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The Ultimate Limit in Measurements by Instrumental Analysis: An Interesting Account of *Schroteffekt* and Shot Noise

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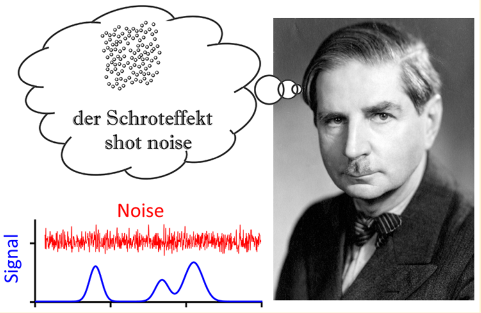
ABSTRACT: Shot noise is one of the essential concepts in instrumental analysis, which places a fundamental limit on quantitative measurements when the magnitude of the analytical signal is very small. The introduction of an abstract scientific concept with a brief historical perspective often shows the human side of science. In the scientific literature, several explanations are provided as to why shot noise is called "shot noise". Some of them are incorrect, and some of them are partially based on personal opinions. In this short communication, the origins of the terms "shot effect" and "shot noise" are traced. The term "shot effect" was initially called *Schroteffekt* in Schottky's 1918 paper, which finally became "shot noise" in the scientific literature written in English in the 1930s. Schottky, who made many fundamental contributions in physics, rarely wrote anything in English. Herein, we briefly clarify what Schottky thought in his own words when he coined this terminology. Several interesting conclusions are made, especially the self-correcting nature of science, which would encourage the young generation of scientists to think critically.



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■ INTRODUCTION

The teaching of scientific concepts with a historical touch often adds a human element to otherwise abstract ideas. We better retain the ideas when an engaging background story of a concept is discussed in the class. The purpose of such conversations is to avoid introducing a new idea in a dry and formal fashion. It is also observed that some students resort to relying on memorization without understanding the meaning of the terminology. This learning approach is rarely helpful in the long term. Tracing the etymology and earliest known uses of scientific terms to understand a concept is often a delightful and rewarding exercise. Three major resources for scientists and educators are *Earliest Known Uses of the Words of Mathematics*,[1] *A Glossary of Coined Names and Words in Science*,[2] and the Ask the Historian[3] series by the *Journal of Chemical Education*. The math collection traces the origin of mathematical terms, symbols, and terminologies such as matrix, group theory, and symbols (∂, σ, Δ, $\overline{x}$). The glossary of coined names focuses on chemical terminologies. It contains significant contributions from one of the authors' own compilation of the history of scientific terms. The "Ask the Historian" series traced the origin of individual concepts, such as the concept of entropy, the universal gas constant R, and so on. All databases give reference to the original publications when traceable. A book particularly useful to advanced organic chemists is *Organic Chemistry, the Name Game* with a discussion of organic chemistry terms, nomenclature, and exciting stories behind them.[4] These databases let us appreciate the very nature of science and its self-correction ability and show how some neat textbook models were initially difficult and insecure explorations by dedicated scientists.

One elusive term that has evaded an explanation of its origin is the concept of "shot noise". The purpose of this communication is to clarify the issue and eliminate the myths associated with the terminology. The concept of shot noise is discussed in most analytical chemistry textbooks in the undergraduate and graduate curriculum, often without explaining why shot noise is so named. Shot noise is a fundamental aspect of spectroscopic measurements, and it is encountered when Poisson statistics govern the counting of objects such as electrons, photons, ions, and molecules or any discrete objects for that matter. Shot noise can be introduced to the students as follows along with the formal derivation, which has appeared in a recent publication of this *Journal*.[5] The derivation (eq 4, *vide infra*) and this communication would serve as a good companion for a lecture on noise sources in instrumental analysis. Poisson statistics state that the standard deviation (σ) of independent random events is equal to the square root of the signal or the number of counted events (N). Stated mathematically

$$\sigma = \sqrt{N} \tag{1}$$

This random fluctuation or noise (σ) is a fundamental limit of quantitative chemical analysis. By analogy, this concept has

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Table 1. Example Explanations of the Origin of the Term "Shot Effect" or "Shot Noise"

