

Signal to noise enhancement of lockin amplifiers

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whose expectation value is

$$E[\hat{R}(m)] = \frac{1}{N} \sum_{k=0}^{N-1} S(k)S(k+m) + R_{nn}(m), \quad (4)$$

where $R_{nn}(m)$ is the noise autocorrelation function.

The variance of the autocorrelation estimate [Eq. (3)] is

$$\begin{aligned} \text{Var}[\hat{R}(m)] = & \frac{\sigma^2}{N^2} (N\sigma^2 + \sum_{k=0}^{N-1} S^2(k) \\ & + \sum_{k=0}^{N-1} S^2(k+m) + 2 \sum_{k=0}^L S(k)S(k+2m)), \quad (5) \end{aligned}$$

where

$$L = \begin{cases} N-1 & \text{for } m \leq N/2 \\ 2(N-m)-1 & \text{for } m > N/2 \end{cases} \quad \text{and } \sigma^2 = \text{Var}[n(t)].$$

For sufficiently large N and m , we can simplify Eq. (5) in certain cases to get

$$\text{Var}[\hat{R}(m)] \approx \frac{\sigma^2}{N} [\sigma^2 + 2S^2] \quad (6)$$

Therefore, the SNIR from a single trigger is

$$(\text{SNIR})_s = (S/\sigma)(E[\hat{R}(m)]/\sqrt{\text{Var}[\hat{R}(m)]})^{-1}. \quad (7)$$

Thus for a given value of SNIR, the averaging has to be done over fewer samples, resulting in a reduction of the total measurement time by a factor of $(\text{SNIR})_s$. The total measurement time becomes significant when the dead time between samples is large, and under such circumstances the correlation estimate $\hat{R}(m)$ may be computed by simple but slow hardware. The signal parameters can be inferred from the autocorrelation estimate after ignoring small values of m .

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Signal to noise enhancement of lock-in amplifiers

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A lock-in amplifier can be considered to be a special case of the more general box-car averager. Expressions for the output noise voltage of lock-in amplifiers are deduced from the corresponding results derived earlier for box-car averagers. Deviations from the simple $(4RC)^{1/2}$ law are shown to exist in the case of nonwhite noise.

Lock-in amplifiers are generally used to recover sinusoidal signals buried in noise. The instrument can also be used when the signal is periodic with an arbitrary but known waveform. A box-car averager, on the other hand, is employed to extract repetitive (though not necessarily periodic) signals of unknown wave-shapes. It has been pointed out by Blume¹ that a lock-in amplifier can be viewed as a special case of the box-car averager when the signal is periodic with a period T which equals exactly twice the gate-width ϵ .

For white noise, Ernst² has shown that in the case of linear signal averaging, the signal to noise improvement ratio (SNIR) is proportional to \sqrt{n} , where n is the number of samples used. However, box-car averagers and lock-in amplifiers use an exponential averaging process. Recently, Neelakantan and Dattagupta³ have calculated the SNIR of box-car averagers. (This paper is hereafter referred to as I). The analysis indicates that the analog of the \sqrt{n} law, i.e., $\text{SNIR} = (2RC/\epsilon)^{1/2}$, is valid only for white noise, and im-

portant deviations from this law exist for nonwhite noise sources. The purpose of this brief note is to point out that for the lock-in amplifiers (with a first order filter), the result⁴ for the output noise quoted as being proportional to $(4RC)^{1/2}$, is valid again for white noise only. Additional expressions for the SNIR of lock-in amplifiers in the case of other noise sources of practical interest are also presented.

