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

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 & Gamble, Miami Valley Laboratories, Cincinnati, OH 45247, U.S.A.

N. OMENETTO

Institute of Inorganic and General Chemistry, University of Pavia, Pavia, Italy

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**Abstract**—This part of the review links up with the tutorial discussion in Part I and gives general signal-to-noise expressions for emission and luminescence spectrometric systems. Tabular presentations are used for the expressions and for comparison of noise sources.

### I. INTRODUCTION

IN PART I, a tutorial discussion of signal-to-noise ratios for idealized spectrometric measurements was given. In Part II, general signal-to-noise expressions will be given for emission and luminescence spectrometric systems, and so more than one noise source will be considered. Liberal use of tables will be made for the expressions as well as for comparison of noise sources. No attempt will be made to derive signal-to-noise ratios in Part II, but rather the reader will be referred to the appropriate literature. In Part II, the aim is to give suitable general signal-to-noise ratio expressions to allow an approximate description of real emission and luminescence spectrometric systems and to compare various instrumental systems with respect to their signal-to-noise ratios.

### II. SIGNAL EXPRESSIONS

No detailed signal expressions will be given here for analytical spectrometric systems [1–4], but rather the general factors limiting the detector signal level in various analytical spectrometric methods will be given and briefly discussed. For a continuum source of radiation, the detected light flux,  $\Phi_{cd}$ , in W, is given by

$$\Phi_{cd} = \int B_{\lambda}(\lambda) L \tau(\lambda) A(\lambda - \lambda_o) d\lambda \quad (\text{II.1})$$

where

$B_{\lambda}(\lambda)$  = spectral radiance of continuum source at  $\lambda$  ( $\text{W cm}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ );

$L$  = optical conductance of optical train (generally limited by dispersive element in spectrometer), i.e. limiting area  $X$  limiting solid angle ( $\text{cm}^2 \text{sr}$ );

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\* Dedicated to the memory of Professor HEINRICH KAISER.

- [1] J. D. WINEFORDNER, *Comparison of Spectroscopic Methods Trace Analysis* (Edited by J. D. WINEFORDNER, Chap. 11, p. 419. John Wiley, New York (1976).
- [2] J. D. WINEFORDNER, S. G. SCHULMAN, and T. C. O'HAYER, *Luminescence Spectrometry in Analytical Chemistry*. John Wiley, New York (1972).
- [3] A. P. THORNE, *Spectrophysics*. Chapman & Hall, and Science Paperbooks, London (1974).
- [4] IUPAC Commission on Spectrochemical and other Optical Procedures, *Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis*—I, *General Atomic Emission Spectroscopy*, *Pure Appl. Chem.* **30**, 653 (1972);—II, *Analytical Flame Spectroscopy and Associated Procedures*, *Pure Appl. Chem.* **45**, 105 (1976); cf. *Spectrochim. Acta* **33B**, 219, 247 (1978).

$\tau(\lambda)$  = transmittance of optical train at  $\lambda$  (dimensionless);

$A(\lambda - \lambda_o)$  = normalized instrumental factor of monochromator with wavelength set at  $\lambda_o$  (dimensionless);

and for a narrow line source, the detected flux,  $\Phi_{ld}$ , in  $W$ , is given by

$$\Phi_{ld} = B(\lambda_o)L\tau(\lambda_o) \quad (II.2)$$

where

$B(\lambda_o)$  = radiance of line source ( $W\text{ cm}^{-2}\text{ sr}^{-1}$ );

$\tau(\lambda_o)$  = transmittance of optical train at  $\lambda_o$ , the center of the spectral line (dimensionless).

To convert  $\Phi$  to a current,  $i$ , or a detector count rate,  $R$ ,

$$\begin{aligned} i &= \gamma\Phi \\ R &= \gamma'\Phi \end{aligned} \quad (II.3)$$

where

$\gamma$  = detector responsivity ( $A\text{ W}^{-1}$ );

$\gamma'$  = detector responsivity (counts  $s^{-1}\text{ W}^{-1}$ ).

To convert from  $\gamma$  to  $\gamma'$ , one needs only to convert from current, in  $C\text{ s}^{-1}$ , to count rate, in  $s^{-1}$ , and so  $\gamma' = \gamma/e\bar{G}$ , where  $e$  is the charge of an electron ( $e = 1.6 \times 10^{-19}\text{ C}$ ) and  $\bar{G}$  is the overall gain of the photodetector. If  $\gamma$  or  $\gamma'$  depend greatly upon wavelength, then spectral quantities should be used, i.e. in terms of currents,

$$i_c = \int B_\lambda(\lambda)L\tau(\lambda)\gamma(\lambda)A(\lambda - \lambda_o)d\lambda \quad (II.4)$$

and

$$i_l = B(\lambda_o)L\tau(\lambda_o)\gamma(\lambda_o). \quad (II.5)$$

Assuming a continuum source with essentially constant spectral radiance,  $B_\lambda(\lambda_o)$ , over the effective spectral bandwidth of the monochromator,  $\Delta\lambda_m$ , in nm, then

$$i_c = B_\lambda(\lambda_o)\Delta\lambda_mL\tau(\lambda_o)\gamma(\lambda_o). \quad (II.6)$$

