical sensor has been investigated. The sensor consists of a selective film coated over an optically transparent electrode (OTE). The mode of detection is attenuated total reflection (ATR). For an analyte to be detected, it must first partition into the sensing film, second be electroactive at the applied potential, and third have a change in its absorbance at the wavelength of light monitored by ATR. Four different excitation potential waveforms were investigated: pulsed, step, triangular, and sinusoidal. Under the condition of continuous cycling of the excitation potential, the optical response approaches a steady-state condition within as few as five cycles. Once the response has reached steady state, ensemble averaging over successive cycles is shown to improve the signal-to-noise ratio, allowing an order of magnitude improvement in the limit of detection. A model sensor consisting of a cationically selective sol−gel-derived Nafion composite film coated on an indium tin oxide OTE is employed to demonstrate the signal acquisition techniques under investigation. Tris(2,2′-bipyridyl)ruthenium(II) chloride was used as a model analyte.

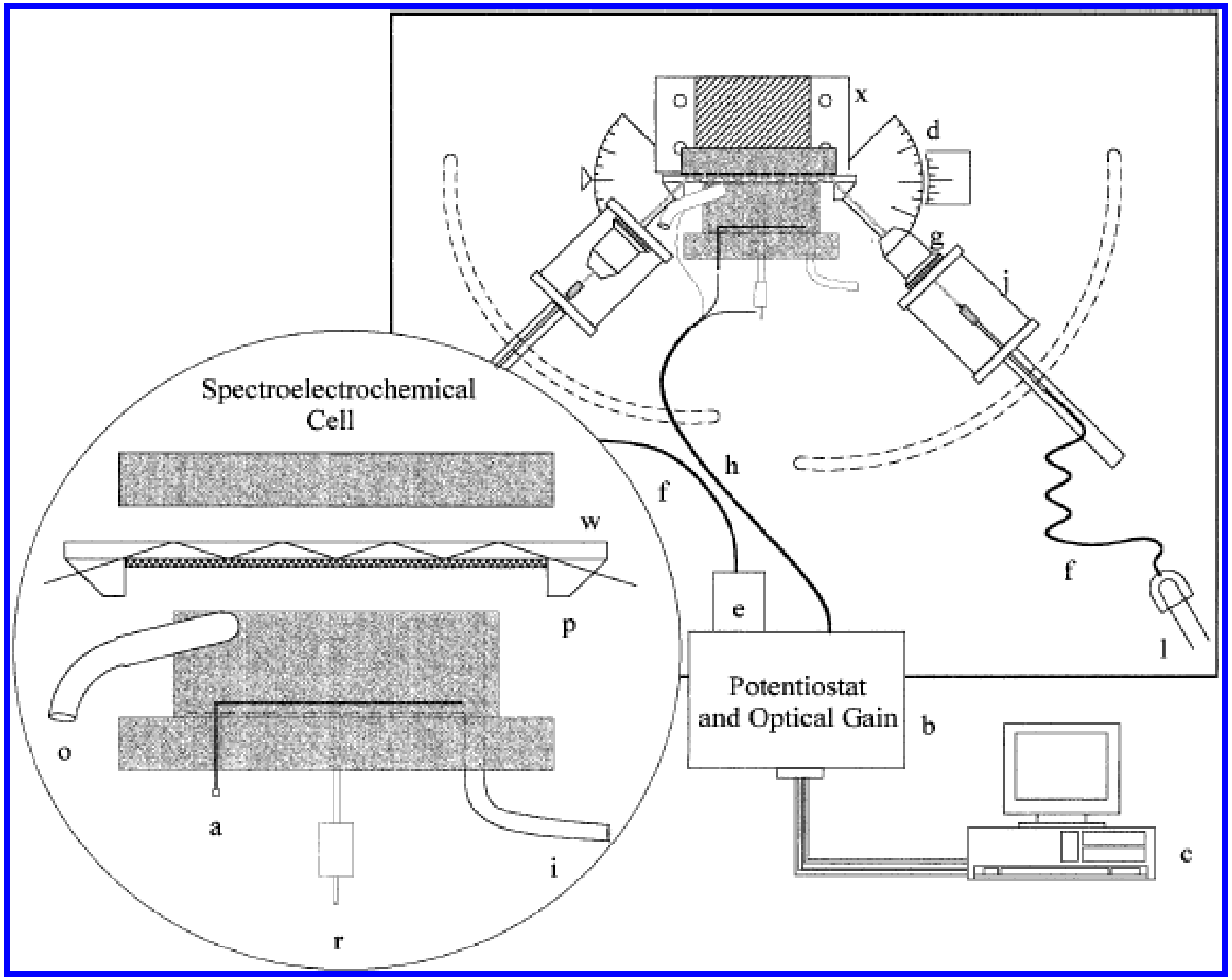


Figure 1. Schematic of experimental layout: l, Panasonic blue LED; f, fiber optic cable; j, Newport fiber coupler; g, microscope objective; d, Berg dial with vernier; x, cell mount with *X*–*Y* translation stage; h, leads for electrodes; e, optical detector; b, potentiostat and optical gain; c, Pentium PC with digital-to-analog processor. Figure inset: p, Schott SF6 coupling prism; w, spin-coated ITO glass electrode; r, Ag/AgCl reference electrode; a, platinum mesh auxiliary electrode; i, sample inlet tubing; o, sample outlet tubing.

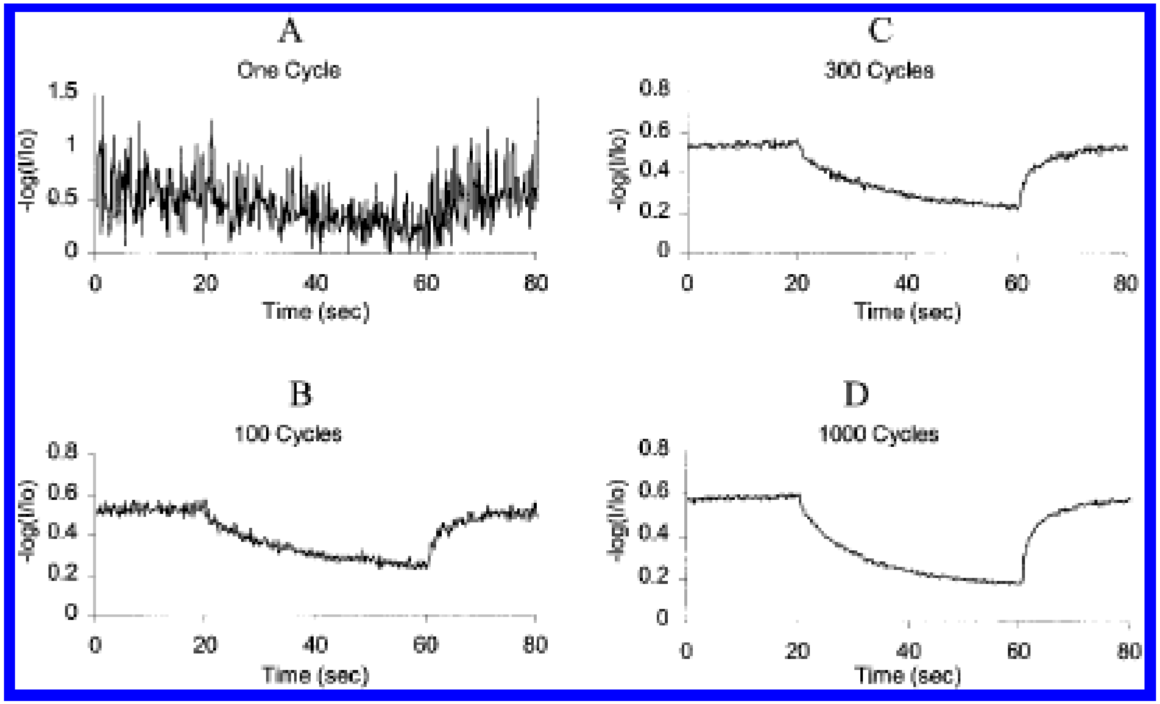


Figure 5. Effect of ensemble averaging on optical response: square wave excitation, τ = 40 s, LED source, PMT detector. (A) Optical response to one cycle of applied potential waveform (S:N = 1.95:1). (B) Averaged optical response for 100 cycles (S:N = 20.90:1). (C) Averaged optical response for 300 cycles (S:N = 35.93:1). (D) Averaged optical response for 1000 cycles (S:N = 60.00:1).

