Spectrochimica Acta, Vol. 33B, pp. 383 to 399
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0031-6987/78/0801-0383$02.00/0

A review and tutorial discussion of noise and signal-to-noise ratios in analytical spectrometry—I. Fundamental principles of signal-to-noise ratios*

C. TH. J. ALKEMADE and W. SNELLEMAN
Fysisch Laboratorium, University of Utrecht, Utrecht, The Netherlands

G. D. BOUTILIER, B. D. POLLARD and J. D. WINEFORDNER
Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.

T. L. CHESTER
Proctor and Gamble, Miami Valley Laboratories, Cincinnati, OH 45247, U.S.A.

N. OMENETTO
Institute of Inorganic and General Chemistry, University of Pavia, Pavia, Italy

(*Received* 3 *February* 1978)

Abstract—This review consists of two parts which discuss signal-to-noise in a tutorial manner. The sources of noise, the mathematical representation of noise, and the major types of noises in emission and luminescence spectrometry are discussed. An extensive treatment of noise and signal-to-noise ratios of paired readings is given using the relation between the auto-correlation function and the spectral noise power. These signal-to-noise expressions under optimized measurement conditions are given in terms of currents and count rates as well as in terms of charge and counts for the cases of d.c. and a.c. measurements; the present treatment is limited to the cases when the background shows only either shot noise or flicker noise. Finally, the consequences of the combination of these noise sources is considered. Signal expressions for optical spectrometry are also given. Tables give the expressions for signal-to-noise ratios in the various cases.

I. INTRODUCTION

THE MEASUREMENT of signals in optical spectrometry is influenced by the presence of spurious signals. Often such spurious signals can be eliminated. However, the quantum nature of radiation causes fluctuations for which the term *shot noise* is colloquial. Shot noise adds an error signal, which is only statistically predictable, to the desired signal. In addition to the statistically predictable shot noise, additional scatter in the signal measured occurs due to *excess low-frequency* (e.l.f.) *noise*; a common case of such noise has a spectral noise power which is roughly inversely proportional to frequency and is termed *flicker noise* or 1/f *noise*. The cause of these noise sources may be found in the light sources, the absorbing medium, the detectors, and the electronic measurement systems used in optical spectrometry. Because of the importance of noise, particularly signal-to-noise ratios in optical spectrometry (actually in all measurements), and because of the lack of a unified treatment of these phenomena, particularly from the standpoint of analytical chemistry, the present manuscript was prepared.

Calculations of shot noise in terms of standard deviations and noise power spectra generally do not present difficulties. But problems arise when e.l.f. noise, e.g. 1/f noise, has to be taken into account, since the integral describing the standard deviation diverges. An adequate description can then be given when use is made of the auto-correlation function of the noise signals and when paired readings are considered. This treatment yields general expressions for the signal-to-noise ratio (S/N). Inserting the specific time

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* Dedicated to the memory of Professor HEINRICH KAISER.

A part of this paper has been presented by one of the authors (C.TH.J.A.) in a colloquium on "The effect of time-correlation in the background fluctuations on the detection limit in analytical spectroscopy" at the Institut für Spektrochemie und Angewandte Spektroskopie, Dortmund, 22nd January 1976, upon invitation by Professor H. KAISER.

response and frequency response of the measuring system and the specific noise power spectrum, one obtains S/N expressions in the various cases, from which the optimal values of the time constants can be derived.

It should be stressed, that even though the expressions are given and discussed for use in analytical optical spectrometry, many of them are directly applicable to other types of spectroscopy, such as absorption spectrometry and also to various types of non-spectroscopic measurements. The calculations for analog readings follow essentially the procedure outlined in [5].

II. NOISE AND SIGNAL-TO-NOISE EXPRESSIONS

II.A. TYPES OF ERRORS AND NOISE SOURCES

The study of noise [1-5] forms part of the discussion of errors in analytical measurements [5]. Errors may be divided into: (i) *systematic errors* [6] which may arise from the measuring procedure itself (sample preparation, etc.) and from unwanted signals produced by background, stray light, detector offset, etc., which can be corrected for by various methods, including blank subtraction, signal modulation, careful calibration, etc.; and (ii) *random errors* or *scatter*, which are a result of reading and digitizing errors which can be easily eliminated by scale expansion, and of random variations with time of physical quantities or parameters that affect the signal reading, called *noise*.

The r.m.s.-value of a noise source and the signal-to-noise ratio are useful parameters to describe analytical figures of merit of procedures [7, 8]. These important analytical figures of merit are: (i) *relative standard deviation*, which is the reciprocal signal-to-noise ratio; (ii) analytical *limit of detection*, which is the amount (or concentration) of analyte that can be detected with a certain confidence level by a given analytical procedure; (iii) the *sensitivity* of the analytical method, which corresponds to the slope of the analytical calibration curve (analyte signal or measure vs concentration or amount of analyte). The limit of detection is defined by

$$c_L \,(\text{or } q_L) \equiv \frac{x_L - \bar{x}_{bl}}{S} = \frac{k\sigma_{bl}}{S} \tag{II.A.1}$$

which ties together two of the analytical figures of merit, namely the limit of detection (concentration, c_L, or amount q_L) and the sensitivity, S; the limit of detection is also related to the blank noise level, σ_{bl}, resulting from a number (16 or more is preferred [7, 8]) of measurements of the blank, i.e. $\bar{x}_{bl}$ and σ_{bl} are the average blank and standard deviation of the blank, and k is a protection factor to give a desired confidence level (a value of $k = 3$ is recommended; if $k = 3$, a 99.86% confidence level occurs).

The spectral noise power (noise power per unit frequency interval) in terms of current fluctuations for *shot noise* is given by

$$(S_i)_{sh}(f) \equiv S_o = 2e \sum_j \bar{i}_j = 2 \sum_j \bar{R}_j e^2 \tag{II.A.2}$$

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[1] R. KING, *Electrical Noise*. Chapman and Hall, London (1966).

[2] B. M. OLIVER and J. M. CASE, *Electronic Measurements and Instrumentation*. McGraw-Hill, New York (1971).

[3] A. VAN DER ZIEL, *Noise in Measurements*. John Wiley, New York (1976).

[4] D. K. C. MCDONALD, *Noise and Fluctuations: An Introduction*. John Wiley, New York (1962).

[5] C. TH. J. ALKEMADE, *5th Intern. Conf. on Atomic Spectroscopy, Melbourne* 1975, Abstracts of papers, The Australian Academy of Science (1975).

[6] T. C. O'HAVER, *Analytical Considerations, Trace Analysis* (Edited by J. D. WINEFORDNER), Chap. 2, p. 15. John Wiley, New York (1976).

[7] H. KAISER, *Two Papers on the Limit of Detection of a Complete Analytical Procedure* (translated by A. C. MENZIES), Hilger, London (1968)/Hafner, New York (1969). Original papers: H. KAISER, *Z. Anal. Chem.* **209**, 1 (1965); **216**, 80 (1966).

[8] IUPAC Commission on Spectrochemical and other Optical Procedures, *Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis—II. Data Interpretation, Pure Appl. Chem.* **45**, 99 (1976); cf. *Spectrochim. Acta* **33B**, 24 (1978).

where e is the elementary charge (in C), i_j is the j-th component in the current, emitted e.g. by a photocathode (in A) and R_j is the corresponding electron count rate (in counts s^{-1}). The spectral noise power considered as a function of frequency f is called the noise spectrum. The dimension of S_i is $[i]^2[t]$. Bars denote average values.