To convert  $\Phi$  to charge,  $q$ , or counts,  $C$ , the counting or integration time,  $\tau_i$ , must be used, i.e.

$$\begin{aligned} q &= i\tau_i = \gamma\Phi\tau_i \\ G &= R\tau_i = \gamma'\Phi\tau_i. \end{aligned} \quad (II.7)$$

### III. SIGNAL-TO-NOISE EXPRESSIONS IN EMISSION AND LUMINESCENCE SPECTROMETRY

#### III.A. EXPRESSIONS FOR $S/N$ FOR SINGLE CHANNEL DETECTORS (PHOTOMULTIPLIERS)

It should be emphasized that in Part I only one noise source was considered in calculating the signal-to-noise ratios. However, when making measurements in analytical spectrometry, more than one noise source occur and so must be considered whatever measurement system is being utilized for the signal measurement. In this section, only emission (atomic and molecular) and luminescence (atomic and molecular) spectrometry will be explicitly considered. No attempt will be made here to give general expressions for absorption (atomic and molecular) spectrometry, although the expressions for emission and luminescence spectrometry can be applied, with some changes, to absorption spectrometry, which is somewhat more complex due to the necessity of making ratio measurements and the non-linearity of absorbance with analyte concentration. The noises occurring in emission and luminescence spectrometry will be explicitly discussed and evaluated in this section, particularly with regard to how the noises combine to give the total noise in the measurement.

In general, shot noises\* are simple to consider since they add quadratically, i.e. no correlation between these noises. Flicker noises\* are much more complicated to handle because they may be dependent, independent, or a combination of dependency and independency. Although high-frequency proportional noises are similar in complexity to flicker noises, they can be omitted in the following treatment because such noises can be minimized by proper selection of the frequency of the measurement system. In the following treatment, flicker noises will be assumed to be completely dependent or completely independent (no correlation coefficients) according to the best experimental evidence available to the authors [5–7]. Although the most general expressions should contain flicker noises with correlation coefficients, such expressions would be exceedingly complex and of little use since correlation coefficients for flicker noises are rarely available. It was necessary in the present treatment to assume the linear addition of analyte emission or luminescence flicker noises to the related “background” flicker noises (background emission in emission spectrometry and source related background, such as scatter and luminescence background in luminescence spectrometry); this addition is not exact because *analyte flicker occurs only during the sample and not the blank*. Nevertheless, the expressions to be given should be good estimates of  $S/N$  for actual experimental situations. Finally, tables of expressions and evaluations of parameters will be utilized where feasible to simplify the expressions and evaluations of the expressions. The  $S/N$  expressions to be given will contain various parameters, such as total measurement time and counting rates, which are evaluated according to the analytical system under study, flicker factors which are evaluated according to the analytical system under study and the measurement method, and constant terms characteristic of the measurement method.

General  $S/N$  expressions (digital case\* only) for atomic or molecular emission spectrometry and for atomic or molecular luminescence spectrometry, are given in Table 1. All terms are defined at the end of the table. The power terms,  $p$ ,  $q$ ,  $r$ ,  $u$ , and  $w$ , are also evaluated in Table 1 for the cases of CW (continuous excitation-continuous emission or luminescence and continuous measurement), AM (amplitude modulation of emitting radiation in emission spectrometry or of exciting source in luminescence spectrometry), WM (wavelength modulation of optical system to produce an a.c. current for the analyte), SM (sample-blank modulation, i.e. repetitive measurement of sample and blank), AM + WM (double modulation where the optical system is slowly wavelength modulated while rapidly amplitude modulating the signal as described above), and AM + SM (double modulation where the sample and blank are repetitively and slowly introduced while the amplitude is rapidly modulated as described above). Other double modulation approaches, as WM + SM, and triple modulation, as AM + WM + SM, result in little gain in analytical figures of merit and are more complex and so will not be discussed here.

A representation of the various modulation approaches for emission and luminescence spectrometry is shown in Fig. 1. Modulation methods are only useful in minimizing flicker noises as is evident from the representations in Fig. 1 (any noise source which is present during both halves of the modulation is reduced since  $\xi$  is given by the appropriate a.c.-expression, i.e.  $\xi_{ai}$  for the synchronous counter, rather than by the d.c. integrator expression,  $\xi_{di}(\xi_{di} > \xi_{ai})$ . The flicker noises, which are reduced by modulation are indicated with + in Table 2.

In Table 3, the appropriate flicker factor,  $\xi_{di}$  or  $\xi_{ai}$  for the d.c. integrator or digital synchronous counter, respectively, are noted. In Table 4, evaluation of the duty factors for the various measurement modes and for the various duty factors in the general noise

\* Refer to Part I.