Software Methods: Boxcar Averaging

This process is some times called co-addition

- **The results of n repeated sets of measurements of the same phenomena are added and the resultant sum is divided by n to obtain an averaging scan**
- **The data will sum coherently, while the random noise should average zero**
- **S/N improve as square-root of n (number of data collected to determine the ensemble averaging)**

Software Methods: Boxcar Averaging

- This is a digital procedure for smoothing irregularities and enhancing the S/N in a wave form

- A group of closely spaced digital data points depicted a slowly changing analog signal are replaced by a single point representing the average of group

- In practice, 2 to 50 points are average to generate a final point

- S/N improve as square-root of n (# of point average in each box-car)

Software Methods: Boxcar Averaging

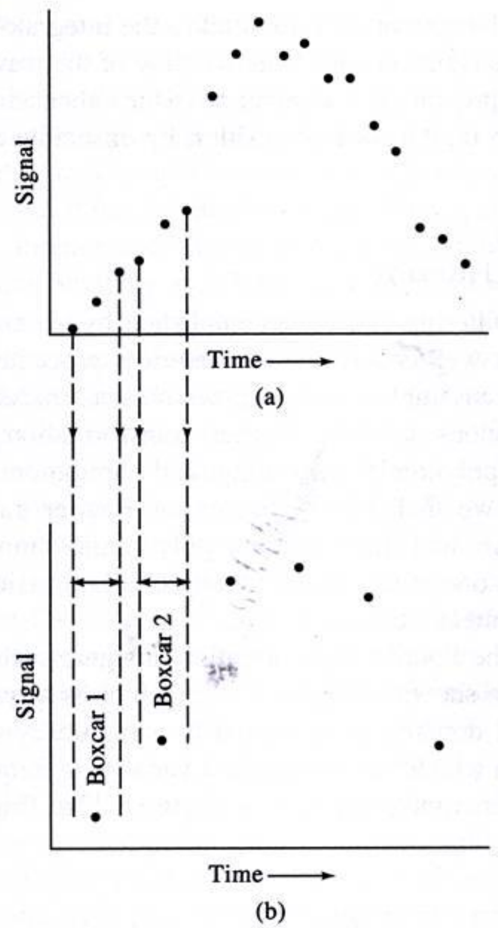
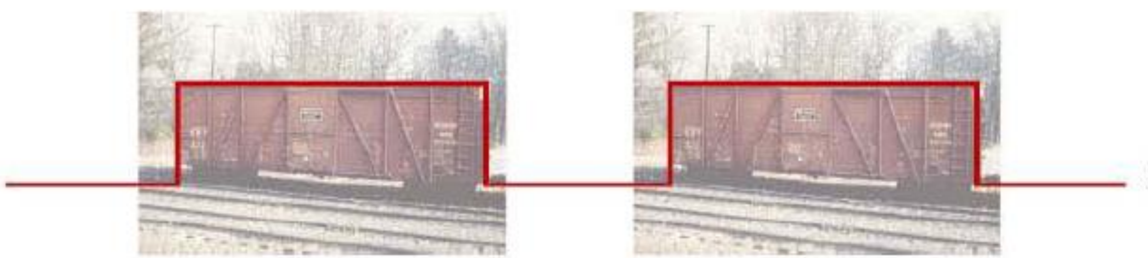


Figure 5-11 Effect of boxcar averaging: (a) original data, (b) data after boxcar averaging. *(Reprinted with permission from G. Dulaney,* Anal. Chem., *1975,* 47, *28A. Copyright 1975 American Chemical Society.)*