	Explanations Offered by Various Scholars	Source (Reference in This Work)
(a)	Shot noise is a short form of Schottky noise.	8
(b)	Schottky himself originally likened the phenomenon to the random audible noise produced by pouring a stream of small shots (German *Schrot*), buckshot perhaps, onto a metal plate. He regarded this analogous to the stream of electrons in the vacuum tubes "impinging" on the anode.	9
(c)	Shot noise is not a corruption of Schottky as some occasionally assert. It is simply that if you hook up an audio system to a source of shot noise biased at a very low current, the resulting sound is much like that of buckshot (pellets) dropping onto a hard surface.	10
(d)	"Shot noise" draws an analogy between electrons and the small pellets of lead that hunters use for a single charge of a gun.	11
(e)	The name is derived from the sound of a fistful of gunshot dropped on the floor (*der Schroteffekt*in German), and not from an abbreviation of the name of the discoverer.	12
(f)	The term shot noise arose on listening to the fluctuations in current in vacuum diodes run in their "temperature-limited" region with headphones. Current variations sound like lead shot raining down on a metal plate.	13
(g)	Unabridged *Oxford English Dictionary*: Shot effect [translating German *Schroteffekt* (W. Schottky 1918, in *Ann. der Physik* LVII. 547), < *schrot* small shot] the fluctuation in the magnitude of the anode current in a thermionic valve due to the random character of electron emission; also any fluctuation having a similar stochastic character.	14
(h)	The actual footnote of Schottky's 1918 paper: *"Diese Bezeichnung ist mit Rücksicht auf die Entstehungsart gewählt; der Ausdruck "Schrot" weist, wie im gewöhnlichen Sprachgebrauch, auf das Auftreten von einer großen Zahl gleichartiger Elementarteilchen hin."* This term is chosen with respect to the origin (of the effect): The term "Schrot" points, as in common linguistic usage, to the occurrence of a large number of uniform elementary particles (translated by the authors).	15

been extended to counting molecules in very small volumes in terms of *molecular shot noise*.[6] These counting problems become important when very small numbers are encountered and need to be measured. For example, in Raman spectroscopy, one photon in 10^6−10^8 photons is inelastically scattered depending on the cross section of the molecule. Fluorescence spectroscopy also relies upon photon counting, especially in very small volumes of dilute solutions or zeptomolar range. In such cases, the signal (N) to noise (σ) ratio becomes very small. If

$$\text{signal} = N \tag{2}$$

$$\text{signal to noise ratio (SNR)} = \frac{N}{\sqrt{N}} = \sqrt{N} \tag{3}$$

then eq 3 shows two critical aspects points for spectroscopic measurements: (i) the noise is present *in* the analytical signal and (ii) as the signal becomes large, shot noise contribution *in* the signal becomes insignificant as SNR becomes very large. A handy analogy of the shot noise limit is given in a Raman spectroscopy monograph by McCreery[7]

> *Consider a person counting cars passing on a highway when the cars occur randomly but at a constant average rate. If only a few cars are counted, the relative standard deviation is high. As the number of cars counted increases by increasing the observation time, the standard deviation increases, but the relative standard deviation decreases and the SNR increases. The relative precision of the determination of the average number of car/min improves as the measurement time increases and more cars are observed.*

■ WHY IS THE SHOT EFFECT CALLED "SHOT EFFECT"?

There are several explanations in books as well as on the Internet that attempt to rationalize the term "shot effect" or "shot noise". Table 1 summarizes the views of various scholars. Unfortunately, some of the explanations are incorrect or partially correct with a few exceptions (Table 1). All the references in Table 1 are very well-cited with more than 100 citations. The most common misconception about shot noise is that it is a short form of Schottky's noise. This is usually seen in web-based presentations, lectures, and even some Ph.D. theses.

