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Description of the Role of Shot Noise in Spectroscopic Absorption and Emission Measurements with Photodiode and Photomultiplier Tube Detectors: Information for an Instrumental Analysis Course

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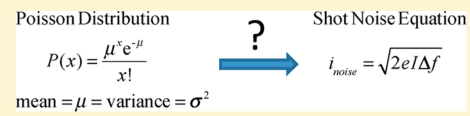
Ⓢ *Supporting Information*

ABSTRACT: A description of shot noise and the role it plays in absorption and emission measurements using photodiode and photomultiplier tube detection systems is presented. This description includes derivations of useful forms of the shot noise equation based on Poisson counting statistics. This approach can deepen student understanding of a fundamental principle that can ultimately limit the sensitivity of a spectroscopic measurement.



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■ INTRODUCTION

A complete understanding of chemical instrumentation requires fundamental knowledge of how signals are generated by an instrument, as well as the sources of noise that ultimately limit the sensitivity of the instrumental measurement. Instrumental analysis textbooks highlight the importance of the signal-to-noise ratio (S/N) and introduce the four general sources of instrumental noise: flicker or $1/f$ noise, environmental noise, thermal or Johnson noise, and shot noise,[1−3] but the equations are provided without derivation. Thomas Coor wrote an excellent background article on signals and noise in chemical measurements for this *Journal* in 1968 that included a derivation of the Johnson noise equation.[4] Coor qualitatively described shot noise and provided the well-known shot noise equation

$$i_{\text{noise}} = \sqrt{2eI\Delta f} \tag{1}$$

where i_{noise} is the standard deviation in the measured current, I is the measured current, e is the fundamental charge of the electron, and Δf is the bandwidth of the measurement, but it did not provide the derivation of the equation from fundamental principles. The original derivation of eq 1 is attributed to Walter Schottky in 1918,[5] but the Schottky paper is written in German and difficult to obtain. Although there is an extensive amount of literature and technical reports written on shot noise,[6−8] we believe there is a lack of integration of these ideas at a level appropriate for advanced undergraduate students. We describe the derivation of the shot noise equation based on Poisson counting statistics and show how the shot noise limit can be calculated for spectroscopic instruments that use photodiode or photomultiplier tube detectors. We feel our description will be useful to both students and instructors of instrumental analysis courses.

Photodiodes (PD) and photomultiplier tubes (PMT) are common detectors used in spectroscopic instrumentation. These detectors work on the basic principle that when photons strike the detector they generate free electrons, and the movement of these electrons results in a measurable current. Shot noise in the current measurement is due to the stochastic nature of the generation of these free electrons. In any given time interval, there will be random fluctuations in the number electrons generated. Poisson statistics for uncorrelated random discrete events states that the standard deviation in the average number of electrons generated, σ_n, occurring randomly in a given time interval is equal the square root of the number of electrons, n

$$\sigma_n = \sqrt{n} \tag{2}$$

For example, if an average of 100 electrons were created during a measurement time, the standard deviation of the average for multiple measurements would be ±10 electrons.

In addition to the current generated from the photons of the light source, there is also a dark current due to the thermal generation of free electrons. The overall shot noise depends on both current sources and the variances of the two noise sources add together

$$\sigma_{\text{total}}^2 = \sigma_{\text{light}}^2 + \sigma_{\text{dark}}^2 = n_{\text{light}} + n_{\text{dark}} \tag{3}$$

or

$$\sigma_{\text{total}} = \sqrt{n_{\text{light}} + n_{\text{dark}}} \tag{4}$$

In the high light limit, as in an absorption experiment, $n_{\text{light}} \gg n_{\text{dark}}$, the photon contributions to the shot noise dominate, and the best signal-to-noise ratio that can be achieved in the high light limit is

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$$S/N = \frac{n_{\text{light}}}{\sqrt{n_{\text{light}}}} \quad (5)$$

In the low light limit, as in an emission experiment without background light, the dark current contribution to the shot noise must be considered, and the best signal-to-noise that can be achieved is

$$S/N = \frac{n_{\text{light}}}{\sqrt{n_{\text{light}} + n_{\text{dark}}}} \quad (6)$$

When only shot noise is considered, it is clear that the signal-to-noise improves with increasing photocurrent in both absorption and emission measurements.

In spectrometers, the detector output is typically measured as a current, I, and the number of electrons generated is determined from the average current and the measurement time, Δt, of the detection system. The measurement time of the detection system is rarely specified directly but is related to the bandwidth, Δf, of the detection electronics. The detection bandwidth may be restricted by a low pass resistor−capacitor (RC) filter, which is often characterized by the 3 dB point, $f_{3\text{dB}}$, in the frequency distribution. The following relationships are used to determine the measurement time from the appropriate detection system parameters

$$\Delta t = \frac{1}{2\Delta f} = \frac{1}{\pi f_{3\text{dB}}} = 2\text{RC} \quad (7)$$

A detailed derivation of these relationships is included in the Supporting Information.