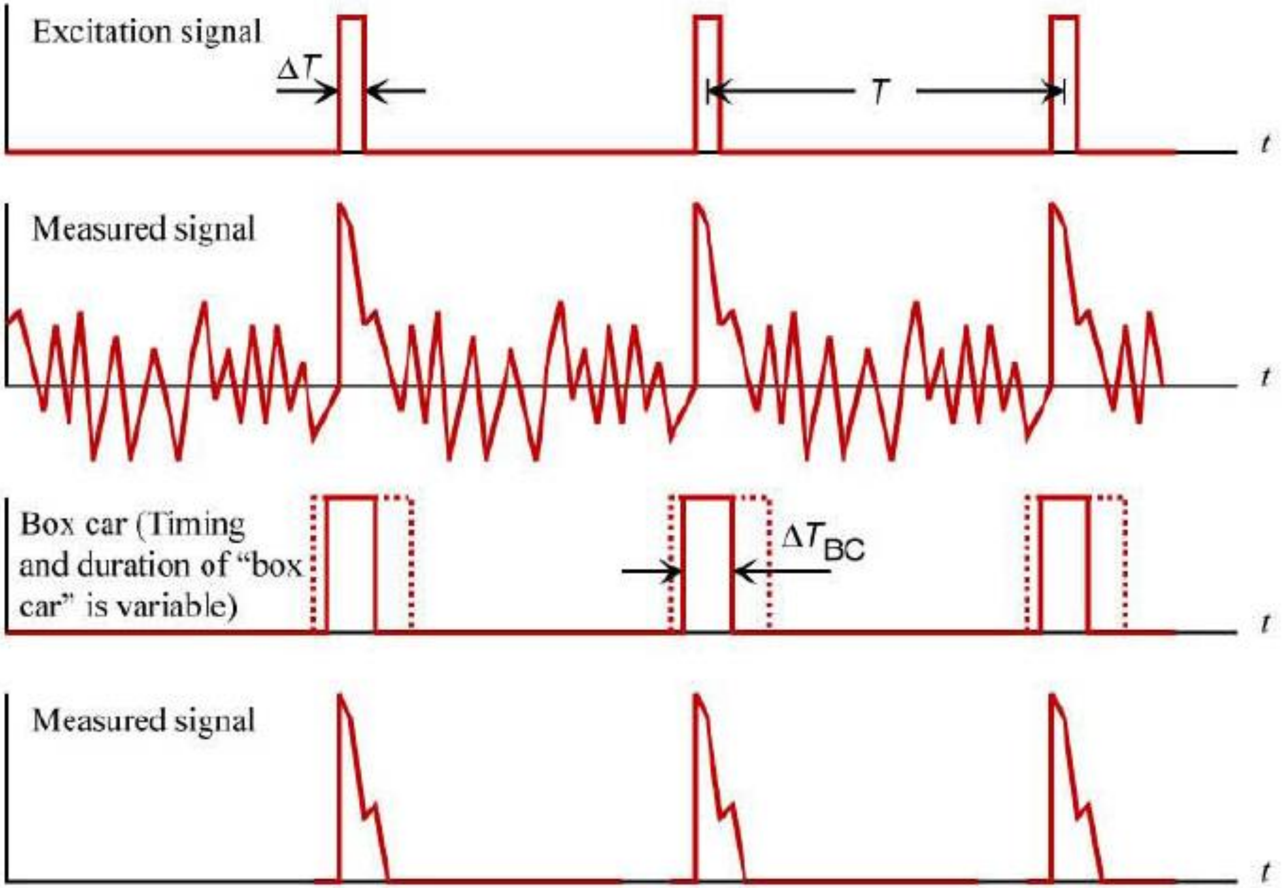
Software Methods: Boxcar Averaging

Why a box-car integrator is called that way?



Software Methods: Boxcar Averaging

- Typical signals:



Anal. Chem. 1999, *71*, 5328−5334

Depth Profiling of Thin Films with Pulsed Glow Discharge Atomic Emission Spectrometry

Chenglong Yang, Kristofor Ingeneri, Matt Mohill, and W. W. Harrison*

Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

The application of microsecond pulsed Grimm glow discharge atomic emission spectrometry for depth profiling of thin films is examined. The effects of pulsed conditions including pulse voltage, pulse frequency, pulse width, and Ar pressure on depth profiling performance were characterized for Zn and Cu coatings on steel. Using optimized conditions, linear calibration curves of coating thickness for Zn (6.1−26.9 μm) and Cu (50−500 nm) on steel were achieved. A precision of 2−5% relative standard deviation was determined. An ultrathin coating of Cu (10 nm) on steel was also measured by this technique.