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

Table 1. General signal-to-noise ratio expressions for emission and luminescence spectrometry with definition of terms

$\frac{S}{N_E} = \frac{S_L}{\sqrt{N_{ES}^2 + N_{BS}^2 + N_{I,S}^2 + N_{DS}^2 + (N_{EF} + 2^q N_{I,F} + 2^q N_{BF})^2 + [2^w N_{DF}]^2 + [2^w N_A]^2}}$		Measurement mode*	$q$	$w$
		CW	1	1
		AM	$\frac{1}{2}$	$\frac{1}{2}$
		WM	$\frac{1}{2}$	$\frac{1}{2}$
		SM	0	$\frac{1}{2}$

$\frac{S}{N_L} = \frac{S_L}{\sqrt{N_{LS}^2 + N_{ES}^2 + N_{I,S}^2 + N_{SS}^2 + N_{BS}^2 + N_{DS}^2 + (N_{LF} + 2^p N_{SF} + 2^q N_{I,F})^2 + 2^p (N_{EF} + 2^q N_{BF})^2 + [2^w N_{DF}]^2 + [2^w N_A]^2}}$		Measurement mode*	$p$	$q$	$r$	$u$	$w$
		CW	1	1	1	1	1
		AM	0	$\frac{1}{2}$	1	1	$\frac{1}{2}$
		WM	1	$\frac{1}{2}$	$\begin{cases} \frac{1}{2} \text{ (continuum)} \\ 1 \text{ (line)} \end{cases}$	$\frac{1}{2}$	$\frac{1}{2}$
		SM	1	0	0	0	$\frac{1}{2}$
		AM + WM	0	0	$\begin{cases} \frac{1}{2} \text{ (continuum)} \\ 1 \text{ (line)} \end{cases}$	1	$\frac{1}{2}$
		AM + SM	1	0	0	0	0

## Definition of terms

- $N_{ES}$  analyte emission shot noise =  $\sqrt{\frac{1}{2} D_{EM} D_{WM} R_{Et_m}}$  (counts)  
 $N_{BS}$  background emission shot noise =  $\sqrt{D_{EM} D_O R_{Bt_m}}$  (counts)  
 $N_{I,S}$  interferent (in matrix) emission shot noise =  $\sqrt{D_{EM} R_{It_m}}$  (counts)  
 $N_{DS}$  detector dark shot noise =  $\sqrt{D_{GD} R_{Dt_m}}$  (counts)  
 $N_{LS}$  analyte luminescence shot noise =  $\sqrt{\frac{1}{2} D_{LM} D_{WM} D_O R_{Lt_m}}$  (counts)  
 $N_{SS}$  scatter (source) shot noise =  $\sqrt{D_{LM} D_{IM} D_O R_{St_m}}$  (counts)  
 $N_{I,L}$  interferent (in sample/blank) luminescence shot noise =  $\sqrt{D_{LM} D_O R_{It_m}}$  (counts)  
 $2^w N_A$  amplifier readout noise (generally negligible in  $S/N$  measurements) (counts)  
 $N_{EF}$  analyte emission flicker noise =  $\frac{1}{2} \xi_{EF} D_{EM} D_{WM} D_O R_{Et_m}$  (counts)  
 $2^q N_{BF}$  background emission flicker noise =  $2^q \xi_{BF} D_{EM} D_{SB} D_O R_{Bt_m}$  (counts)  
 $2^q N_{I,F}$  interferent (in emission) flicker noise =  $2^q \xi_{I,F} D_{EM} R_{It_m}$  (counts)  
 $2^w N_{DF}$  detector dark flicker noise =  $2^w \xi_{DF} D_{GD} R_{Dt_m}$  (counts)  
 $2^r N_{SF}$  scatter (source) flicker noise =  $2^r \xi_{SF} D_{IM} D_{LM} D_{SB} D_O R_{St_m}$  (counts)  
 $2^u N_{I,L}$  interferent (in sample/blank) luminescence flicker noise =  $2^u \xi_{I,L} D_{LM} D_O R_{It_m}$  (counts)  
 $N_{LF}$  analyte luminescence flicker noise =  $\frac{1}{2} \xi_L D_{LM} D_{SB} D_O R_{Lt_m}$  (counts)  
 $S_E$  analyte emission signal =  $\frac{1}{2} D_{EM} D_{WM} R_{Et_m}$  (counts)  
 $S_L$  analyte luminescence signal =  $\frac{1}{2} D_{LM} D_{WM} D_O R_{Lt_m}$  (counts)  
 $t_m$  measurement time for one spectral component(s) (see Fig. 4 and text)  
 $D_{LM}$  amplitude modulation factor for luminescence spectrometry (dimensionless)  
 $D_{EM}$  emission modulated factor for emission spectrometry (dimensionless)  
 $D_{SB}$  sample-blank factor, fraction of time sample is "on" (dimensionless)  
 $D_{WM}$  wavelength modulation factor (dimensionless)  
 $D_{IM}$  wavelength modulation factor for narrow line (dimensionless)  
 $D_O$  factor for correction for emission in luminescence spectrometry, fraction of time emission or luminescence (equal times) is measured (dimensionless)  
 $D_{GD}$  gated detector factor to account for fraction of time detector is gated "on" (dimensionless)  
 $R_E$  photoelectron counting rate of analyte emission ( $s^{-1}$ )  
 $R_B$  photoelectron counting rate of background emission ( $s^{-1}$ )  
 $R_{I_e}$  photoelectron counting rate of interferent in emission spectrometry, assumed to be in both blank and sample ( $s^{-1}$ )  
 $R_S$  photoelectron counting rate of source scatter in luminescence spectrometry ( $s^{-1}$ )  
 $R_{I_l}$  photoelectron counting rate of interferent luminescence in luminescence spectrometry, assumed to be in sample and blank ( $s^{-1}$ )  
 $R_D$  detector dark counting rate of detector ( $s^{-1}$ )  
 $R_L$  photoelectron counting rate of analyte luminescence ( $s^{-1}$ )  
 $\xi_{EF}$  flicker factor for analyte emission flicker (dimensionless)  
 $\xi_{I,F}$  flicker factor for emission interferent flicker factor (dimensionless)  
 $\xi_{BF}$  flicker factor for background emission flicker factor (dimensionless)  
 $\xi_{SF}$  flicker factor for source scatter (in luminescence spectrometry) flicker factor (dimensionless)  
 $\xi_{I,L}$  flicker factor for luminescence interferent (in luminescence spectrometry) flicker factor (dimensionless)  
 $\xi_{DF}$  detector flicker factor (dimensionless)  
 $\xi_{LF}$  flicker factor for analyte luminescence (dimensionless)