Excess low-frequency noise has a noise power spectrum which increases towards low frequencies; its dependence on frequency is often given by $f^{-\alpha}$ where α is about unity (flicker noise). In spectrometry, l/f noise is the most common and so will be the only one discussed in detail. The frequency below which l/f noise becomes important depends on the noise source and the signal level and can vary from less than 1 Hz to frequencies over 1000 Hz. This noise will be termed flicker noise throughout this paper despite the use of this term for a variety of other concepts (flicker noise is certainly a more-used term for l/f noise than fluctuation noise which has been used by some workers for l/f noise). The cause of flicker noise is not well-known. Various models for l/f noise in electronics have been developed [3] but most seem to have little relationship with spectrometric systems. The major sources of flicker noise involve random drift of light sources, analyte production, and detection. The spectral noise power in terms of current fluctuations for *flicker noise* is given by

$$(S_i)_{fl}(f) = \sum_j \frac{K_j^2}{f}\,\bar{i}_j^2 = \sum_j \frac{K_j^2}{f}\,\bar{R}_j^2 e^2 \tag{II.A.3}$$

where f is the frequency, K_j^2 is a constant with dimension unity which describes the low-frequency stability of the noise source and i_j and R_j are as defined previously. We note that the flicker noise power varies as $\bar{i}^2$ whereas the shot noise power varies as $\bar{i}$; the r.m.s.-value of the flicker noise is thus proportional to the mean current (so-called proportional noise).

Apart from the noise components mentioned there may occur peaks in the noise power spectrum which are, for example, due to oscillations in the flame-burner system, such as vortex formation in the gas flows and resonances in the tubings. They may extend to the audible frequency range and are then called *whistle noise*. The noise power in such peaks is also proportional to the square of the photocurrent, as in the case of e.l.f. noise.

Another source of noise existing in electrical circuits and components but insignificant compared to the other noises when photomultipliers are used is the *thermal* (*Johnson*) *noise* due to random thermal motion of electrical charge carriers in any conductor.

When combining noises of different origins into a total noise expression, the method of addition must be carefully considered. For example, if two noises with r.m.s.-values σ_a and σ_b exist together, the r.m.s.-value of the total noise, σ_T, is given by

$$\sigma_T = (\sigma_a^2 + \sigma_b^2 + 2C\sigma_a\sigma_b)^{1/2} \tag{II.A.4}$$

where C is a correlation coefficient; $|C|$ ranges between $|C| = 1$, in the case of complete statistical correlation, and $|C| = 0$ in the case when both noises are completely uncorrelated. Statistical correlation may exist when both noises have a common origin (e.g. fluctuations in the flame temperature).

II.B. Mathematical Treatment of Noise

Because noise is a sequence of unpredictable events, it is impossible to predict a future value based upon previous values. However, by means of probability theory, it is possible to state the chance that a certain process will be in a certain state at a certain time [1, 3], yielding a distribution of probabilities for the possible states. A well-known distribution is the *Poisson distribution*. It is found when events occur independently, e.g. in time. Then the variance of n events occurring in a time period of given length equals the mean value of n, found when the measurement is repeated a large number of times:

$$\text{var}\, n = \sigma_n^2 = \bar{n} \tag{II.B.1}$$

where σ_n is the standard deviation of n.

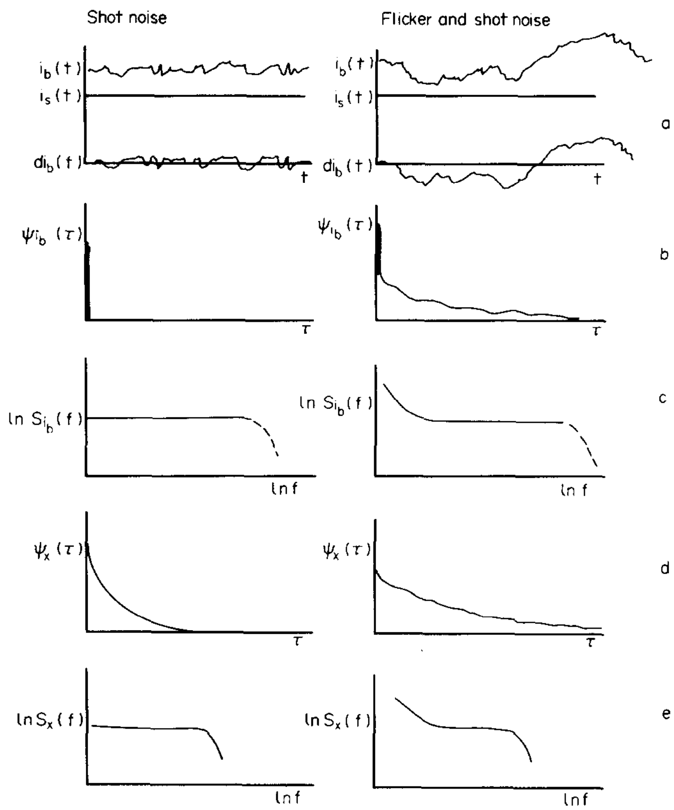

Fig. 1. Representation of shot noise and flicker noise + shot noise.
a. Background photocurrent $i_b(t)$, signal photocurrent $i_s(t)$ and background current fluctuations $di_b(t) \equiv i_b(t) - \bar{i}_b(t)$ vs time t.
b. The auto-correlation functions ψ_{i_b} as a function of the time shift τ.
c. Spectral noise power S_{i_b} as a function of frequency f, with a high-frequency cut-off due to the apparatus used.
d. The auto-correlation function ψ_x of the meter deflections as a function of time shift τ.
e. Spectral noise power S_x of the meter deflections as a function of frequency f.

In this paper the emphasis is on the signal-to-noise ratio (S/N) of a measurement, which is the ratio of a signal to the standard deviation of the noise, as measured in the readings of a meter or an integrator.

In order to be able to compare the signal-to-noise ratios obtained with different types of noise and with different measuring procedures, and to find optimum values of the various characteristic times, one may with advantage make use of the relation between the *auto-correlation function* and the *spectral noise power* involved (see Fig. 1).

The auto-correlation function of a continuously fluctuating signal $dx(t)$ is given by

$$\psi_x(\tau) \equiv \overline{dx(t)\,dx(t+\tau)}, \qquad \text{(II.B.2)}$$

where a bar denotes the average of a large number of values found at different times t for constant time difference τ. In problems of fluctuations, one generally makes $\overline{dx(t)} = 0$ by subtracting the average value from the signal. For a signal based on a purely statistical sequence of pulses (e.g. emission of photoelectrons in the case of a photocurrent in an ideal photomultiplier tube, upon which falls a constant light signal), $\psi_x(\tau)$ differs from zero only for $\tau = 0$, i.e. $\psi_x(\tau) = 0$ for $\tau \neq 0$. The values of $dx(t)$ at different times t are completely uncorrelated and the auto-correlation function is simply a delta-function at $\tau = 0$. This case is typical for shot noise. However, other noise sources may have a different character; in the case of e.l.f. noise the values $dx(t)$ and $dx(t + \tau)$ do show a statistical correlation also for large τ, i.e. $\psi_x(\tau)$ differs from zero also for $\tau \neq 0$. Statistical correlation for $\tau \neq 0$ also occurs when shot noise is amplified and registered by an instrument that has a "memory", e.g. due to the incorporation of an RC-filter.

To obtain an expression of the noise in the frequency domain, use can be made of the Wiener–Khintchine theorem [3, 9], which relates the auto-correlation function to the spectral noise power $S_x(f)$ through a Fourier transformation:

$$S_x(f) = 4 \int_0^\infty \overline{\mathrm{d}x(t)\,\mathrm{d}x(t+\tau)} \cos(\omega\tau)\,\mathrm{d}\tau \tag{II.B.3}$$

$$= 4 \int_0^\infty \psi_x(\tau) \cos(\omega\tau)\,\mathrm{d}\tau,$$

and

$$\psi_x(\tau) = \int_0^\infty S_x(f) \cos(\omega\tau)\,\mathrm{d}f \tag{II.B.4}$$

with $\omega \equiv 2\pi f$.