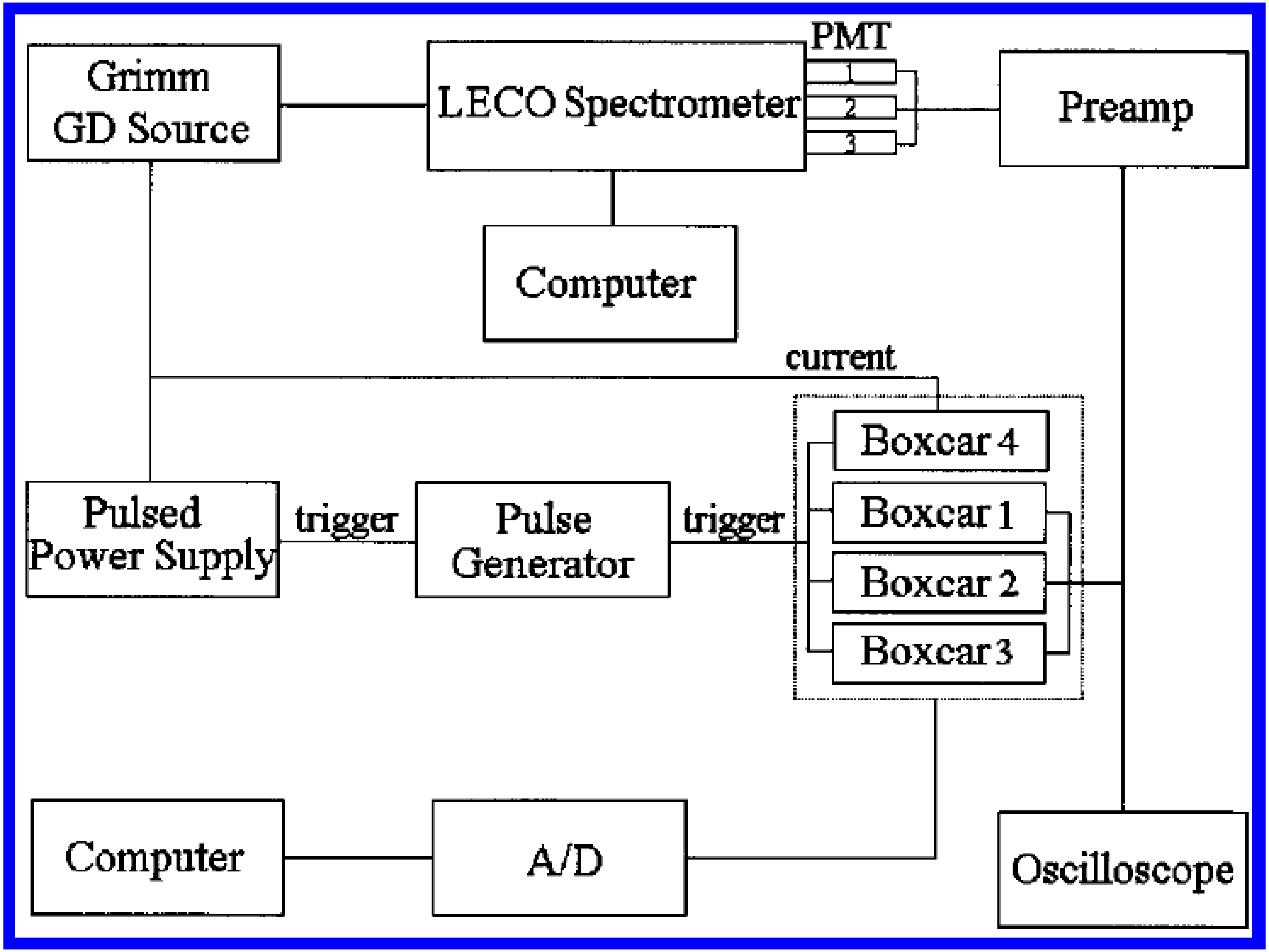


Figure 1. Schematic diagram of pulsed Grimm GD spectrometer and gated detection system for depth profiling.