SHOT NOISE IN A PHOTODIODE DETECTOR

Light striking the depletion zone of a photodiode creates electron−hole pairs that are accelerated by the electric field in the depletion zone and result in a measurable current through the diode. Assuming the high light limit, the measured current is proportional to the photon flux of the light source. For a measurement time of Δt, the number of electrons generated is

$$n = \frac{I\Delta t}{e} \quad (8)$$

where I is the measured current and e is the charge of an electron ($e = 1.6 \times 10^{-19}$ C). From Poisson statistics, the standard deviation in the number of electrons is

$$\sigma = \sqrt{n} = \sqrt{\frac{I\Delta t}{e}} \quad (9)$$

The current fluctuation is

$$i_{\text{noise}} = \frac{\sqrt{n}\,e}{\Delta t} = \sqrt{\frac{I\Delta t}{e}}\,\frac{e}{\Delta t} = \sqrt{\frac{Ie}{\Delta t}} \quad (10)$$

This is the form of the shot noise equation originally shown by Schottky.[5] To convert eq 10 into the form of eq 1, we use the relationship between measurement time and detection bandwidth to get

$$i_{\text{noise}} = \sqrt{2eI\Delta f} \quad (1)$$

If the detection system bandwidth is given by $f_{3\text{dB}}$, or by an RC time constant, the expressions become

$$i_{\text{noise}} = \sqrt{eI\pi f_{3\text{dB}}} = \sqrt{\frac{eI}{2\text{RC}}} \quad (11)$$

Quantitative calculation of the shot noise limit for photodiode detectors is straightforward since the standard equation applies. In most photodiode detection systems, a preamplifier circuit converts the current to voltage and this voltage is read by the processing electronics. Our analysis does not include the noise contribution from the processing electronics, which varies greatly with the electronic design of the system. In a real detection system with known bandwidth, the detection current can be measured and its standard deviation compared to the limiting value of eq 1 to determine how close the noise in the real system is to the fundamental shot noise limit.

SHOT NOISE IN A PHOTOMULTIPLIER TUBE DETECTOR[9]

For a photomultiplier tube, the measured anode current, I, results from the dynode multiplication of electrons emitted at the photocathode by the incident photons. Again assuming the high light limit, the number of electrons emitted at the cathode is

$$n = \frac{I\Delta t}{Ge} \quad (12)$$

where I is the measured anode current and G is the overall gain of the photomultiplier tube. The standard deviation is

$$\sqrt{n} = \sqrt{\frac{I\Delta t}{Ge}} \quad (13)$$

and the fluctuation in the anode current is given by

$$i_{\text{noise}} = \frac{\sqrt{n}\,Ge}{\Delta t} = \sqrt{\frac{I\Delta t}{Ge}}\,\frac{Ge}{\Delta t} = \sqrt{\frac{IGe}{\Delta t}} \quad (14)$$

For the different representations of detection bandwidth the expressions become

$$i_{\text{noise}} = \sqrt{2IGe\Delta f} = \sqrt{IGe\pi f_{3\text{dB}}} = \sqrt{\frac{IGe}{2\text{RC}}} \quad (15)$$

The overall gain of the photomultiplier must be included for quantitative calculations of the shot noise limit in photomultiplier detection systems. The gain of the photomultiplier tube as a function of bias voltage is provided in the specification sheet for a particular detector.[10] There are also contributions to the shot noise due to the multiplicative effect of the secondary electrons emitted at each dynode. In the Supporting Information, we show how the noise contributions from the dynodes are included in the model and also show that their contributions are small with large secondary electron coefficients.

SUMMARY

The elegant simplicity of the square root relationship between the mean and the standard deviation of number of events in Poisson statistics lies at the heart of understanding the fundamental limitation of many chemical measurements. Spectroscopic measurements with photodiodes or photomultiplier tubes provide excellent working examples because the measured current can be readily transformed into the number of events. These examples can be presented to students in problem sets or in the laboratory. We use a laboratory exercise where students measure the signal-to-noise for a PMT signal and compare the measured value to the theoretical shot noise limit. This exercise is described in the Supporting

Information. Ideally, working with these examples will provide insights for students to recognize the role of Poisson statistics in any measurement involving a finite number of events.

■ ASSOCIATED CONTENT

Supporting Information

A detailed derivation of the relationships between measurement time and detection bandwidths; an analysis of the noise contribution from the dynodes of a PMT; a description of an example laboratory exercise that illustrates the shot noise limit of a PMT detection system. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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