The Fourier transform of a delta-function, which describes $\psi_x(\tau)$ for shot noise, is a constant. The transform shows that the shot noise power is evenly distributed over a large (ideally infinite) range of frequencies because of which it is also called *white noise* (cf. equation II.A.2).

When a noise signal passes a measuring system, its statistical properties will generally be changed. When a meter with time constant τ_c is used, this meter will, through its inertia, introduce a correlation-in-time which makes the auto-correlation function of the meter fluctuations due to the (originally) white noise differ from zero also for $\tau \neq 0$ (see Fig. 1). It also changes the auto-correlation function of the e.l.f. noise; consequently the related noise power spectra are also changed. When an integrating measuring system is used, an analogous effect occurs. For white noise, integrated over a time τ_i, a correlation will exist between the results of two integrations when they are taken less than τ_i seconds apart. When they are taken more than τ_i seconds apart, the results are again strictly uncorrelated. For e.l.f. noise a similar reasoning holds, i.e. an *extra* correlation is introduced in the noise signal when the integrator readings are taken less than τ_i seconds apart; when the readings are taken more than τ_i seconds apart, only the correlations in the original signal contribute to the correlation in the readings.

To relate the standard deviation of the noise, which is needed for the calculations of the signal-to-noise ratio, to the auto-correlation function and the spectral noise power, we follow the procedure outlined in [5].

When one works near to the detection limit, which is set by the background fluctuations, one usually applies *paired readings*. The background, which has been admitted to the measuring system during a time long compared to the time constant of the system, is read just before the signal to be measured is admitted at $t = t_o$, its value is subtracted from the signal-plus-background reading made τ_s seconds later; τ_s is called the sampling time. This difference, Δx, is taken to be the *signal reading corrected for background*:

$$\Delta x = x_{s+b}(t_o + \tau_s) - x_b(t_o). \tag{II.B.5}$$

Equation II.B.5 can be rewritten as

$$\Delta x = x_s(t_o + \tau_s) + [\mathrm{d}x_b(t_o + \tau_s) - \mathrm{d}x_b(t_o)] \tag{II.B.6}$$

where $\mathrm{d}x_b(t)$ is the statistical fluctuation in the meter deflection or integrator output due to the background alone. The signal-to-noise ratio (S/N) is then the signal reading, $x_s(t_o + \tau_s)$, divided by the standard deviation, $\sigma_{\Delta x}$, in the *difference* of the background fluctuations occurring τ_s seconds apart (see Fig. 2). We assume the noise in the signal to be insignificant as compared to the background noise and so

$$\frac{S}{N} = \frac{x_s(t_o + \tau_s)}{\sigma_{\Delta x}} \tag{II.B.7}$$

[9] R. B. Blackman and J. W. Tukey, *The Measurement of Power Spectra*. Dover, New York (1958).

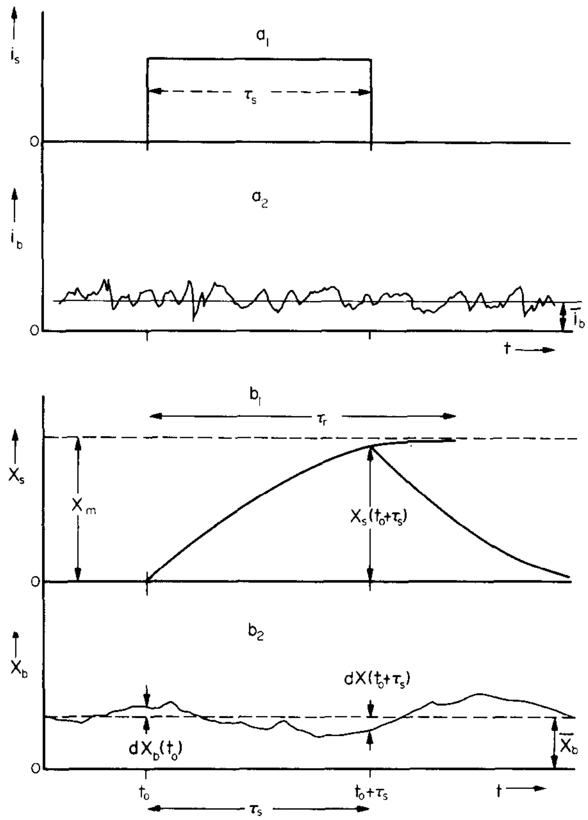

Fig. 2. Representation of signal and noise measured with a meter.
a_1. Signal photocurrent, i_s, vs time; a_2. Fluctuating background photocurrent, i_b, vs time.
b_1. Meter deflection for signal, x_s, vs time; b_2. Meter deflection for background, x_b, vs time.

with

$$\sigma_{\Delta x} = \left\{\overline{[\mathrm{d}x_b(t_o + \tau_s) - \mathrm{d}x_b(t_o)]^2}\right\}^{1/2}. \tag{II.B.8}$$

From equation II.B.8, the variance $\sigma_{\Delta x}^2$ can be straightforwardly expressed as

$$\sigma_{\Delta x}^2 = \overline{\mathrm{d}x_b(t_o + \tau_s)^2} + \overline{\mathrm{d}x_b(t_o)^2} - \overline{2\mathrm{d}x_b(t_o + \tau_s)\,\mathrm{d}x_b(t_o)}. \tag{II.B.9}$$

Because the background fluctuation is assumed to be *stationary*, each of the first two terms in the right-hand side of the latter equation is equal to σ_b^2 which is the *time-independent* variance of $\mathrm{d}x_b(t)$. From the very definition of the auto-correlation function, $\sigma_{\Delta x}^2$ may be rewritten as

$$\sigma_{\Delta x}^2 = 2\sigma_b^2 - \overline{2\mathrm{d}x_b(t_o + \tau_s)\,\mathrm{d}x_b(t_o)} = 2[\psi_x(0) - \psi_x(\tau_s)], \tag{II.B.10}$$

where

$$\psi_x(0) = \overline{\mathrm{d}x_b(t_o + \tau_s)^2} = \overline{\mathrm{d}x_b(t_o)^2} = \sigma_b^2$$

and

$$\psi_x(\tau_s) = \overline{\mathrm{d}x_b(t_o + \tau_s)\,\mathrm{d}x_b(t_o)}.$$

To calculate $\sigma_{\Delta x}^2$, the auto-correlation function is expressed in terms of the spectral noise power $S_{i_b}(f)$ of the background current fluctuations and in the characteristics of the measuring system, using the Wiener–Khintchine theorem. Therefore $\psi_x(\tau_s)$ may be expressed as

$$\psi_x(\tau_s) = \int_0^{\infty} S_x(f)\cos(2\pi f\tau_s)\,\mathrm{d}f \tag{II.B.11}$$

where

$$S_x(f) = S_{i_b}(f)|G(f)|^2 \tag{II.B.12}$$

and $G(f)$ is the frequency response of the (linear) measuring-read out system. In other words, the spectral noise power of the meter fluctuations is the product of the spectral noise power of the background current fluctuations, S_{i_b}, and the squared absolute value of the frequency response of the measuring system, $|G(f)|^2$, including the amplification of the photomultiplier detector. Since noise power is a squared quantity, one needs here the square of the absolute value of the frequency response; phase-shifts and the associated complex form of the frequency response do not enter in the calculation of noise signals. Substituting equation II.B.12 into equation II.B.11 gives

$$\psi_x(\tau_s) = \int_0^\infty S_{i_b}(f)|G(f)|^2 \cos(2\pi f\tau_s)\,\mathrm{d}f. \tag{II.B.13}$$

Using equation II.B.13, equation II.B.10 for $\sigma_{\Delta x}^2$ may be rewritten as

$$\sigma_{\Delta x}^2 = 2\int_0^\infty S_{i_b}(f)|G(f)|^2\{1 - \cos(2\pi f\tau_s)\}\,\mathrm{d}f, \tag{II.B.14}$$

because $\cos(2\pi f\tau_s) = 1$ for $\tau_s = 0$; $\sigma_{\Delta x}^2$ is therefore a function of the sampling time τ_s; and as $\tau_s \to 0$ both $\sigma_{\Delta x}$ and x_s approach zero.