\* Explained in the text (section III.A). See also Fig. 1.

expressions defined in Table 2 (at end of table) are given. The duty factor is generally defined as the fractional on time for any given process by any type of measurement made.

The expressions in Table 1 with the definition and evaluation of terms in Tables 1, 3, and 4 describe all measurement modes in emission and luminescence spectrometry except for those cases where the emission source in emission spectrometry or the excitation source in luminescence spectrometry is pulsed and the detector-electronics system is gated with or without time delay between the termination of excitation and the initiation of measurement [6, 8]. In Table 4, expressions for duty factors to describe source pulsing-detector gating are given with definition of terms. The duty factors,  $D_{EM}$  and  $D_{LM}$ , replace the values of  $\frac{1}{2}$  or 1 in Table 4 for CW, AM, WM, SM, AM + WM, and AM + SM measurement modes. The CW mode for source pulsing-detector gating implies that a blank is determined in order to correct for background, interferent, and dark counts in emission and for background, interferent, scatter, and dark counts in luminescence. The AM mode for source pulsing-detector gating implies that a blank is determined as above for the CW mode but also in between source pulses for a time period of  $t_g$  (s) dark counts are observed in emission spectrometry and dark counts, analyte emission, and background emission are observed in luminescence spectrometry. The other modes have not been used for analytical emission and luminescence spectrometry but would involve the following: WM mode means that every other pulse is "on" wavelength and alternate pulses are "off" wavelength in either emission or luminescence spectrometry—again a blank must be "run"; SM mode means that one or more pulses occur for the sample and one or more (the same number as for the sample) occur for the blank and then the process is repeated for either emission or luminescence spectrometry—in this case, in luminescence spectrometry, a separate source of measurement must be "run" to determine the emission signal; double modulation methods, AM + WM and AM + SM are of interest only for luminescence spectrometry and involve a combination of the above modes. Therefore, to obtain the appropriate  $S/N$  expression, one takes the appropriate expression from Table 1 with noise terms described by the expressions at the end of the table; the flicker factors are those listed in Table 3 and Table 2 of Part I. The duty factors, except for  $D_{EM}$ ,  $D_{LM}$ , and  $D_{GD}$  are those in Table 4 and the ones for  $D_{EM}$ ,  $D_{LM}$  and  $D_{GD}$  are given in Table 5. The power coefficients,  $p$ ,  $q$ ,  $r$ ,  $u$ , and  $w$  are the same as in Table 1. In Table 6, a comparison of pulsing methods with respect to noise reduction are given.

### III.B. EXPRESSIONS FOR $S/N$ FOR MULTICHANNEL DETECTORS (IMAGE DEVICES)

The  $S/N$  expressions [7] in Table 1 with term definitions in Tables 1, 3, 4, and 5 apply to either single channel detectors (photon detectors) or multichannel detectors [image devices, such as, vidicons (V), silicon intensified (SIT) vidicons, intensified silicon intensifier target (ISIT) vidicons, secondary emission conduction (SEC) vidicons, solid state diode arrays (SSDA), etc.]. Image dissectors (ID), generally considered to be in the image device category, are actually single channel (with rapid slew rate) detectors. The only significant differences between single- and multi-channel detectors in terms of  $S/N$  are: (i) with multi-channel devices, the number of channels illuminated and measured must be considered; and (ii) with multichannel devices, it is usually not possible to assume that amplifier noise is negligible as is "always" the case with photo-multipliers. Cross channel interference, e.g. blooming, pin-cushion effect, etc., in some image devices will cause only small errors in the signal-to-noise ratios as long as the spectral image covers more than 2 channels and only the middle channels are measured. In addition, multichannel detectors are difficult to use in the modulated modes unless the modulation frequency is low, say 30 Hz or less. Therefore, it is necessary to define two parameters characteristic of the channels (effectively individual photon detectors)

