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A review and tutorial discussion of noise and signal-to-noise ratios in analytical spectrometry—III. Multiplicative noises*

C. TH. J. ALKEMADE and W. SNELLEMAN

Fysisch Laboratorium, Rijksuniversiteit Utrecht, Princetonplein 5, 3508 TA Utrecht, The Netherlands

and

G. D. BOUTILIER† and J. D. WINEFORDNER

Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.

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Abstract—In this review, signal-to-noise ratios are discussed in a tutorial fashion for the case of multiplicative noise. Multiplicative noise is introduced simultaneously with the analyte signal and is therefore much more difficult to reduce than additive noise. The sources of noise, the mathematical representation of noise, and the major types of noises in emission and luminescence spectrometry are discussed. If the limiting source of noise is multiplicative white noise, the signal-to-noise ratio for optimal sampling time τ_s increases as the square root of the response or integration time of the readout and is independent of the rate at which sample and reference are measured. The variation of multiplicative flicker noise with variation in sampling time, τ_s, time interval between sample and reference measurements, T, and response (τ_r) or integration (τ_i) time is discussed in some detail. The optimal system for the case of multiplicative noise is a dual channel approach in which the sample and reference are measured simultaneously and a ratio of signals is taken. Although the best reference in most cases of interest to analytical chemists is a calibration standard, it is often impossible to measure a sample and a calibration standard simultaneously and so an internal standard, a detector monitoring the source intensity, etc., may be useful.

NOMENCLATURE

t	time
$i_s(t)$	"input" signal of the analytical sample
$i_r(t)$	"input" signal of reference parameter
τ_s	sampling time
T	time interval between sample and reference measurements
C_s	analyte sample concentration
C_r	reference parameter value
$G(t)$	"multiplication factor" containing a stationary Gaussian noise process $dG(t) = G(t) - \bar{G}$
$\bar{G}$	average multiplication factor
$dG(t)$	$\equiv G(t) - \bar{G}$
$A(t)$	"multiplied" signal $[A(t) = G(t)i(t)]$
τ_c	RC time constant
$x(t)$	meter deflection
$\sigma^2_{C_s}$	variance of the analyte sample concentration
$\psi_G(t')$	autocorrelation function of noise $dG(t)$
$S_G(f)$	spectral noise power of noise $dG(t)$
τ_G	correlation time of noise $dG(t)$
τ_r	response time ($\tau_r = 2\pi\tau_c$)
τ_m	total measurement time
β	$2\pi\tau_s/\tau_r$
α	T/τ_s.

1. INTRODUCTION

IN PARTS I [1] and II [2], a tutorial discussion of signal-to-noise ratios and general signal-to-noise (S/N) ratio expressions were given for emission and luminescence

* Dedicated to the memory of Professor HEINRICH KAISER.

† Present address: Department of Chemistry, University of Georgia, Athens, GA 30602, U.S.A.

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[1] C. TH. J. ALKEMADE, W. SNELLEMAN, G. D. BOUTILIER, B. D. POLLARD, J. D. WINEFORDNER, T. L. CHESTER, and N. OMENETTO, *Spectrochim. Acta* **33B**, 383 (1978).

[2] G. D. BOUTILIER, B. D. POLLARD, J. D. WINEFORDNER, T. L. CHESTER, and N. OMENETTO, *Spectrochim. Acta* **33B**, 401 (1978).

spectrometric systems considering only additive noises, i.e. noises which are independent of the presence of a signal. The signal was considered to be constant, and all fluctuations when taking a meter or integrator reading of signal plus background were caused by fluctuations of the background. In Part II, a term due to analyte flicker noise was given in an approximate fashion so that eventually the S/N ratio would reach a constant value with increasing signal level, as is the case in real spectrometric systems. Other discussions of S/N ratios have used this same approach [3–5]. In this paper, we will treat multiplicative noise on a more general, mathematical basis, again using paired measurements.

In the discussion of additive noise, it was assumed that fluctuations in the meter deflection due to a fluctuating quantity in the spectrometric system constituted a stationary fluctuation process. The background current, i_b, was assumed to have been applied to the meter for a long time before a reading was taken. In the case of multiplicative noise, noise is introduced simultaneously with a signal due to the analyte. The noise is dependent upon the signal level, which may vary with time, and, in the reading, also upon the frequency characteristic of the measuring device (meter of integrator). We consider paired measurements, that is the measurement of a reference signal followed by the measurement of an analyte signal. Since these signals are read after a finite sampling time τ_s, which may be shorter than the response time τ_r, a stationary fluctuation process. The background current, i_b, was assumed to have been nor for the fluctuations inherent in the signal. It is therefore necessary to deal with the temporal response of the meter to a *non*-stationary fluctuation process.