It should be noticed that the factor $1 - \cos 2\pi f\tau_s\,(= 2\sin^2 \pi f\tau_s)$ stems from the use of paired readings. The noise components having frequencies f for which $f\tau_s = 1, 2, 3$, etc. are completely rejected.

The signal deflection, $x_s(t_o + \tau_s)$, due to a constant signal current i_s that is instantaneously applied to the input at time t_o is

$$x_s(t_o + \tau_s) = Gi_s x(\tau_s) \tag{II.B.15}$$

where G is the d.c. response of the detector plus measuring system, and $x(\tau_s)$ is the normalized time response of the system used (meter or integrator) to a unit step function. Introducing the normalized frequency response of the measuring system

$$g(f) \equiv \frac{G(f)}{G(0)} \equiv \frac{G(f)}{G}. \tag{II.B.16}$$

equation II.B.7 for the signal-to-noise ratio finally becomes

$$\frac{S}{N} = \frac{i_s x(\tau_s)}{\left[2\int_0^\infty S_{i_b}(f)|g(f)|^2\{1 - \cos(2\pi f\tau_s)\}\,\mathrm{d}f\right]^{1/2}} \tag{II.B.17}$$

This equation is the general expression for the signal-to-noise ratio with dominant background noise in the case of paired readings with a d.c. measuring system (meter or integrator).

To optimize the S/N ratio for specific situations we have to introduce in equation II.B.17:

(a) the background noise spectrum S_{i_b} (white noise or flicker noise)
(b) the time response $x(\tau_s)$ of the meter or the integrator used, and the associated normalized frequency response $g(f)$,

and to determine the dependence of the S/N thus found on the sampling time τ_s and the other time parameters.

II.C. Expressions for Noise and Signal-to-Noise for Shot and Flicker Noise

In this section, we shall assume that the photon irradiance to be measured has been converted to an electrical signal through the photocathode of a photomultiplier. Signals and noises will be given in both analog and digital form in terms of rates (current or count rate) and integrations (charge or counts), respectively. All currents, i, or count rates, R, refer to *primary* (or *cathode*) currents or count rates, respectively. The multiplication noise of the photomultiplier will, for simplicity, be neglected [3]. An anodic current, i_a, is related to the cathodic current, i_c, by

$$i_a = i_c G_{pm} \tag{II.C.1}$$

where G_{pm} is the average gain of the photomultiplier. This expression can be used if one wishes to convert final expressions for S/N to anodic currents. It will be assumed throughout this manuscript that systematic errors, e.g. offsets due to amplifier, dark current/stray light, etc., are accounted for, whereas fluctuations and random drift, i.e. noise, are treated in the following cases.

II.C.1. *d.c. measurement in the presence of background shot noise*

In this case, a constant signal current i_s is assumed to be applied to the input at $t = t_o$ whereas the background current i_b is assumed to be continuously present.

Case 1: *Current meter or rate meter*. The step response of a meter damped by an RC-filter (see Fig. 2), i.e. the normalized response of a meter when a constant d.c. current is suddenly applied at $t = t_o$, is

$$x(\tau_s) = 1 - \exp(-\tau_s/\tau_c) \qquad (\text{for } \tau_s \geqq 0) \tag{II.C.2}$$

where the meter time constant $\tau_c = RC$. The response time of the meter is defined as

$$\tau_r \equiv 2\pi\tau_c. \tag{II.C.3}$$

After a time τ_r, the meter has reached its final deflection within 0.2%. The squared absolute value of the normalized frequency response of such a meter is

$$|g(f)|^2 = \frac{1}{1 + (2\pi\tau_c f)^2} = \frac{1}{1 + (f\tau_r)^2}. \tag{II.C.4}$$

Inserting equations II.C.2 through II.C.4 into equation II.B.17, with $S_{i_b}(f) = S_o$ for shot noise, one obtains

$$\frac{S}{N} = \frac{i_s\{1 - \exp(-2\pi\tau_s/\tau_r)\}}{\left\{2\int_0^\infty \frac{S_o\{1 - \cos(2\pi f\tau_s)\}}{1 + f^2\tau_r^2}\,\mathrm{d}f\right\}^{1/2}}. \tag{II.C.5}$$

The integral in equation II.C.5 can be evaluated by using:

$$\int_0^\infty \frac{\sin^{-2} x}{\pi^2 + x^2}\,\mathrm{d}x = \tfrac{1}{4}(1 - e^{-2\pi})$$

which yields:

$$\frac{S}{N} = \frac{i_s\{1 - \exp(-2\pi\tau_s/\tau_r)\}^{1/2}}{(\pi S_o/\tau_r)^{1/2}}. \tag{II.C.6}$$

For fixed τ_r, the maximum value of S/N is reached for $\tau_s = \infty$ and is

$$\frac{S}{N} = \frac{i_s}{(\pi S_o/\tau_r)^{1/2}} = \frac{i_s}{(2\pi e\bar{i}_b)^{1/2}}\tau_r^{1/2}. \tag{II.C.7}$$

Since this value is reached within 0.1% for $\tau_s = \tau_r$, the sampling time τ_s can be restricted to that value. A larger value of τ_s is only a waste of time; a smaller value yields a smaller S/N ratio. Equation II.C.7 shows that the S/N ratio is proportional to the square root of τ_r and thus improves with increasing response time τ_r, provided $\tau_s \gtrsim \tau_r$.

If one substitutes $i = Re$ for a rate meter system, equation II.C.7 becomes

$$\frac{S}{N} = \frac{R_s}{(2\pi\bar{R}_b)^{1/2}}\tau_r^{1/2} \tag{II.C.8}$$

which shows that the dependence of S/N on τ_r is independent of the system used.

Case 2: Analog or digital integrator. The response of an integrator when a constant current i_s is applied during a sampling or integration time τ_i is given by

$$y(\tau_i) = Gi_s\tau_i \qquad (\text{for } \tau_i \geqq 0).$$

G is the combined gain of the photomultiplier and the electronic amplifier before the signal is supplied to the integrator.

The square absolute value of the complex frequency response of the integrator output over the integration time τ_i is (see Appendix 1)

$$|G(f)|^2 = \frac{1 - \cos(2\pi f\tau_i)}{2\pi^2 f^2} G^2. \tag{II.C.10}$$

Using these equations and equations II.B.7 and II.B.14 i.e. taking paired readings of two consecutive integration periods τ_i yields with $S_{i_b} = S_o$:

$$\frac{S}{N} = \frac{i_s\tau_i}{\left[2S_o\int_0^\infty \frac{\{1 - \cos(2\pi f\tau_i)\}^2}{2\pi^2 f^2}\,df\right]^{1/2}} \tag{II.C.11}$$

which yields, with $\int_0^\infty \frac{\sin^4 z}{z^2}\,dz = \pi/4$,

$$\frac{S}{N} = \frac{i_s}{S_o^{1/2}}\tau_i^{1/2}. \tag{II.C.12}$$

We can also obtain this ratio indirectly by considering the integrator as a limiting case of a current meter with very large response time. We shall therefore here derive the S/N ratio from equation II.C.5 by assuming $\tau_s \ll \tau_r$. Then the (very slow) meter acts as an integrator.