The analysis is identical to that of the box-car averager except that the gate-width ϵ is to be set equal to $T/2$, where T is the signal time-period. Using Eq. (20) of I, we have

$$(\text{SNIR})_{\text{white noise}} = (4RC/T)^{1/2} \quad (2)$$

the familiar result for lock-in amplifiers.⁴

In real life one often encounters band-limited noise such as the one with an exponential correlation function with a time constant α^{-1} , say [cf., Eq. (21) of I]. Using Eq. (22) of I, the output noise voltage in this case can be written

$$\langle V_{NO}^2 \rangle = \frac{\lambda \langle V_N^2 \rangle}{\lambda^2 - \alpha^2} \left((1 - \exp(-\lambda T))^{-1} \{ (\lambda - \alpha) + (\lambda + \alpha) \exp(-\lambda T) - 2\lambda \exp[-(\lambda + \alpha)T/2] \} + 2\lambda \frac{[\cosh \lambda T/2 - \cosh(\alpha T/2)]}{\sinh(\lambda T/2)[\exp(\alpha T + \lambda T/2) - 1]} \right), \quad (2)$$

where $\lambda = (RC)^{-1}$, $\langle V_N^2 \rangle$ is the mean-square input noise voltage, and where we have assumed that $n\lambda T \gg 1$.

The SNIR, derived from Eq. (2), is much more complicated than given by the simple white noise expression of Eq. (1). As is discussed in I, the "intergate" correlations, which are negligible for white noise, lead to a

higher output noise and hence a poorer SNIR in the case of nonwhite noise sources.

Usually, a white noise is fed through a bandpass filter to the input of a lock-in amplifier. The resultant input noise is of the exponential-cosine type [cf., Eq. (31) of I]. As remarked in I, the SNIR can be easily evaluated from Eq. (2) above, and again a simple $(4RC)^{1/2}$ law does not emerge.

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High pressure pressure-jump apparatus

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A pressure jump relaxation technique is described to study fast reactions in solution under pressure up to 1.5 kbar. The mechanical relaxation time of the instrument is 0.5 ms.

A recent review¹ indicates how the use of pressure as a variable in chemical kinetics, has contributed to our understanding of the mechanisms of reactions in solution. Fast reaction techniques introduced by Eigen and De Maeyer² have deepened our understanding of the kinetics of molecular interactions. The field has recently been reviewed with regard to pressure as a variable.³ Pressure jump relaxation techniques have a number of advantages compared with temperature jump methods especially in the biological field.⁴ It is therefore desirable to adapt the pressure jump technique for work under high pressure. Brower⁵ described an instrument with a quick-release pressure valve and obtained a pressure drop with a relaxation time of about 10 ms. Similar instruments have been described.^{6,7} We describe an instrument based on a different principle with a mechanical relaxation time of 0.5 ms.

The basic principle of the apparatus can be described as follows: The pressure drop is realized by expanding a small volume which is done by displacing a piston over a small distance. This method of pressure jump has considerable advantages over the conventional pressure jump techniques where a bursting membrane is used as a pressure drop device. The principle advantage is that the pressure drop can be easily controlled. In addition with the use of a bursting membrane device under pressure, one would need an assembly disassembly cycle of the apparatus after each pressure jump. The mechanical valve we use was originally developed in our laboratory for pressure jump techniques at normal pressure.⁸ A similar system has been described.⁹

Figure 1 shows the basic design of the apparatus. The main cell body is made of stainless steel. The volume of the observation chamber (A) is about 1 ml. The windows consist of a polished quartz cylinder with partial conical shape at the side of the observation chamber. This provides room for a viton ring. The windows are sealed against the pressure bomb with the viton ring by a screw bolt. This window design can be used up to 2 kbar. A Teflon membrane (B) separates the observation chamber (A) from the chamber (C). The apparatus is loaded by carefully filling the observation chamber with the solution after which the membrane is put in its proper position. The membrane is held in place by screwing in the upper part of the apparatus containing pressure drop device including hammer and piston. The chamber (C) contains pressure inlet and pressure recording with a pressure transducer.¹⁰ The system can be cut off from the main pressure line by a high pressure valve. The piston (D) (SHSS steel) is supported by a stepped piston arrest (G) (hardened carbon steel) which is displaced by a hammer stroke (H). The displacement is controlled by the barrier which is mounted in (J). The gear ball (I) smoothens the displacement of the stepped piston arrest. The spring (F) gives additional speed to the piston. The whole setup is firmly mounted on a heavy support to ground the mechanical vibrations provoked by the hammer stroke. It was found that mechanical vibrations persist for half a second if the apparatus is not properly grounded. Almost complete disappearance of the vibrations is observed when the whole system is placed on the laboratory floor. The apparatus