2. ASSUMPTIONS

The assumptions used in this model of multiplicative noise (see Fig. 1) are

(i) the input signal, $i_s(t)$, of the analytical sample and the reference signal, $i_r(t)$, (i.e. the signals at the "input" of the whole analytical measuring system) are noise-free;

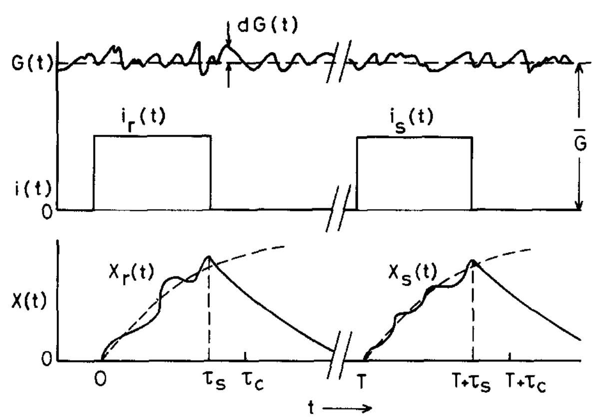

Fig. 1. Representation of analyte signal and reference signal measured with a d.c. meter. $x_r(t)$ = meter deflection due to reference as a function of time t; $x_s(t)$ = meter deflection due to analyte sample; $i_r(t)$ = reference "input" signal; $i_s(t)$ = analyte "input" signal; τ_s = sampling time; τ_c = time constant of meter damped by RC-filter; T = time interval between analyte and reference measurements; $G(t)$ = multiplication factor; $\bar{G}$ = average multiplication factor; $dG(t)$ = deviation of $G(t)$ from $\bar{G}$.

[3] 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).
[4] G. D. BOUTILIER, J. D. BRADSHAW, S. J. WEEKS, and J. D. WINEFORDNER, *Appl. Spectrosc.* **31**, 307 (1977).
[5] R. P. COONEY, G. D. BOUTILIER, and J. D. WINEFORDNER, *Anal. Chem.* **49**, 1048 (1977).

(ii) the time-dependence of the input signals is a step function:

$$i_r(t) = i_r \quad \text{for} \quad 0 < t < \tau_s,$$
$$i_s(t) = i_s \quad \text{for} \quad T < t < T + \tau_s$$

and $i_s(t) = i_r(t) = 0$ for t outside the given intervals; we assume $T \geq \tau_s$ and call τ_s the sampling time;

(iii) at $t = 0$ and $t = T$, the meter deflection caused by the preceding signal has decayed or been reset to zero;

(iv) no additive noises are present;

(v) i_s is proportional to the analyte sample concentration (C_s) and i_r is proportional to a reference parameter (C_r) which may be a calibration standard, an excitation source intensity in luminescence spectrometry, etc;

(vi) a "multiplication factor," $G(t)$, contains a stationary, Gaussian noise process which produces multiplicative noise, and is given by $G(t) = \bar{G} + dG(t)$; $\bar{G}$ contains any constant parameter that may occur in the conversion of "input signal" to "meter deflection" (apart from the time constant; see below); $G(t)$ is, in general, not dimensionless;

(vii) after "multiplication," the input signal $i(t)$ is transformed into the "multiplied" signal $A(t) \equiv G(t)i(t)$; $dA(t) = i(t)dG(t)$ is the noise in the multiplied signal;

(viii) the meter deflection $x(t)$ and the multiplied signal $A(t)$ are related by

$$A(t) = \frac{\mathrm{d}x}{\mathrm{d}t} + \frac{x}{\tau_c}, \tag{1}$$

where τ_c is the time constant of the (linear) meter with exponential time-response;

(ix) the estimate of the analyte concentration, C_s, is given by

$$C_s = \frac{x_s(T + \tau_s)}{x_r(\tau_s)} C_r. \tag{2}$$

Several points should be carefully noted. The noise in the multiplicative factor, $G(t)$, is itself a stationary noise process, but the noise in $x(t)$ is not a stationary noise process. Examples of a fluctuating multiplication factor in atomic emission spectrometry may be the thermal excitation factor in the presence of temperature fluctuations, the rate of sample supply, the internal amplification factor of the photomultiplier tube, and the electronic amplification factor. The reference signal, i_r, and the reference parameter, C_r, have been defined in a completely general way. The most common case in analytical spectrometry is that the reference is a standard of known analyte concentration. It is possible that other references may be used, such as an internal standard.