One obtains with the approximation $1 - \exp(-2\pi\tau_s/\tau_r) \approx 2\pi\tau_s/\tau_r$ and writing τ_i for τ_s

$$\frac{S}{N} = \frac{i_s 2\pi\tau_i/\tau_r}{\left[2S_o\int_0^\infty \frac{1 - \cos(2\pi f\tau_i)}{f^2\tau_r^2}\,df\right]^{1/2}} \tag{II.C.13}$$

and for fixed, large τ_r with the substitution $z \equiv 2\pi f\tau_i$:

$$\frac{S}{N} = \frac{i_s}{(\frac{1}{2}S_o)^{1/2}}\tau_i^{1/2} \tag{II.C.14}$$

because

$$\int_0^\infty \frac{1 - \cos z}{z^2}\,dz = \pi/2$$

or

$$\frac{S}{N} = \frac{i_s}{(e\bar{i}_b)^{1/2}}\tau_i^{1/2} = \frac{R_s}{(\bar{R}_b)^{1/2}}\tau_i^{1/2}. \tag{II.C.15}$$

However, when paired integrator readings are made, a first (background) integration starts at $t_o - \tau_s$ and a second (background + signal) integration starts at t_o. We are thus dealing here with the fluctuations in the difference of *two* consecutive background integrations, each during τ_i seconds. This adds a factor $\sqrt{2}$ to the r.m.s. noise expression in equation II.C.13. The final expression becomes therefore

$$\frac{S}{N} = \frac{i_s}{(2e\bar{i}_b)^{1/2}}\tau_i^{1/2} = \frac{R_s}{(2\bar{R}_b)^{1/2}}\tau_i^{1/2}. \tag{II.C.16}$$

Comparing equation II.C.7 and equation II.C.16 for equal sample time τ_s, one finds an improvement of a factor $\pi^{1/2} \approx 1.8$ in S/N when an integrator is used.

The derivation of equation II.C.16 is only a demonstration of the calculation method used. The same result can be obtained directly from the properties of the Poisson-distribution. The r.m.s. value of the fluctuations in the difference of two consecutive background integrations, each during τ_i seconds, is $\sqrt{\bar{N}_b} = (2\bar{R}_b\tau_i)^{1/2}$; herein $\bar{N}_b$ is the mean total number of background counts during a time interval $2\tau_i$. The ratio of the signal $R_s\tau_i$ and this r.m.s.-value yields equation II.C.16. However, this simple approach fails for e.l.f. noise and for the case of a current or rate meter where the meter characteristics must be taken into account.

II.C.2. *d.c. measurement in the case of background flicker noise*

Case 1: *Current meter or rate meter*. Substitution of the spectral noise power for flicker noise $S_{i_b}(f) = K^2\bar{i}_b^2/f$ into equation II.B.17 yields:

$$\left.\frac{S}{N}\right)_f^{\mathrm{dm}} = \frac{i_s[1-\exp(-2\pi\tau_s/\tau_r)]}{\left\{2K^2\bar{i}_b^2\int_0^\infty \frac{1-\cos(2\pi f\tau_s)}{f(1+f^2\tau_r^2)}\,\mathrm{d}f\right\}^{1/2}}. \tag{II.C.17}$$

This expression is valid for any τ_s and τ_r, but can be evaluated only by numerical methods. It is possible to simplify this expression by introducing two new variables with dimension unity. Let β and z be defined as

$$\beta \equiv 2\pi\tau_s/\tau_r = \tau_s/\tau_c \tag{II.C.18}$$

$$z \equiv 2\pi f\tau_s. \tag{II.C.19}$$

Substitution of these new variables into equation II.C.17 leads to

$$\left.\frac{S}{N}\right)_f^{\mathrm{dm}} = \frac{i_s\{1-\exp(-\beta)\}}{\left\{2K^2\bar{i}_b^2\int_0^\infty \frac{1-\cos z}{z(1+z^2/\beta^2)}\,\mathrm{d}z\right\}^{1/2}} \tag{II.C.20}$$

or

$$\left.\frac{S}{N}\right)_f^{\mathrm{dm}} = \frac{i_s}{(2K^2\bar{i}_b^2)^{1/2}}f(\beta) \tag{II.C.20}$$

where

$$f(\beta) \equiv \frac{(1-\exp(-\beta)]}{\left\{\int_0^\infty \frac{1-\cos z}{z(1+z^2/\beta^2)}\,\mathrm{d}z\right\}^{1/2}}. \tag{II.C.21}$$

Numerical evaluation [5] of $f(\beta)$ gives a maximum of approximately 0.88 at β approximately equal to 0.8, i.e. $\tau_s \approx \tau_r/8$ or $\tau_s \approx 0.8\tau_c$, and $f(\beta)$ falls to zero as β tends toward zero or infinity. A plot of $f(\beta)$ vs β is given in Fig. 3.

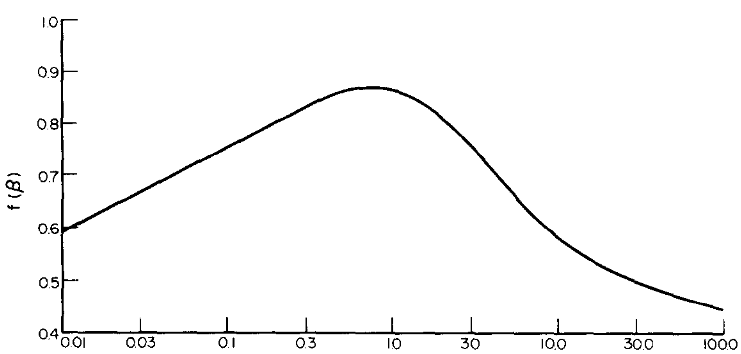

Fig. 3. Single-logarithmic plot of the function $f(\beta)$ defined in equation II.C.21 with $\beta \equiv 2\pi\tau_s/\tau_r$. One can prove that $f(\beta)$ tends asymptotically to zero as $1/\sqrt{\ln\beta}$ for $\beta\to\infty$, and as $1/\sqrt{\ln(\beta^{-1})}$ for $\beta\to 0$.

The important point is thus that the maximum S/N for flicker noise is dependent only on the *ratio* τ_s/τ_r and *not* on τ_s and τ_r individually. So there is no gain in S/N here when we make $\tau_r(=8\tau_s)$ longer. Evidently in the flicker noise limited case, the increased smoothing effect of a longer time constant $\tau_r = 2\pi\tau_c$ is just offset by the increase in low-frequency noise from the equally longer sampling time τ_s, due to the 1/f-dependence of the flicker noise power spectrum. One can also show that for a noise power proportional to $f^{-\alpha}$ with $\alpha > 1$, the S/N ratio even decreases when τ_r (and τ_s) are increased.