The other common version is that the term shot noise is analogous to the noise of shots falling on a hard surface. These misconceptions are understandable given that Schottky (Figure 1), who coined this term as *Schroteffekt* in 1918,[15] rarely published in English. His original paper on shot noise was never translated to the best of our knowledge. In this paper, he studied the fluctuations of electrical current in high-vacuum amplifier tubes based on the thermionic emission of electrons from heated cathodes. Assume a simple case of a hot cathode in an amplifier tube and an anode. The *elementary process* referred to below implies an independent transition of a quantum of elementary charge between the hot cathode and the anode. Schottky described this process (translated into English by the authors) as[15]

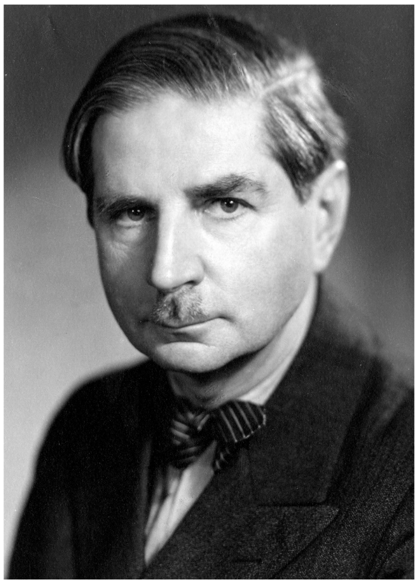

Figure 1. Physicist Walter Hans Schottky (23 July 1886−4 March 1976). Photograph reproduced with permission from Siemens Historical Institute, Berlin, Germany.

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[B]ecause of the atomistic constitution of electricity, the transfer of electricity is not a uniformly flowing current, but a hail of quantum charges "ein Hagel von Ladungsquanten" which would give a reason for fluctuations in flux even for regular temporal distribution. Their frequency would be determined by the number of particles transferred per second.

Later, Schottky introduced his famous *Schroteffekt* concept (translated into English by the authors) as follows:[15]

The amplitude of the average alternating current of a certain period induced by the "Schroteffekt" is proportional (under given average discharge current) to the square root of the elementary electric charge, which is transported from one electrode to another during an elementary process.

The derivation of the modern version of this relation is given in a recent publication from simple statistical principles.[5]

$$i_{\text{noise}} = \sqrt{2eI\Delta f} \tag{4}$$

In this equation, i_{noise} is the standard deviation in the measured current, I is the measured current, e is the charge of the electron, and Δf is the bandwidth of the measurement. This explanation is followed by a footnote given in Schottky's paper (see Table 1, h) (translated into English by the authors):[15]

This term is chosen with respect to the origin of the effect: The term "Schrot" points, as in common linguistic usage, to the occurrence of a large number of uniform elementary particles.

The word *Schrot* has two meanings in German. The first meaning refers to a quantity of coarsely ground grains (which is an uncountable noun), and the second meaning is the lead shot used in firearms (Figure 2). Schottky did not explicitly imply the terminology of firearms in his original explanation; instead, he implied the usage of the word *Schrot* as in common use to represent a large number of uniform-sized elementary particles *(einer großen Zahl gleichartiger Elementarteilchen)* in vacuum tubes. Schottky wanted to emphasize the nature of graininess or discreteness of a large number of identical and uniform elementary particles. The year 1918 was the end of World War I; the word *Schrot* could be in the mind of Schottky. The imagery of independent shots (electrons) traveling as a hail of independent particles from one electrode to the another is indeed an appealing description. As it is clear now, Schottky's original choice of *Schroteffekt* had nothing to do with any audible noise originating from falling on a hard surface or noise disturbance in headphones, as believed by some writers. The preceding analogy becomes clear from Figure 2. The previous analogy of hail of charged quanta ("*ein Hagel von Ladungsquanten*"), as an example of Poisson statistics, is also a good analogy of counting discrete events.

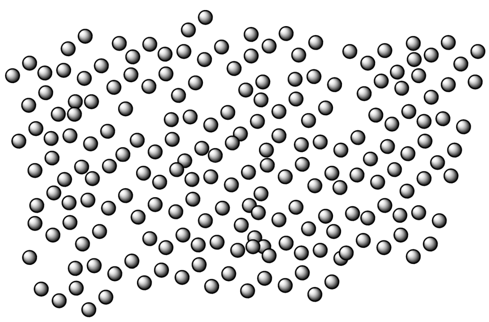

Figure 2. Schematic of lead shots typically used in the munition. The word *Schrot* represents small balls of lead metal for the cartridges of certain firearms. In the modern terminology, *Schroteffekt* reflects the noise (statistical error) in counting a large number of quantized uniform particles such as electrons, ions, and photons.