3. General Expression for the Relative Variance

From equation (2), the differential of C_s may be written as

$$\frac{dC_s}{C_s} = \frac{dx_s(T + \tau_s)}{\overline{x_s(T + \tau_s)}} - \frac{dx_r(\tau_s)}{\overline{x_r(\tau_s)}}, \tag{3}$$

where the bar denotes an ensemble average, and the variance of C_s, $\sigma^2_{C_s}$, is given by

$$\sigma^2_{C_s} = \overline{\left[\frac{dx_s(T + \tau_s)}{\overline{x_s(T + \tau_s)}} - \frac{dx_r(\tau_s)}{\overline{x_r(\tau_s)}}\right]^2} C_s^2. \tag{4}$$

The relative variance of C_s may be written as

$$\frac{\sigma^2_{C_s}}{C_s^2} = 2\left[\frac{\overline{dx_r(\tau_s)^2}}{\overline{x_r(\tau_s)}^2} - \frac{\overline{dx_r(\tau_s)dx_s(T + \tau_s)}}{\overline{x_r(\tau_s)} \cdot \overline{x_s(T + \tau_s)}}\right], \tag{5}$$

where use has been made of the fact that $\overline{(dx_s/\bar{x}_s)^2} = \overline{(dx_r/\bar{x}_r)^2}$. The S/N ratio is given by C_s/σ_{C_s}. We wish to find how the S/N ratio depends on τ_s, τ_c, and T (see Fig. 1 for definition of all terms) for given statistical properties of $dG(t)$ and what the optimum measurement conditions are.

From the definition of $A(t)$ and $G(t)$ and integration of equation (1), the expression for $\overline{x(\tau_s)}$ is

$$\overline{x(\tau_s)} = i\tau_c\bar{G}[1-\exp(-\tau_s/\tau_c)], \tag{6}$$

where $\overline{x(\tau_s)}$ is either $\overline{x_r(\tau_s)}$ or $\overline{x_s(T+\tau_s)}$ and i is either i_r or i_s, respectively. When $A(t)$ is an arbitrary function of t for $t>0$ and zero for $t<0$, the general solution of equation (1) is

$$x(\tau_s) = x(0)\exp(-\tau_s/\tau_c) + \exp(-\tau_s/\tau_c)\int_0^{\tau_s} \exp(u/\tau_c)A(u)\,du, \tag{7}$$

where u is a dummy integration variable [6]. Treating the meter deflection from the reference signal, $x_r(\tau_s)$, and using the definitions of $A(t)$ and $G(t)$ with $x(0)=0$, it follows from equation (7) that

$$x_r(\tau_s) = i_r\tau_c\bar{G}[1-\exp(-\tau_s/\tau_c)] + i_r\exp(-\tau_s/\tau_c)\int_0^{\tau_s}\exp(u/\tau_c)dG(u)\,du \tag{8}$$

or [see equation (6)]

$$x_r(\tau_s) = \overline{x_r(\tau_s)} + dx_r(\tau_s) \tag{9}$$

and $dx_r(\tau_s)$ is given by

$$dx_r(\tau_s) = i_r\exp(-\tau_s/\tau_c)\int_0^{\tau_s}\exp(u/\tau_c)dG(u)\,du. \tag{10}$$

In an analogous way we find that the expression for the meter deflection due to the analyte signal is

$$x_s(T+\tau_s) = \overline{x_s(T+\tau_s)} + dx_s(T+\tau_s), \tag{11}$$

where

$$\overline{x_s(T+\tau_s)} = i_s\tau_c\bar{G}[1-\exp(-\tau_s/\tau_c)] \tag{12a}$$

and

$$dx_s(T+\tau_s) = i_s\exp(-\tau_s/\tau_c)\int_T^{T+\tau_s}\exp[(v-T)/\tau_c]dG(v)\,dv, \tag{12b}$$

where v is also a dummy variable for integration.

To find the expression for $\overline{dx_r(\tau_s)dx_s(T+\tau_s)}$, equations (10) and (12b) are multiplied and ensemble averaged (cf. [6], equation (60a)). It is found that

$$\overline{dx_r(\tau_s)dx_s(T+\tau_s)} = i_ri_s\exp(-2\tau_s/\tau_c)\overline{\int_0^{\tau_s}du\int_T^{T+\tau_s}\exp[(u+v-T)/\tau_c]dG(u)dG(v)\,dv}. \tag{13}$$

The ensemble average over a double integral may be replaced by a double integral over an ensemble average. Equation (13) can be rewritten as

$$\overline{dx_r(\tau_s)dx_s(T+\tau_s)} = i_ri_s\exp(-2\tau_s/\tau_c)\int_0^{\tau_s}du\times\int_T^{T+\tau_s}dv\exp[(u+v-T)/\tau_c]\overline{dG(u)dG(v)}. \tag{14}$$