[8] N. OMENETTO, G. D. BOUTILIER, S. L. WEEKS, B. W. SMITH and J. D. WINEFORDNER, *Anal. Chem.* **49**, 1076 (1977).

of image devices if single- and multi-channel devices are to be compared for spectrometric measurements: area per channel,  $A_k$ ; and the efficiency per channel (counts per photon per channel),  $q_k$ . Thus, to compare photomultiplier detectors with each other or with image devices, it is necessary to transform all detector count rates, in counts  $s^{-1}$ , to photon irradiances,  $E_p$ , in photons  $s^{-1} cm^{-2}$ , and so measurement of radiative process,  $i$ , with image devices results in

$$R_{i(\text{image})} = \sum_k E_{pk} A_k q_k \quad (\text{III.B.1})$$

where the summation is over the number of channels (64, 128, 256, 512, 1024, etc.) illuminated with the spectral line or band of interest. For a photomultiplier (PM) detector

$$R_{i(\text{PM})} = E_p A q \quad (\text{III.B.2})$$

where the terms are as defined above and refer to the illuminated region of the photocathode.

Some image devices are divided horizontally into two rows of 128, 256, ... channels in order to allow correction for dark counts (if correction is done after each scan of the channels, this is effectively amplitude modulation which reduces dark flicker noise, i.e.  $\xi_{ai}$  applies to the dark flicker noise rather than  $\xi_{di}$ ). Because the signal is a result of the subtraction of the dark measure from the spectral plus dark measure, the dark current and amplifier noises are both measured using both halves of the image device, whereas all radiative processes are measured only during the processing of the illumination half of the device. This approach corresponds to the AM measurement mode for both emission and luminescence spectrometry (see Tables 3 and 4, and Table 3, Part I). If the entire image device is illuminated, this corresponds to the CW mode. In both the CW and AM modes, a blank must be separately measured. The other measurement modes, WM, SM AM + WM, and AM + SM are either difficult or impossible to perform or are not necessary with image devices. Source pulsing-detector gating is possible with image devices but only in the CW and AM modes. The flicker factors for all noises except dark flicker noise in the AM mode where  $\xi_{dc}$  is applicable, are given by the d.c. expressions for the integrator case in Table 2, Part I. The constants,  $p$ ,  $q$ ,  $r$ ,  $u$ , and  $w$  in the  $S/N$  expressions are as defined in Table 1.

The amplifier noise,  $N_A$ , for single channel detectors is determined by the equivalent

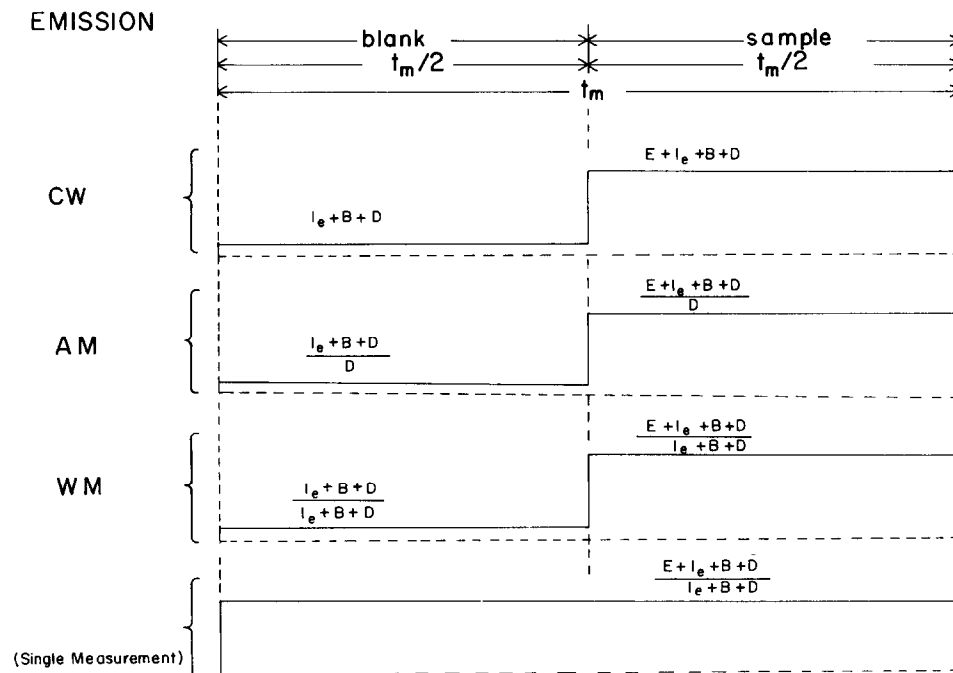


Fig. 1(a).