The optimum S/N for background flicker noise is therefore

$$\left.\frac{S}{N}\right)_f^{dm\ max} = \frac{i_s}{\{2.6K^2\bar{i}_b^2\}^{1/2}} \equiv \frac{i_s}{2\xi_{dm}\bar{i}_b} \tag{II.C.22}$$

where $\xi_{dm} \equiv 0.81K$ is defined as the flicker factor for single d.c. measurements.*

For the digital case of a photon count rate meter in the presence of background flicker noise, equation II.C.19 may be rewritten, using $i = Re$, as

$$\left.\frac{S}{N}\right)_f^{dm\ max} = \frac{R_s}{\{2.6K^2\bar{R}_b^2\}^{1/2}} = \frac{R_s}{2\xi_{dm}\bar{R}_b}. \tag{II.C.23}$$

Case 2: Analog or digital integrator. As in the case of shot noise, the integrator response $x(\tau_s)$ and the associated (normalized) frequency response, together with the expression for the spectral noise power for flicker noise, are to be inserted into equations II.B.7 and II.B.14, which yields

$$\left.\frac{S}{N}\right)_f^{di} = \frac{i_s\tau_i}{\left[2K^2\bar{i}_b^2\displaystyle\int_0^\infty \frac{\{1-\cos(2\pi f\tau_i)\}^2}{2\pi^2 f^3}\,df\right]^{1/2}}. \tag{II.C.24}$$

Writing $z = 2\pi f\tau_i$, we obtain

$$\left.\frac{S}{N}\right)_f^{di} = \frac{i_s\tau_i}{\left[4K^2\bar{i}_b^2\tau_i^2\displaystyle\int_0^\infty \frac{(1-\cos z)^2}{z^3}\,dz\right]^{1/2}}. \tag{II.C.25}$$

The integral [14] is equal to ln 2 ≈ 0.695 and the ratio becomes

$$\begin{aligned}\left.\frac{S}{N}\right)_f^{di} &= \frac{i_s\tau_i}{[4K^2\bar{i}_b^2\tau_i^2 \ln 2]^{1/2}} \\ &= \frac{i_s}{K\bar{i}_b(4\ln 2)^{1/2}} \equiv \frac{i_s}{2\xi_{di}\bar{i}_b}\end{aligned} \tag{II.C.26}$$

where $\xi_{di} = 0.83K$ is the flicker factor for single integrator measurements.

It should be noted that the S/N is again independent of integration time and essentially the same as the maximum S/N for the case of a current meter when flicker noise prevails.

* Note: To avoid confusion we have defined the flicker factor, ξ, in this part for *single* measurements. This conforms with the definition of ξ in previous papers [10–13]. However, it should be stressed that flicker factors are primarily applicable to paired measurements and so, for the above cases, the flicker values for paired measurements are $2\xi_{dm} = 1.61K$ and $2\xi_{di} = 1.67K$. However, the expressions for S/N are the same whether ξ is defined for single- or paired-measurements.

[10] J. D. WINEFORDNER, R. AVNI, T. L. CHESTER, J. J. FITZGERALD, L. P. HART, D. J. JOHNSON and F. W. PLANKEY, *Spectrochim. Acta* **31B**, 1 (1976).

[11] G. D. BOUTILIER, J. D. BRADSHAW, S. J. WEEKS and J. D. WINEFORDNER, *Appl. Spectrosc.* **31**, 307 (1977).

[12] R. P. COONEY, G. D. BOUTILIER and J. D. WINEFORDNER, *Anal. Chem.* **49**, 1048 (1977).

[13] N. OMENETTO, G. D. BOUTILIER, S. J. WEEKS, B. W. SMITH and J. D. WINEFORDNER, *Anal. Chem.* **49**, 1075 (1977).

[14] I. S. GRADSHTEYN and I. M. RYZHIK, *Tables of Integrals, Series and Products* (translated by A. JEFFREY). Academic Press, New York (1965).

For a digital system in the integration mode with background flicker noise, equation II.C.26 becomes

$$\left.\frac{S}{N}\right)_f^{\mathrm{di}} = \frac{R_s \tau_i}{(2.6K^2 \overline{R_b^2} \tau_i^2)^{1/2}} = \frac{R_s}{2\xi_{\mathrm{di}} \overline{R_b}}. \tag{II.C.27}$$

II.C.3. *a.c. measurement in the presence of background noise*

For the case of a.c. measurements, it is assumed that the signal is repetitively turned on and off at some frequency f_{mod} and that only the a.c. component is amplified and demodulated in the analog case. Signal noise is again not considered here. The signal currents are modulated d.c. currents. The measurement system is again assumed to respond linearly. The exact value of S/N will also depend on the modulation wave form and the reference wave form for the case of lock-in amplifiers; the expression for the S/N will therefore include a constant factor, F, of the order of unity depending on the measurement system.

The S/N ratio depends essentially on whether or not the background with noise is also modulated. When the noise originates from the flame background emission which is modulated by a rotating chopper together with the emission signal, essentially the *same* S/N expressions apply as in the case of d.c. measurements. This holds because the same e.l.f. noise components (near 0 Hz) that interfere with the measurement of the d.c. signal are now transferred, together with the signal, to a frequency band around f_{mod}. Thus, in the case of pure shot noise, equation II.C.16 applies also in the a.c. case, apart from a numerical factor F, while τ_r now refers to the response of the readout meter of the a.c. system. With flicker noise, we essentially obtain the same S/N expression as in the d.c. case, if we again choose an optimal ratio of sampling time to response time. The modulation frequency is irrelevant in these cases. Modulation is thus not advantageous as far as the S/N is concerned; often it may even cause a slight deterioration, as the chopper throws away part of the emission signal that is available in the flame.

A different situation exists if only the signal to be measured is modulated but not the fluctuating background. This occurs for example when the noise originates from the dark current of the photodetector or when the supply of metal-salt solution to the flame is modulated but not the flame background. Such a situation may also be found with double-beam set-ups in which the modulated emission signal is effectively differentiated from an underlying unmodulated background spectrum.

We shall derive an expression for the S/N ratio, analogous to equation II.B.17, that holds when the signal but not the background is modulated at frequency f_{mod}. We assume that after a.c. amplification of the modulated signal and the background noise, synchronous demodulation takes place. The demodulated signal is supplied to a d.c. current or rate meter or to an integrator or counter. We again suppose that paired readings are taken, as before.

After demodulation the signal is essentially a d.c. current whose value depends on the a.c. amplification factor and the modulating and demodulating wave forms (including the duty factor). The signal reading can be represented by $Fi_s x(\tau_s)G(f_{\mathrm{mod}})$, where F is a factor, usually of order unity, that takes into account the effects of the (de-)modulating wave form, i_s is the signal current at the photocathode, $x(\tau_s)G(f_{\mathrm{mod}})$ is the response of the amplifier + read-out system (including the internal amplification factor of the photomultiplier) to a unit a.c. input current at f_{mod}, as a function of sampling or integration time τ_s. It is assumed that the a.c. signal current has the optimal phase with respect to that of the a.c. reference signal driving the synchronous demodulator.

After demodulation, the a.c. components of the unmodulated background current, i_b, at the photocathode, having frequencies around f_{mod}, produce a low-frequency noise current near 0 Hz. Since the frequency bandwidth of the measuring system is determined by the time constant or integration time of the read-out system, which is usually of the order of 1 s or larger, this bandwidth is small compared to f_{mod} (which may be typically 50 Hz or higher). Consequently, only the a.c. components of the background current in a relatively narrow frequency band around f_{mod} contribute to the noise in the read-out system. Since the spectral noise power, $S_{i_b}(f)$, of the background fluctuations will not vary markedly within this narrow band, we can regard the spectral noise power of the *demodulated* background current noise as being constant within the relevant frequency band and having a spectral noise power proportional to $S_{i_b}(f_{mod})$. (The proportionality constant will drop out when we consider the *S/N ratio.*)

Consequently, the situation as regards signal and noise, considered at the read-out system, is essentially the same as that in the measurement of a d.c. signal in the presence of white noise. We can thus apply here essentially the same expression for the S/N ratio as given in equation II.B.17, while replacing therein $S_{i_b}(f)$ by the factor $S_{i_b}(f_{mod})$ and adding a numerical factor F:

$$\frac{S}{N} = \frac{Fi_s x(\tau_s)}{\left[2S_{i_b}(f_{mod}) \int_0^\infty |g(f)|^2 \{1 - \cos(2\pi f \tau_s)\}\, df\right]^{1/2}}. \tag{II.C.28}$$

Here $g(f)$ describes the normalized frequency response of the read-out system, that is, of that part of the measuring system that follows the demodulation stage. Note that $g(f)$ drops to zero when f falls outside the frequency bandwidth.