Because $dG(t)$ has been defined as a stationary noise process, it is possible to define the time-independent auto-correlation function of $dG(t)$ by

$$\psi_G(t') = \overline{dG(t)dG(t+t')}. \tag{15}$$

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

The factor $\overline{dG(u)dG(v)}$ is therefore equal to $\psi_G(v-u)$. Rearranging equation (14) and replacing the integration variable v by $v=y+u$ for given u results in

$$\overline{dx_r(\tau_s)dx_s(T+\tau_s)} = i_r i_s \exp(-2\tau_s/\tau_c)\int_0^{\tau_s} du \exp[(2u-T)/\tau_c] \times \int_{T-u}^{T-u+\tau_s} \exp(y/\tau_c)\psi_G(y)\,dy, \quad (16)$$

with $0 \leq u \leq \tau_s < T$. This is the general expression for

$$\overline{dx_r(\tau_s)dx_s(T+\tau_s)}.$$

In an entirely analogous fashion to that in which the expression for $\overline{dx_r(\tau_s)dx_s(T+\tau_s)}$ was obtained, the expression for $\overline{dx_r(\tau_s)^2}$ is found to be

$$\overline{dx_r(\tau_s)^2} = i_r^2 \exp(-2\tau_s/\tau_c)\int_0^{\tau_s} du \exp(2u/\tau_c)\int_{-u}^{-u+\tau_s} \exp(y/\tau_c)\psi_G(y)\,dy \quad (17)$$

and similarly for $\overline{dx_s(T+\tau_s)^2}$.

Substituting equations (6), (16) and (17) into equation (5) and putting $\overline{x_r(\tau_s)} = \overline{x_s(T+\tau_s)}$ and $i_r = i_s$ (for convenience only) the expression for the relative variance C_s is

$$\frac{\sigma_{C_s}^2}{C_s^2} = \frac{2\exp(-2\tau_s/\tau_c)}{\tau_c^2\bar{G}^2[1-\exp(-\tau_s/\tau_c)]^2} \times \left\{\int_0^{\tau_s} du \exp(2u/\tau_c)\int_{-u}^{-u+\tau_s} \exp(y'/\tau_c)\psi_G(y')\,dy' - \int_0^{\tau_s} du \exp[(2u-T)/\tau_c]\int_{T-u}^{T-u+\tau_s} dy \exp(y/\tau_c)\psi_G(y)\right\}. \quad (18)$$

The substitution $y = y' + T$ and combination of the integrals over y' yields

$$\frac{\sigma_{C_s}^2}{C_s^2} = \frac{2\exp(-2\tau_s/\tau_c)\int_0^{\tau_s} du \exp(2u/\tau_c)\int_{-u}^{-u+\tau_s} dy' \exp(y'/\tau_c)[\psi_G(y') - \Psi_G(y'+T)]}{\tau_c^2\bar{G}^2[1-\exp(-\tau_s/\tau_c)]^2}. \quad (19)$$

From the Wiener–Khinchine theorem,

$$\Psi_G(\tau_s) = \int_0^{\infty} S_G(f)\cos(2\pi f\tau_s)\,df, \quad (20)$$

where $S_G(f)$ is the spectral noise power, we deduce

$$\psi_G(y') - \psi_G(y'+T) = 2\int_0^{\infty} S_G(f)\sin \pi f(2y'+T)\sin(\pi fT)\,df. \quad (21)$$

Substituting equation (21) into (19) gives the final, general expression for the relative variance of C_s

$$\frac{\sigma_{C_s}^2}{C_s^2} = \frac{4\exp(-2\tau_s/\tau_c)\int_0^{\tau_s} du \exp(2u/\tau_c)\int_{-u}^{-u+\tau_s} dy' \exp(y'/\tau_c)\int_0^{\infty} df S_G(f)\sin\{\pi f(2y'+T)\}\sin(\pi fT)}{\tau_c^2\bar{G}^2[1-\exp(-\tau_s/\tau_c)]^2} \quad (22)$$

with $0 \leq u \leq \tau_s < T$ and $-u \leqslant y' \leq -u+\tau_s$.

For the purpose of evaluation of equation (22), the order of integration may be changed. Equation (22) may be rewritten as

$$\frac{\sigma^2_{C_s}}{C_s^2}=\frac{4\exp(-2\tau_s/\tau_c)\int_0^\infty df S_G(f)\sin\pi f T\int_0^{\tau_s}du\exp(2u/\tau_c)\int_{-u}^{-u+\tau_s}dy'\exp(y'/\tau_c)\sin\pi f(2y'+T)}{\tau_c^2\bar{G}^2[1-\exp(-\tau_s/\tau_c)]^2}. \tag{23}$$

With the use of

$$\int\exp(a\omega)\sin b\omega\, d\omega=\frac{\exp(a\omega)[a\sin b\omega-b\cos b\omega]}{a^2+b^2},$$

the integral over y' may be evaluated and is given by

$$\int_{-u}^{-u+\tau_s}dy'\exp(y'/\tau_c)\sin\{\pi f(2y'+T)\}$$
$$=\frac{\tau_c\exp(-u/\tau_c)}{1+(2\pi f\tau_c)^2}\{\exp(\tau_s/\tau_c)[\sin\{\pi f(-2u+2\tau_s+T)\}-2\pi f\tau_c\cos\{\pi f(-2u+2\tau_s+T)\}]$$
$$-[\sin\{\pi f(-2u+T)\}-2\pi f\tau_c\cos\{\pi f(-2u+T)\}]\}. \tag{24}$$