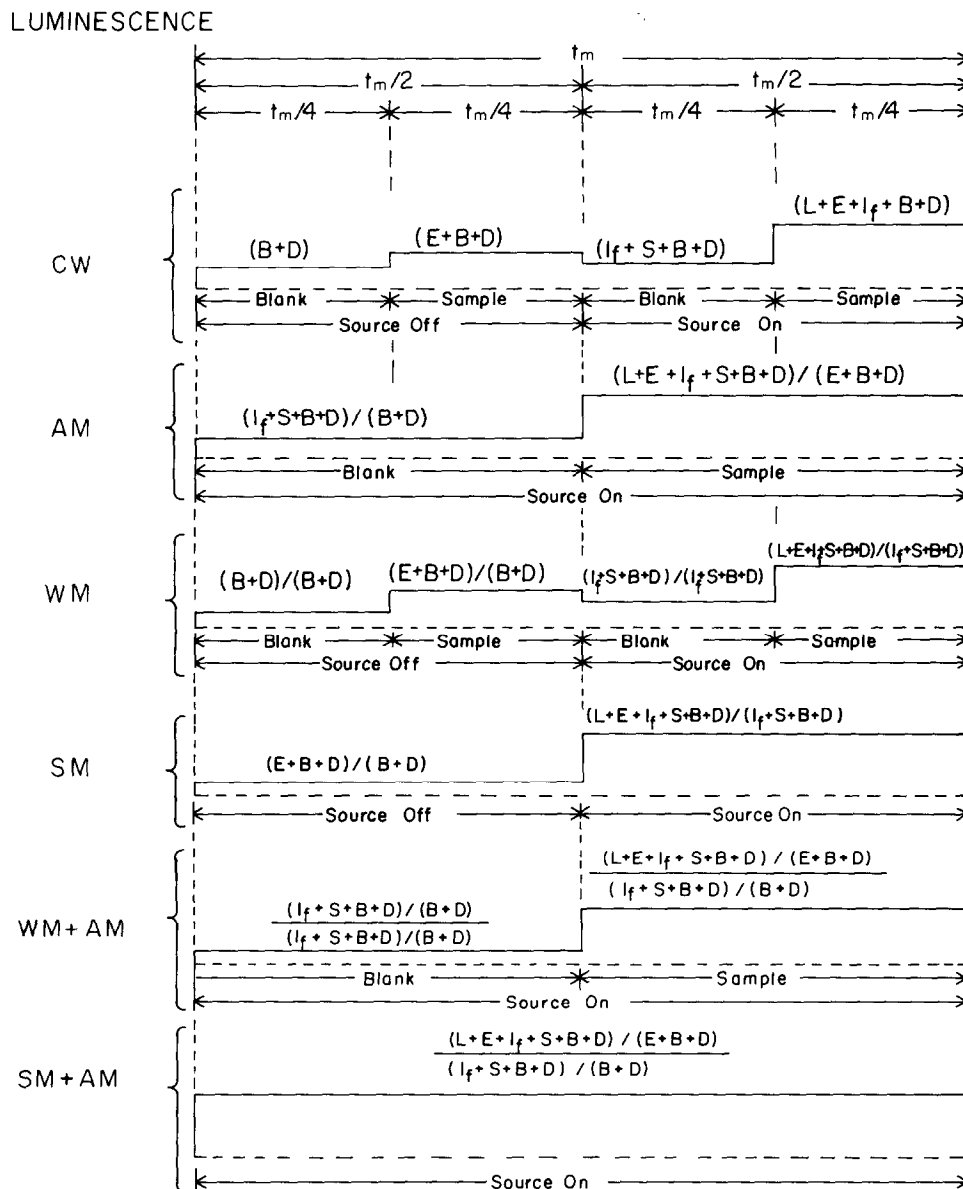


Fig. 1(b).

Fig. 1. Representation of measurement sequence and presence of noise sources for emission (Fig. 1a) and luminescence (Fig. 1b) spectrometry. The symbol  $t_m$  is the measurement time per spectral component and the symbols: CW = continuous "wave" measurement; AM = amplitude modulation; WM = wavelength modulation; SM = sample modulation; Blank means blank is being measured; Sample means sample is being measured; Source on and Source off for the Luminescence case means the source is on or off, respectively, during the measurement. The other symbols are:  $I_f$  = fluorescence interferent assumed to be molecular band;  $I_e$  = emission interferent assumed to be molecular band;  $E$  = analyte emission;  $L$  = analyte luminescence;  $B$  = background emission from cell itself, e.g. flame;  $D$  = detector dark signal;  $S$  = scatter interference. The summations in brackets, ( ), above the measurement segments represent the signal components (and thus noise components) which are present during those segments. If a ratio appears as it does in all a.c. cases, i.e. in AM, WM, SM, and all double modulation cases, this represents the signal (and noise) components present during modulation. In the cases of double modulation, a ratio of 2 ratios is given, i.e. in WM + AM, the terms  $[(a)/(b)]/[(c)/(d)]$  are defined as:  $a$  = noise sources present with chopper open and "on" wavelength,  $b$  = noise sources present with chopper closed and "on" wavelength,  $c$  = noise sources present with chopper open and "off" wavelength, and  $d$  = noise sources present with chopper closed and "off" wavelength, and in SM + AM, the terms  $[(a)/(b)]/[(c)/(d)]$  are defined as:  $a$  = noise sources present with chopper open and sample "on",  $b$  = noise source present with chopper "off" and sample "on",  $c$  = noise source present with chopper "on" and blank "on", and  $d$  = noise source present with chopper "off" and blank "on".