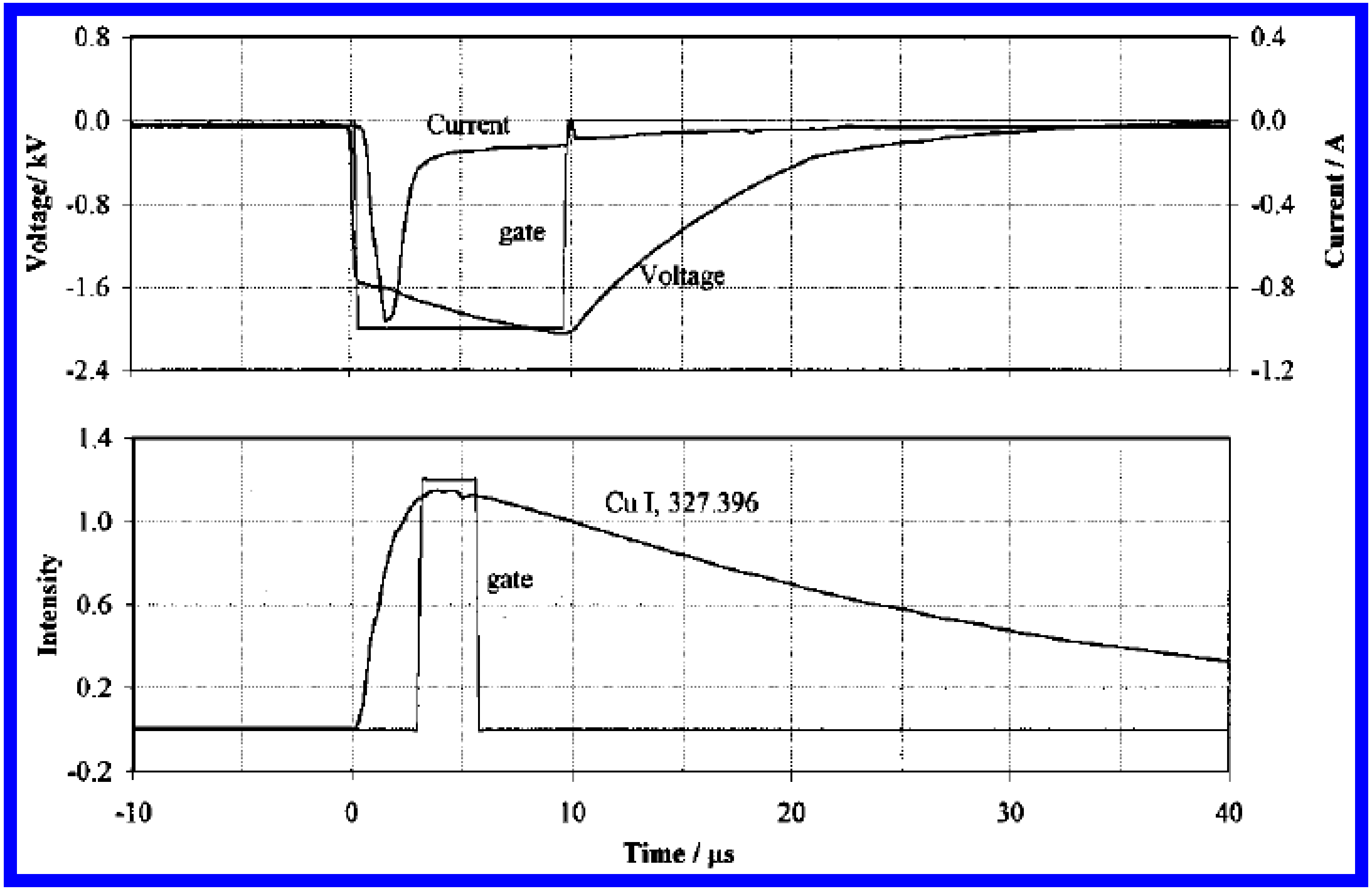


Figure 2. Typical temporal profiles for pulsed Grimm GD. Cu cathode.