The integral over u may be evaluated in four parts using the same solution as applied to the integral over y' twice along with

$$\int\exp(a\omega)\cos b\omega\, d\omega=\frac{\exp(a\omega)[a\cos b\omega+b\sin b\omega]}{a^2+b^2}.$$

Applying these solutions, the expression for the relative variance of C_s becomes

$$\frac{\sigma^2_{C_s}}{C_s^2}=\frac{4}{\bar{G}^2[1-\exp(-\tau_s/\tau_c)]^2}\int_0^\infty\frac{df S_G(f)\sin^2(\pi f t)}{1+(2\pi f t_c)^2}$$
$$\times[\exp(-2\tau_s/\tau_c)+1-2\exp(-\tau_s/\tau_c)\cos(2\pi f\tau_s)]. \tag{25}$$

Up to this point, the derivation for the relative variance of C_s is general for arbitrary $S_G(f)$, τ_s, τ_c and T, subject to the constraints of the assumptions. The divergency of flicker noise as $f\to 0$ is neutralized by the squared sine function of frequency, f, in equation (25). Because equation (25) cannot be evaluated for arbitrary $S_G(f)$, τ_s, τ_c and T, specific assumptions will be made for certain cases.

4. Signal-to-Noise Ratio Expressions for Various Cases

4.1 *Direct current measurement with a current meter for white noise*

A case of interest is the case of a white noise spectrum. It is possible to define a correlation time, τ_G, of noise $dG(t)$ by

$$\tau_G\equiv\frac{\int_0^\infty\psi_G(y)\,dy}{\psi_G(0)}=\frac{1}{2}\frac{\int_{-\infty}^{+\infty}\psi_G(y)\,dy}{\psi_G(0)}, \tag{26}$$

where $\psi_G(0)=\overline{dG(t)^2}$. The value of $\psi_G(y)$ differs noticeably from zero only for $|y|\lesssim\tau_G$, and $\tau_G\ll\tau_s$, τ_c and T. For this case, $S_G(f)$ is a constant over the relevant frequency range and falls off at very high frequencies $2\pi f\gtrsim\tau_G^{-1}$. Starting from equation (19), $\psi_G(y'+T)\simeq 0$ because $(y'+T)\gg\tau_G$. Because $\psi_G(y')$ exists only for $y'\approx 0$, the integral over y' can be approximated by $\int_{-\infty}^{+\infty}\psi_G(y')\,dy'$. It is a valid approximation as for $0\le u<\tau_s$ the integration limits of y', viz. $-u$ and $-u+\tau_s$, are negative and positive, respectively. From equation (26), the definition of $\psi_G(y')$, and the approximation of the integral over y′, equation (19) becomes

$$\frac{\sigma_{C_s}^2}{C_s^2}=\frac{4\exp(-2\tau_s/\tau_c)\int_0^{\tau_s}\exp(2u/\tau_c)\,du\overline{dG^2}\tau_G}{\tau_c^2\bar{G}^2[1-\exp(-\tau_s/\tau_c)]^2}. \tag{27}$$

Making the substitution $z=2u/\tau_c$ and evaluating equation (27) gives

$$\frac{\sigma_{C_s}^2}{C_s^2}=\frac{2\overline{dG^2}\tau_G[1-\exp(-2\tau_s/\tau_c)]}{\bar{G}^2\tau_c[1-\exp(-\tau_s/\tau_c)]^2}. \tag{28}$$

From the definition, $\overline{dG^2}=\psi_G(0)$, the inverse Wiener–Khinchine theorem, and equation (26) we have

$$\overline{dG^2}=S_G(0)/4\tau_G. \tag{29}$$

Substituting equation (29) into (28) yields

$$\frac{\sigma_{C_s}^2}{C_s^2}=\frac{S_G(0)[1-\exp(-2\tau_s/\tau_c)]}{2\bar{G}^2\tau_c[1-\exp(-\tau_s/\tau_c)]^2}. \tag{30}$$

This result can also be obtained by solving equation (25), for $S(f)=$ constant, directly with the use of the integrals

$$\int_0^\infty\frac{\cos(ax)\,dx}{\beta^2+x^2}=\frac{\pi}{2\beta}\exp(-a\beta)\quad\text{and}\quad\int_0^\infty\frac{\cos(ax)\cos(bx)dx}{\beta^2+x^2}=\frac{\pi}{4\beta}[\exp\{-|a-b|\beta\}+\exp\{-(a-b)\}\beta].$$