Table 2. Flicker noises reduced\* by modulation techniques

Emission <sup>†</sup>						
Measurement mode	$N_{EF}$	$N_{BF}$	$N_{I,F}$	$N_{DF}$		
CW <sup>‡</sup>	—	—	—	—		
AM	—	—	—	+		
WM	—	+	+ <sup>γ</sup>	+		
SM	—	+	+ <sup>γ</sup>	+		
Luminescence <sup>†</sup>						
Measurement mode	$N_{LF}$	$N_{EF}$	$N_{BF}$	$N_{SF}$	$N_{I,F}$	$N_{DF}$
CW <sup>‡</sup>	—	—	—	—	—	—
AM	—	—	+	—	—	+
WM	—	—	+	+	+ <sup>¶γ</sup>	+
SM	—	—	+	+	+ <sup>¶γ</sup>	+
WM + AM <sup>§</sup>	—	—	+	+	+ <sup>¶γ</sup>	+
SM + AM <sup>§</sup>	—	—	+	+	+ <sup>¶γ</sup>	+

\* + means noise is reduced; — means noise is not reduced. Since the signal level in each of the cases is essentially the same, any + value means an increase in  $S/N$ .

<sup>†</sup> It is assumed that blank has all matrix components of sample. If not, the noises indicated by  $\gamma$  are not reduced by modulation.

<sup>‡</sup> Since CW is not modulation case, no flicker noises are reduced; it is included in the table for completeness.

<sup>§</sup> Although some flicker noise reduction occurs in all of these cases, the two double modulation cases allow measurement of signal due only to luminescence with 1 or 2 measurements during time  $t_m$  whereas 2 or 4 measurements within same time must be used for SM or WM alone, respectively (see Fig. 1).

<sup>¶</sup> If the interference is not present in the sample cell when blank is introduced, i.e. a matrix related flicker interference, then no reduction occurs ( $\gamma$  symbol applies).

Table 3. Evaluation of flicker factors\* in emission and luminescence spectrometry

Emission						
Measurement mode	$\xi_{EF}$	$\xi_{BF}$	$\xi_{I,F}$	$\xi_{DF}$		
CW	DC	DC	DC	DC		
AM	DC	DC	DC	AC		
WM	DC	AC	AC	AC		
SM	DC	AC	AC	AC		
Luminescence						
Measurement mode	$\xi_{LF}$	$\xi_{EF}$	$\xi_{BF}$	$\xi_{I,F}$	$\xi_{SF}$	$\xi_{DF}$
CW	DC	DC	DC	DC	DC	DC
AM	DC	AC	AC	DC	DC	AC
WM	DC	DC	AC	AC	AC	AC
SM	DC	DC	AC	AC	AC	AC
AM + WM	DC	AC	AC	AC	AC	AC
AM + SM	DC	AC	AC	AC	AC	AC

\* The flicker factors are either given by the d.c. integrator case or the a.c. synchronous counter case in Table 2, Part 1.

Table 4. Evaluation of duty factors in emission and luminescence spectrometry

Emission*						
Measurement mode	$D_{EM}$	$D_{WM}$	$D_{GD}$			
CW†	1	1	1			
AM†	$\frac{1}{2}(1)^\ddagger$	1	1			
WM	1	$\frac{1}{2}$	1			
SM	1	1	1			
Luminescence*						
Measurement mode	$D_{LM}$	$D_{WM}$	$D_{SB}$	$D_{IM}$	$D_O$	$D_{GD}$
CW†	1	1	$\frac{1}{2}$	1	$\frac{1}{2}$	1
AM†	$\frac{1}{2}(1)^\ddagger$	1	$\frac{1}{2}$	1	1	1
WM	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}(\text{line})^\ddagger$	$\frac{1}{2}$	1
SM	1	1	1	1(cont)†	$\frac{1}{2}$	1
AM + WM	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}(\text{line})^\ddagger$	$\frac{1}{2}$	1
AM + SM	$\frac{1}{2}$	1	1	1(cont)†	1	1

\*  $D_{EM} = \frac{1}{2}$  if the emission is *modulated* in emission spectrometry;

$D_{EM} = 1$  if the emission is *not modulated* in emission spectrometry;

$D_{WM} = \frac{1}{2}$  if wavelength modulation is used and 1 if it is not used;

$D_{LM} = \frac{1}{2}$  if the source of excitation in luminescence spectrometry is modulated;

$D_{LM} = 1$  if the source of excitation in luminescence spectrometry is not modulated;

$D_{SB} = \frac{1}{2}$  for paired sample-blank measurements;

$D_{SB} = 1$  for sample modulation;

$D_{GD} = 1$  if the detector is "on" during the entire measurement;