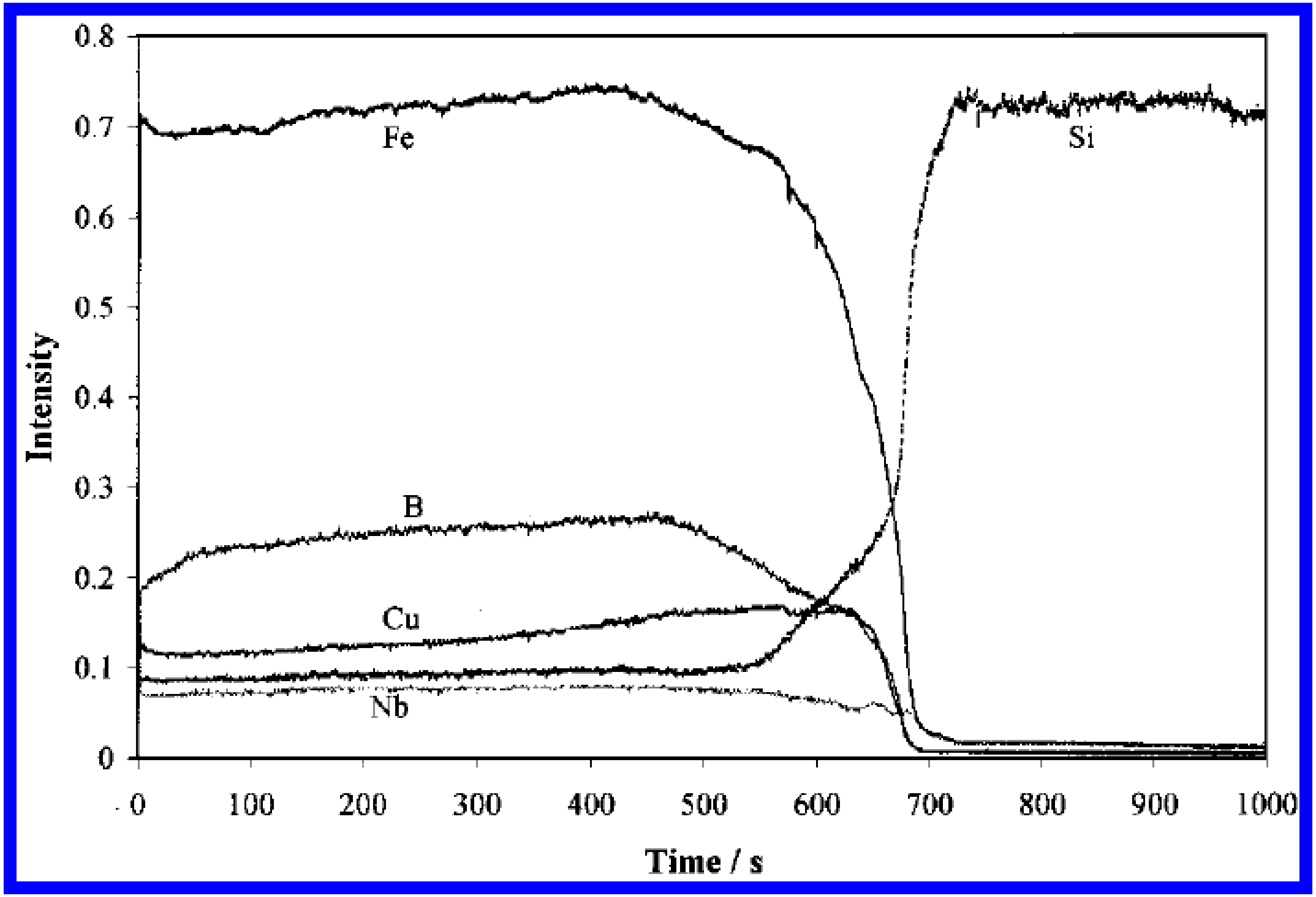


Figure 12. Depth profile of 300-nm FeSiB−CuNb on a silicon wafer with the following conditions: pulse voltage of 1200 V, frequency of 200 Hz, pulse width of 10 μs, and 4 Torr pressure.