The S/N ratio becomes

$$\frac{S}{N}=\frac{\bar{G}\sqrt{(2\tau_c)}[1-\exp(-\tau_s/\tau_c)]}{\sqrt{\{S_G(0)[1-\exp(-2\tau_s/\tau_c)]\}}}. \tag{31}$$

The S/N ratio is found to be independent of T, or in other words, the S/N ratio is unaffected by the time between measurement of the reference signal and the analyte signal. The S/N ratio is maximum when $\tau_s\to\infty$. In actual measurements, the maximum S/N ratio is practically attained when $\tau_s\simeq 2\pi\tau_c$ where $2\pi\tau_c$ is defined as the response time, τ_r; in terms of the response time, the maximum signal-to-noise is given by

$$\left(\frac{S}{N}\right)_{max}=\bar{G}\sqrt{\left[\frac{\tau_r}{\pi S_G(0)}\right]}. \tag{32}$$

When this equation is compared with the expression for the case of additive background shot noise, it is seen that the S/N ratio increases in both cases with $\sqrt{(\tau_r)}$. It is noted that the expression for shot noise should not be substituted here for $S_G(0)$ because $S_G(0)$ does not represent shot noise but is of different, multiplicative origin. All that can be specified is that for the white noise case $S_G(0)$ is constant. The S/N ratio will also increase as $\sqrt{[S_G(0)]}$ decreases.

4.2 *Direct current measurement with an integrator for white noise*

Equation (31) was derived for a current meter damped by an RC filter. If, as in the treatment of additive noise [1], the integrator is considered as a limiting case of a current meter with a very large response time by assuming $\tau_s\ll\tau_r$ and identifying τ_s by the integration time τ_i, equation (31) becomes in the limit of $\tau_c(=\tau_r/2\pi)\to\infty$

$$\frac{S}{N}=\frac{\bar{G}\sqrt{(2\tau_c)}}{\sqrt{[S_G(0)]}}\cdot\frac{\tau_i/\tau_c}{\sqrt{(2\tau_i/\tau_c)}}=\frac{\bar{G}\sqrt{(\tau_i)}}{\sqrt{[S_G(0)]}}, \tag{33}$$

which differs by a factor $\sqrt{\pi}$ from the expression in equation (32), as was also found in the case of additive noise [1]. Note that S/N increases $\propto\sqrt{\tau_i}$ and is independent of T.

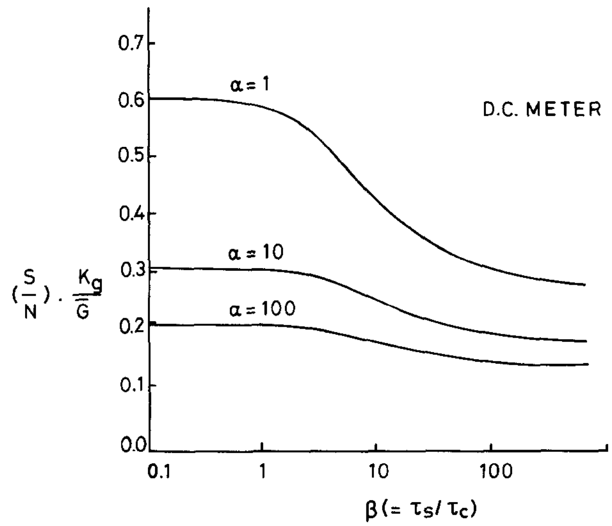

Fig. 2. Plot of $S/N \cdot K_g/\bar{G}[\equiv f(\alpha, \beta)]$ vs β for d.c. meter system with $\alpha(\equiv T/\tau_s) = 1$, 10 and 100 in the case of flicker noise.

4.3 *Direct current measurement with a current meter for flicker noise*

Starting with equation (25) and making the following substitutions

$$S_G(f) \equiv K_g^2/f; \quad \beta \equiv 2\pi\tau_s/\tau_r = \tau_s/\tau_c; \quad z \equiv 2\pi f\tau_s; \quad \alpha \equiv T/\tau_s \qquad (\alpha \geq 1),$$

gives

$$\frac{\sigma_{C_s}^2}{C_s^2} = \frac{4K_g^2}{\bar{G}^2[1-\exp(-\beta)]^2} \int_0^\infty \frac{dz \sin^2(\frac{1}{2}\alpha z)}{z(1+z^2/\beta^2)} [\exp(-2\beta) + 1 - 2\exp(-\beta)\cos z], \qquad (34)$$

or

$$\frac{S}{N} = \frac{\bar{G}}{K_g} f(\alpha, \beta), \qquad (35)$$

where

$$f(\alpha, \beta) \equiv \left\{ 4 \int_0^\infty \frac{dz \sin^2(\frac{1}{2}\alpha z)}{z(1+z^2/\beta^2)} \cdot \frac{\exp(-2\beta) + 1 - 2\exp(-\beta)\cos z}{[1-\exp(-\beta)]^2} \right\}^{-1/2}. \qquad (36)$$