When a current or rate meter with a time constant τ_c is used, we find in the case of background *shot noise* by putting $S_{i_b}(f_{mod}) = 2e\bar{i}_b$ and taking $\tau_s = \tau_r(=2\pi\tau_c)$ (compare with equation II.C.17)

$$\left.\frac{S}{N}\right)_{sh}^{am} = \frac{Fi_s}{(2\pi e\bar{i}_b)^{1/2}}\tau_r^{1/2}. \tag{II.C.29}$$

In this case, a.c. modulation offers no gain in S/N when compared to a d.c. measurement for equal response time of the meter. In digital measurements, we have (compare equation II.C.8):

$$\left.\frac{S}{N}\right)_{sh}^{am} = \frac{FR_s}{(2\pi\bar{R}_b)^{1/2}}\tau_r^{1/2} \tag{II.C.30}$$

which is identical to the S/N ratio for the analog measurement.

In the case of background *flicker noise*, we obtain, by putting $S_{i_b}(f_{mod}) = K^2\bar{i}_b^2/f_{mod}$ and taking again $\tau_s = \tau_r$,

$$\left.\frac{S}{N}\right)_{f}^{am} = \frac{Fi_s(\tau_r f_{mod})^{1/2}}{\pi^{1/2}K\bar{i}_b} \equiv \frac{Fi_s}{\sqrt{2}\,\xi_{am}\bar{i}_b}\tau_r^{1/2}. \tag{II.C.31}$$

with*

$$\xi_{am} \equiv K(\pi/2f_{mod})^{1/2}.$$

Comparing the latter expression with equation II.C.22, we see that application of a.c. modulation yields an improvement in S/N by a factor of the order of $(\tau_r f_{mod})^{1/2}$ if the background is not modulated. Introducing the noise bandwidth Δf of the whole a.c. measurement system, which is determined by the response time $\tau_r = 2\pi\tau_c$ of the d.c. read-out system according to

$$\Delta f = \pi/2\tau_r \tag{II.C.32}$$

we find a gain factor to be of the order of $(f_{mod}/\Delta f)^{1/2}$, which can be made quite large in practice by choosing a large f_{mod} and a small Δf. Note that the noise bandwidth of the whole a.c. measuring system is determined by the time response of the d.c. read-out meter.

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* Note that for paired measurements, $\sqrt{2}\xi_{am} = K(\pi/f_{mod})^{1/2}$ and $\sqrt{2}\xi_{ai} = K/f_{mod}^{1/2}$ occur.

Table 1. Signal-to-noise ratio expressions for individual shot and flicker noises and several measurement systems

Measurement system	Shot noise		Flicker noise	
	d.c.	a.c.	d.c.	a.c.
Current meter ($\tau_s = \tau_r$)	$\frac{i_s\sqrt{\tau_r}}{(2\pi e\bar{i}_b)^{1/2}}$	$\frac{Fi_s\sqrt{\tau_r}}{(2\pi e\bar{i}_b)^{1/2}}$	$\frac{i_s}{2\xi_{dm}\bar{i}_b}$	$\frac{Fi_s\sqrt{\tau_r}}{\sqrt{2}\,\xi_{am}\bar{i}_b}$
Rate meter ($\tau_s = \tau_r$)	$\frac{R_s\sqrt{\tau_r}}{(2\pi\bar{R}_b)^{1/2}}$	$\frac{FR_s\sqrt{\tau_r}}{(2\pi\bar{R}_b)^{1/2}}$	$\frac{R_s}{2\xi_{dm}\bar{R}_b}$	$\frac{FR_s\sqrt{\tau_r}}{\sqrt{2}\,\xi_{am}\bar{R}_b}$
Current integrator	$\frac{i_s\sqrt{\tau_i}}{(2e\bar{i}_b)^{1/2}}$	$\frac{Fi_s\sqrt{\tau_i}}{(2e\bar{i}_b)^{1/2}}$	$\frac{i_s}{2\xi_{di}\bar{i}_b}$	$\frac{Fi_s\sqrt{\tau_i}}{\sqrt{2}\,\xi_{ai}\bar{i}_b}$
Digital integrator	$\frac{R_s\sqrt{\tau_i}}{(2\bar{R}_b)^{1/2}}$	$\frac{R_s\sqrt{\tau_i}}{(2\bar{R}_b)^{1/2}}$	$\frac{R_s}{2\xi_{di}\bar{R}_b}$	$\frac{FR_s\sqrt{\tau_i}}{\sqrt{2}\,\xi_{ai}\bar{R}_b}$

When the read-out system is an integrator, the same extra gain factor in S/N is obtained as compared to the use of a current meter, as occurs in the d.c. case (see Section II.C.1, case 2). The flicker factor is $\xi_{ai} = K/(2f_{\mathrm{mod}})^{1/2}$ (see note on p. 395).

The gain in S/N ratio, when a.c. detection with unmodulated background signal is used, can also be understood by considering the a.c. measurement as a repetition of N d.c. measurements with $(\tau_s)_{dc} = 1/2f_{\mathrm{mod}}$ and $(\tau_s)_{ac} = N(\tau_s)_{dc}$. The expected gain is a factor $N^{1/2}$, if the statistical errors in the d.c. measurements are uncorrelated. This is the case indeed since every d.c. measurement consists of two paired readings, which eliminate the correlation caused by the e.l.f. components in the noise. The factor $N^{1/2}$ is easily seen to equal the gain factor $(f_{\mathrm{mod}}/\Delta f)^{1/2}$ obtained above.

II.D. Optimization of Electrical Measurement Parameters

Table 1 lists the S/N ratios for background shot and flicker noises for a.c. and d.c. systems using integration or meter read-out. Table 2 lists the a.c. and d.c. flicker factors for comparison.

II.D.1. *Shot noise*

For d.c. measurement systems, the S/N will improve as the square root of the response time, τ_r, and the integration time, τ_i, for current (count rate) meters and integrators, respectively. For current meter systems, taking a sampling time equal to response time gives S/N of 99.9% of the maximum attainable at fixed response time. For a fixed measurement time, there is no difference in making multiple sets of paired measurements at small response time or one set of paired measurements with response time of one-half the total measurement time. For the same response time, an a.c. system gives an S/N a factor of $\sqrt{2}$ poorer than the d.c. system because of rejection of half the signal in case of square-wave modulation. Therefore, modulation of the signal, regardless of the modulation frequency will not improve S/N in the case of shot noise.

Table 2. Expressions for flicker factors,* ξ, for several measurement approaches

Measurement device	d.c.	a.c.
Current or rate meter	$\xi_{dm} \equiv (0.65\,K^2)^{1/2} = 0.81K$	$\xi_{am} \equiv K(\pi/2f_{\mathrm{mod}})^{1/2}$
Integrator	$\xi_{di} \equiv (\ln 2K^2)^{1/2} = 0.83K$	$\xi_{ai} \equiv K/(2f_{\mathrm{mod}})^{1/2}$
Synchronous counter	—	$\xi_{si} \equiv K(\ln 2/f_{\mathrm{mod}})^{1/2}$

* Note that the ξ factors are defined for single measurements (see footnotes on pp. 393 and 395 concerning paired measurements).

II.D.2. *Flicker noise*

For d.c. measurement systems, the best S/N, obtainable by choosing sampling time $\tau_s \approx \tau_r/8$ in the case of meter readings, is independent of response time τ_r or integration time in the case of integration measurements. It is best, then, for fixed measurement time, τ_m, to make the integration or response time as small as possible (until shot noise becomes dominant over flicker noise) and repeat the measurement N times alternately turning the signal "on" and "off" but not the background. This increases S/N by a factor of $N^{1/2}$. This conclusion has been indicated by SNELLEMAN [15] and has also been reached by LÉGER *et al.* [16]. It is therefore seen to be most advantageous to "modulate" a d.c. system i.e. to use an a.c. system in the case of background flicker noise. It is again important to note that *the gain of a modulated system is only realized if the signal and not the background is modulated.* If both are modulated, then the d.c. expressions for background flicker noise apply (with appropriate duty factors) because the 1/f spectrum has been moved to the modulation frequency.