■ HOW DID THE "SHOT EFFECT" BECOME "SHOT NOISE"?

The next logical question one may ask is this: Why is the shot effect explained above now called shot noise? The term noise may bring an "audible" sensation to mind, yet it should be made quite clear that the modern concept of noise is very abstract. The general meaning of noise can be explained as random or irregular fluctuations or disturbances in the current or voltage that are not part of a signal (whether the signal is audible or not), or that interfere with or obscure a signal. Thus, noise is something unwanted in the simplest possible terms. Not surprisingly, the term "noise" has its roots in telephone and telegraph science where the word "noise", in a technical and audible sense, was used as early as 1923, according to the unabridged *Oxford English Dictionary*. Yeang gives an interesting account of the history of various noises.[16] Thus, there is no audible noise due to the phenomenon of the shot effect itself. However, one may perceive this phenomenon as a "fluctuation", an audible noise with the help of a suitable device such as an audio system. This audible noise could have led to explanations b and c in Table 1.

When did "shot effect" become "shot noise"? The earliest known usage of shot noise is a study from 1930 of Bell Laboratories: A Study of Noise in Vacuum Tubes and Attached Circuits.[17] In that text, the author uses the terminology of "shot effect" and "shot-effect noise". However, in a figure caption, the author shows a curve with a label "shot noise". The curve showed the filament heating power in watts vs. noise power. Thus, in 1934, Johnson, again from Bell Laboratories, explains that[18]

Anyone who has had his favorite radio hours ruined by statics knows the effect of an incoherent background of noise (...) At one time, it seems that other sources of noises of purely local origin, such as poor batteries, loose contacts (...), might be eliminated entirely so that the circuits would be capable of amplifying any signal, no matter how small. It was found, however, that noise level cannot be lowered indefinitely; that there are limits below which, in the nature of things, noise cannot be reduced.

This is the same Johnson who has a noise named after him, "Johnson's noise", due to thermal agitation of electrons in circuits. Note how relevant his statements are today, from an analytical chemist's perspective. Instruments cannot measure any arbitrarily dilute solution of an analyte because its signal will be comparable to the fundamental types of noise we just discussed above. As a side note, the German equivalent of the "shot noise" is *Schrotrauschen*, which can be considered as a replacement of *Schroteffekt*. Interestingly, the word "*rauschen*" means noise, with an audible connotation of the rustling of wind or leaves. This terminology did not appear until the late 1930s as far as we could trace it back.[19]

■ CONCLUSIONS

A summary of explanations and the opinions of various scholars is shared on the origin of the term "shot noise". Shot noise is an important concept in analytical chemistry and detector technology (e.g., optical detectors, mass spectrom-

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eters, and ion counters). Optical detector manufacturers usually strive to be shot-noise limited. However, being shot-noise limited does not necessarily mean the best possible detector. Schottky's explanation is provided from his original paper for choosing this name. His logic of choosing this name is different from the opinions of some authors who have rationalized the choice of "shot noise" in modern books.

Several lessons can be drawn from this communication that will be beneficial to future scientists. As per the idiom "paper never refused ink", research students should develop a habit of cross-checking facts from various sources. Second, we often have an unshakable faith in peer-reviewed articles. Many excellent research papers have honest mistakes, and human errors, including this 1918 paper of Schottky's.[15] Some of them get corrected, and some of them remain unnoticed. Schottky made a mistake in the integration of a function in deriving a relation for the shot effect, which gave rise to an erroneous value of the elementary charge. This error was addressed by Johnson of Bell Laboratories (the man behind "Johnson's noise").[20] The beauty of science is its self-correction, and this comes from the habit of cross-checking experimental results and comparative analysis of literature. As scientists, we should remember that there is no authority or hierarchy in science. Only experimental facts dictate the fate of a theory. A significant amount of information is available at the fingertips of everyone these days, yet the very same information can be quite misleading if we as students, teachers, and scientists do not develop a habit of critical reading from multiple resources.

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Notes

The authors declare no competing financial interest.

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