The S/N ratio for this case is plotted in Figs. 2 and 3. The function $f(\alpha, \beta)$ was evaluated by numerical integration for several cases of constant α and constant β, respectively. At

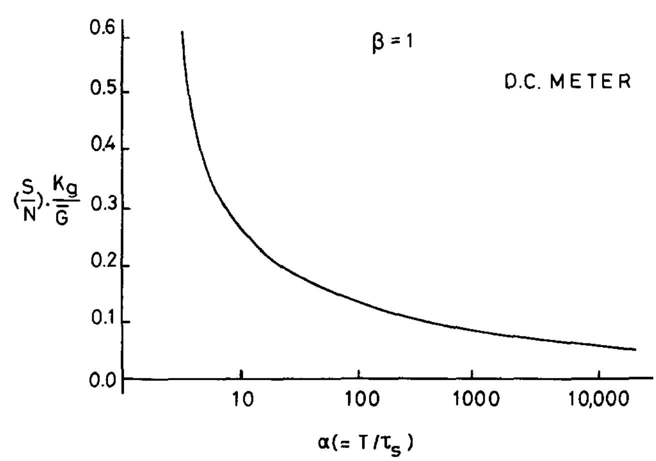

Fig. 3. Plot of $S/N \cdot K_g/\bar{G}[\equiv f(\alpha, \beta)]$ vs α for d.c. meter system with $\beta(\equiv \tau_s/\tau_c) = 1$ in the case of flicker noise.

constant $\alpha = T/\tau_s$, the S/N ratio remains approximately constant for $\beta < 1$, but decreases for $\beta > 1$. From the definition of β and τ_r, τ_s is optimum when $\tau_s \leq \tau_c$. The S/N ratio decreases rapidly with increasing α (note that the lowest possible value of α is 1). The maximum S/N ratio possible, for $\alpha = 1$ and $\tau_s \leq \tau_c$, for a paired measurement is found from Figs. 2 and 3

$$\left(\frac{\mathrm{S}}{\mathrm{N}}\right)_{\max} = \frac{0.6\,\bar{G}}{K_g}. \tag{37}$$

4.4 *Direct current measurement with an integrator for flicker noise*

Using similar approximations as in the case for an integrator with white noise and identifying again τ_s ($\tau_s \ll \tau_r$) with the integration time τ_i, choosing the lowest possible value of $T = \tau_i$, noting the limit of $\tau_c^2/1 + (2\pi f \tau_c)^2$ as $\tau_c \to \infty$ is $1/4\pi^2 f^2$, the expression for the relative variance of C_s [equation (25)] becomes, after substituting $S_G(f) = K_g^2/f$ and $z' = \pi f \tau_i$,

$$\frac{\sigma_{C_s}^2}{C_s^2} = \frac{4K_g^2}{\bar{G}^2} \int_0^\infty \frac{\sin^4 z'\,\mathrm{d}z'}{(z')^3}. \tag{38}$$

The solution to this integral is ln 2, so the signal-to-noise ratio becomes

$$\frac{\mathrm{S}}{\mathrm{N}} = \frac{\bar{G}}{2K_g\sqrt{(\ln 2)}}, \tag{39}$$

for the limiting case of $T = \tau_i$ and $\tau_r (= 2\pi\tau_c) \to \infty$. Note that this result is independent of integration time.

An alternative method of solving for the relative variance of C_s is to return to equation (22) and make several approximations to get a solution which is general for $T \geq \tau_i$. We identify again $\tau_i = \tau_s$, and assume $\tau_i \ll \tau_c$, as in the case of an integrator with white noise. Starting from equation (22), setting $S_G(f) = K_g^2/f$ for flicker noise, and approximating $\exp(2u/\tau_c)$, $\exp(-2\tau_s/\tau_c)$, and $\exp(y'/\tau_c)$ by unity and $1-\exp(-\tau_s/\tau_c)$ by τ_s/τ_c for $\tau_c \to \infty$ gives

$$\frac{\sigma_{C_s}^2}{C_s^2} = \frac{2K_g^2}{\bar{G}^2}\left\{\tfrac{1}{2}\left(\frac{T}{\tau_i} - 1\right)^2 \ln(T - \tau_i) + \tfrac{1}{2}\left(\frac{T}{\tau_i} + 1\right)^2 \ln(T + \tau_i) - \left(\frac{T}{\tau_i}\right)^2 \ln T - \ln \tau_i\right\}. \tag{40}$$

It can be shown that the expression between braces in equation (40) depends only on the *ratio* T/τ_i.