In an a.c. system, it is advantageous to make $\Delta f/f_{\mathrm{mod}}$ small. For a narrow band tuned amplifier, it may be difficult to keep the amplifier tuned to f_{mod} if the device providing the modulation (e.g., a mechanical chopper) drifts in frequency. To a limit, one could use a wider band a.c. amplifier at a higher frequency. The most attractive solution, however, is the use of a phase sensitive (lock-in) amplifier or synchronous photon counter which can achieve very narrow bandwidths without suffering from drift in the modulation device.

Two remarks about the suppression of e.l.f. noise should still be made. Equation II.C.31 indicates an unlimited increase in S/N when f_{mod} is increased. However, it should be remembered that shot noise always remains present. Therefore, the gain in S/N by modulation is limited to that modulation frequency at which $(S/N)_{\mathrm{shot}} \approx (S/N)_{\mathrm{flicker}}$. At modulation frequencies above this limit, flicker noise still decreases, but the shot noise is unaffected by modulation and thus sets a final limit to the S/N gain by modulation. An example can be found in fluorescence measurements, where by modulation of the background lamp and a.c. detection at f_{mod}, the e.l.f. noise of the flame radiation is not detected. The optimum S/N is reached when shot noise of the flame radiation is found to become dominant in the measurement. A further increase of f_{mod} does not yield a further gain.

In the second place, the equations also indicate (for d.c. shot noise and a.c. shot noise or flicker noise) an unlimited gain in S/N when the sampling time (and the response time) is (are) increased. However, in practice, after a certain time, a new source of e.l.f. noise or drift, hitherto unnoticed because it was small, will become dominant. When this e.l.f. noise can be located, an extra modulation can again suppress it, but the story will repeat itself. An example is the use of a double-beam instrument in which one photomultiplier detects the background i_b and another background + signal, $i_b + i_s$. In first instance, e.l.f. noise in i_b is suppressed. In second instance the mutually different variation of the amplification factor of the two photomultipliers with time (e.g. fatigue effects of the order of 0.1%) may form a new source of *modulated* e.l.f. noise.

II.D.3. *High-frequency whistle noise*

High-frequency proportional noise may be avoided through careful choice of the modulation frequency. If one has knowledge of the noise power spectrum of the background, this is a simple matter. In many cases, however, one may not have such knowledge nor the facilities for its determination. The alternative is to try several modulation frequencies and pick the one giving the best S/N.

Acknowledgement—One of the authors (GDB) wishes to acknowledge the support of a fellowship sponsored by the Proctor & Gamble Company.

[15] W. SNELLEMAN, Ph.D. thesis, University of Utrecht (1965).
[16] A. LÉGER, B. DELMAS, J. KLEIN and S. DECHEVEIGNE, *Rev. Phys. Appl.* **11**, 309 (1976).

APPENDIX 1. DERIVATION OF FREQUENCY RESPONSE OF INTEGRATOR OUTPUT

The (complex) transfer function, i.e. the ratio of the a.c. response $B(t)$ of the integrator circuit to an a.c. input signal $A(t) = A_m \exp(j\omega t)$ after an integration time τ_i is found as follows

$$\begin{aligned} B(t) &= \int_{t-\tau_i}^{t} A_m \exp(j\omega t')\,\mathrm{d}t' \\ &= A_m \exp(j\omega t)[1 - \exp(-j\omega\tau_i)]/j\omega \\ &= A(t)[1 - \exp(-j\omega\tau_i)]/j\omega. \end{aligned}$$

The transfer function is therefore

$$T(f) \equiv B(t)/A(t) = [1 - \exp(-j\omega\tau_i)]/j\omega.$$

The ratio of the spectral noise power at the output and the input of the integrator is, with $\omega = 2\pi f$ and $e^{j\alpha} = \cos\alpha + j\sin\alpha$

$$|T(f)|^2 = \frac{1 - \cos 2\pi f\tau_i}{2\pi^2 f^2}.$$

APPENDIX 2

Comments on *Spectrochimica Acta* **31B**, 1 (1976).

In the previous article, *A comparison of signal-to-noise ratios for single channel methods (sequential and multiplex) vs multichannel methods in optical spectroscopy* by J. D. WINEFORDNER, R. AVNI, T. L. CHESTER, J. J. FITZGERALD, L. P. HART, D. J. JOHNSON, and F. W. PLANKEY, *Spectrochim. Acta* **31B**, 1 (1976) several errors and inconsistencies were present and kindly pointed out by C. TH. J. ALKEMADE, as follows:

1. It was not clearly stated that the systems were compared on the basis of an integration system, i.e. a photon counter with a digital counter.
2. In the sentence after (1a) $\overline{\Delta i_f(f)}$ should be $(\overline{\Delta i_f(f)^2})^{1/2}$.
3. Equation 2 should not be given in terms of counts but rather in terms of a rate. Equation 2, should be

$$\overline{R_p(f)^2} = \frac{K^2 R_p}{f}. \tag{2}$$

4. Below equation 2, R_p is the photo-count rate and not the photon flux.
5. Equation 3 for the fluctuation (flicker) noise in terms of counts should be as per the derivation in this manuscript (Section II, Case 2) to give for paired measurements

$$N_f^2 = \frac{K^2 R_p^2}{\pi^2} \int_0^{\infty} \frac{(1 - \cos 2\pi f t_c)^2}{f^3}\,\mathrm{d}f = 4(\ln 2) K^2 R_p^2 t_c^2.$$

6. Setting $\xi^2 = 4(\ln 2) K^2$ then gives Equation 4

$$N_f = \xi R_p t_c.$$

7. Paired measurements were not considered, which was an oversight. Since ξ was arbitrarily chosen in value, we could choose a slightly smaller ξ, consider paired measurements, and recalculate the values in Table 4 and obtain approximately the same values. Such calculations are available upon request from one of the authors (JDW). In any case, this does *not* in any way alter the conclusions drawn on the comparison of the four types of spectral measurement systems.
8. In Appendix A, Equation A1 should be

$$i_p = ReG\eta\xi = R_p eG \quad \text{or} \quad i_p = CR_p$$

where R is the photon flux and R_p is the photo-count rate. Equation 3 should be

$$\overline{\Delta i_p} = (2eG\Delta f i_p)^{1/2} = (2e^2G^2R_p/2t_c)^{1/2} = C(R_p/t_c)^{1/2} = C(N_p^2/t_c^2)^{1/2} = \frac{CN_p}{t_c}.$$

Equation A4 should be

$$\overline{\Delta i_f} = K i_p (4\ln 2)^{1/2} = \frac{CN_f}{t_c}. \tag{A4}$$

NOTATION

i_s	signal primary photocurrent
i_b	background primary photocurrent
$\bar{i}_b$	average background photocurrent
x_s	signal meter deflection
x_b	background meter deflection
$\bar{x}_b$	average background deflection
t	time
t_o	sample producing signal introduced
τ_s, τ_i	sampling time, integration time
τ_c	time constant of meter damped by RC-filter
τ_r	response time of meter deflection
$\mathrm{d}x_b(t_o)$	fluctuation in background deflection from $\bar{x}_b$ at t_o
$\mathrm{d}x_b(t_o + \tau_s)$	fluctuation in background deflection from $\bar{x}_b$ at $t_o + \tau_s$