With a fixed integration time τ_i, the minimum value of T is given by $T_{\min} = \tau_i$ (see assumptions). Solving for the S/N ratio gives

$$\frac{\mathrm{S}}{\mathrm{N}}(T_{\min} = \tau_i) = \frac{\bar{G}}{2K_g\sqrt{(\ln 2)}}, \tag{41}$$

which is the same result as that obtained in equation (39).

If $T \gg \tau_i$, the S/N ratio as a function of T/τ_i is asymptotically given by

$$\frac{\mathrm{S}}{\mathrm{N}}(T \gg \tau_i) \to \frac{\bar{G}}{K_g\sqrt{3 + 2\ln(T/\tau_i)}}. \tag{42}$$

As T/τ_i increases, the S/N ratio decreases, but slowly.

Since the S/N ratio does not depend on T and τ_i separately but only on their ratio, we can improve the S/N for a fixed total measurement time, τ_m, by making n repeated, paired measurements of reference and sample with $T = \tau_i$ and $n = \tau_m/2\tau_i$, and averaging the results. This increases the S/N ratio as given by equation (39) by a factor of $\sqrt{n}$. This conclusion has been reached by SNELLEMAN [7] and LÉGER *et al.* [8] for the case of additive flicker noise. In practice, there is a fundamental limit to the amount of

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

improvement that may be achieved by this procedure. In the model for multiplicative noise, only multiplicative noise sources have been treated. All signals in analytical spectrometry will also have shot noise, and if the integration time becomes short enough, the shot noise may become the dominant noise source. In this case, there will be no further improvement in S/N ratio as n is increased for given τ_m. (For the case of multiplicative white noise, there will be no difference between making one set of paired measurements of sample and reference or n sets during the same total measurement time.) The general conclusion is that the optimum S/N ratio will be achieved when the sample and reference pair are measured so rapidly in alternate succession during the measurement time, that shot noise becomes the prevailing noise source.

5. Conclusions

The major conclusions which can be drawn from our theoretical treatment of S/N ratios are as follows.

(i) For the cases of white noise, whether additive or multiplicative, the S/N ratio increases as the square root of the response time, τ_r, or the integration time, τ_i, for current meters and integrators respectively.

(ii) For additive background shot noise limited cases, modulation techniques will give S/N ratios $\sqrt{2}$ time poorer; sample- and wavelength-modulation are an exception, because it is necessary to measure the blank regardless.

(iii) For the cases of white noise, whether additive or multiplicative, the S/N ratio is independent of the rate at which sample and background or sample and reference are measured.

(iv) For the case of multiplicative flicker noise measured with a meter system and fixed $\beta \equiv 2\pi\tau_s/\tau_r$, the S/N ratio decreases as $\alpha \equiv T/\tau_s$ increases above the minimum value of $\alpha = 1$.

(v) For the case of multiplicative flicker noise measured with a meter system and fixed $\alpha \equiv T/\tau_s$, the S/N ratio is approximately constant for $0.1 \leq \beta \leq 1$ ($\beta \equiv 2\pi\tau_s/\tau_r$) and decreases for $\beta > 1$.

(vi) For the case of multiplicative flicker noise measured with a meter system, the optimum S/N ratio is achieved with $\alpha \equiv T/\tau_s = 1$ and $\beta \equiv 2\pi\tau_s/\tau_r \leq 1$.

(vii) For the case of multiplicative flicker noise measured with an integration system and $\tau_s = \tau_i$, the S/N ratio is optimum for the minimum value of $T = \tau_i$ (i.e. $\alpha = 1$) and decreases for $\alpha > 1$.

(viii) For the case of multiplicative flicker noise measured with an integration system and $\tau_s = \tau_i$, the S/N ratio in the limit of $T \gg \tau_i$ is proportional to $1/\{3 + 2\ln(T/\tau_i)\}^{1/2}$.

(ix) For the cases of multiplicative flicker noise measured with either a meter or integration system it is optimum for $\alpha = 1$ to make the integration or response time, for fixed τ_s/τ_r, as short as practical and repeat the pair of measurements n times for fixed total measuring time τ_m.

(x) The optimal system in most cases of multiplicative flicker noise is to use a dual channel approach to measure sample and reference simultaneously and to take their ratio; this approach is necessary in some experiments such as those using pulsed lasers for spectroscopy because the noise caused by effects such as spatial variation in the beam profile will be unrelated from pulse to pulse; in such a case where sample and reference are measured simultaneously (i.e., $T = 0$), multiplicative noise will be minimized and additive noise will become dominant.

(xi) The best reference in many cases is a calibration standard, but it is often impossible to measure a sample and standard simultaneously; in these situations an internal standard, an excitation source intensity, etc. can be measured simultaneously with the sample and the S/N ratio will be improved if the *source of multiplicative noise* affects *both* in the same manner and is a significant source of noise.