$D_{GD} < 1$  if the detector is gated;

$D_{IM} = 1$  if the exciting source in atomic fluorescence spectrometry is a continuum source;

$D_{IM} = \frac{1}{2}$  if the exciting source in luminescence spectrometry is a line source;

$D_O = 1$  if the analyte emission in luminescence spectrometry is automatically compensated for as in AM;

$D_O = \frac{1}{2}$  if a separate "source off" measurement must be made in luminescence spectrometry to compensate for analyte emission as in CW, WM, and SM cases;

† Only these two measurement modes are of importance for image device detectors with image detectors, all duty factors are as shown except for the case of background emission shot and flicker noise in the AM mode where  $D_{EM}$  and  $D_{IM}$  are both as shown in parentheses.

‡ "line" means a line interferent; "cont" means a continuum interferent.

noise input of the system and is usually negligible with analog systems and is always negligible with digital systems (photon counting). However, with image devices, the amplifier-electronics measurement noise,  $N_A$ , is determined not only by the equivalent noise input but also by the readout procedure for the device. For example, the total measurement time,  $t_m$ , is given by

$$t_m = 2[t_s n_s + t_d n_s n_d] \quad (\text{III.B.3})$$

for the case where equivalent measurement times are used for the blank and sample and  $t_s$  is the scan time for the channels (assuming equal time per channel),  $t_d$  is the time allowed for integration over and above the times between scans (integration times are in multiples of scan times),  $n_s$  is the number of scans (interrogation) of the channels of the image device, and  $n_d$  is the number of target integrations [0, 1, 2, ...]. Because the amplifier noise is determined approximately by shot noise [7],

$$N_A = N_a \sqrt{n_s} = N_a \sqrt{\frac{t_m}{2(t_s + n_d t_d)}} \quad (\text{III.B.4})$$

Table 5. Duty factors\* for pulsed source-gated detector cases

Pulsed source-gated detector—no time resolution (no delay between pulsing and detection)	
$d_{AM} \text{ or } d_{EM} = \frac{f\{t_g - \tau_i[1 - e^{-t_g/\tau_i}]\}}{[1 - e^{-1/f\tau_i}]}$	
$d_{GD} = ft_g.$	
Pulsed source-gated detector—with time resolution (delay of $t_d$ , s between pulsing and detection)	
$d_{AM} \text{ or } d_{EM} = \frac{f\tau_i[1 - e^{-t_g/\tau_i}][1 - e^{-t_d/\tau_i}]e^{-t_d/\tau_i}}{[1 - e^{-1/f\tau_i}]}$	
$d_{GD} = ft_g.$	

## Definition of terms

$t_p$	pulse width of source (assuming rectangular pulse), s
$t_g$	gate width of detector (assuming rectangular gate), s
$t_d$	delay time between end of excitation and beginning of measurement
$f$	repetition rate of source (gate), Hz
$\tau_i$	lifetime of radiative process, i, s

\* The duty factors,  $d_{AM}$  or  $d_{EM}$ , become  $ft_g$  in the event that the radiative process,  $i$ , is not pulsed.

where  $N_a$  is the amplifier noise per half channel or channel (depending on whether the image device is split into 2 rows or 1 row of channels) per scan, i.e. amplifier noise *only* occurs when the image device is scanned. Because amplifier noise can often be the limiting noise with image devices (V, SSDA, and sometimes SIT), the importance of

Table 6. Noises\* reduced by source pulsing/detector gating†

Emission					
Temporal mode	$N_E$	$N_{I_e}$	$N_B^{\ddagger}$	$N_D$	
C/C‡	—	—	—	—	
P/G	—	—	—	+	
P/G/T	—	—(+)\$	—(+)\$	+	
Luminescence					
Temporal mode	$N_L$ or $N_E$	$N_{I_f}$	$N_S$	$N_B^{\parallel}$	$N_D$
C/C‡	—	—	—	—	—
P/G	—	—	+	+	+
P/G/T	—	—(+)\$	+	+	+

\* Noises are either shot,  $S$ , or flicker,  $F$ , noises. Any + value means the noise is reduced and — means no change in noise due to mode. Also, any + value implies an increase in  $S/N$  since the signal levels in all cases are assumed identical; — value means no improvement in  $S/N$ .

† C/C = "source" continuously on; detector continuously on;

P/G = pulsed "source"-gated detector; no time resolution;

P/G/T = pulsed "source"-gated detector; with time resolution;

The P/G and P/G/T modes can be operated in the CW, AM, WM, SM, AM + WM, and AM + SM modulation modes as described in the text.

‡ C/C = reference for comparison.

§ If interferent emission or luminescence decays faster than analyte emission or luminescence, then noise is reduced and  $S/N$  is increased.

¶ The background in emission is pulsed with the analyte emission.

|| The background in luminescence is *not* pulsed with the analyte luminescence.

Table 7. Relative signal-to-noise ratios for comparing image detectors with photomultiplier detectors for emission and luminescence spectrometry\*†

Noise type	Detector type‡							
Device	V		SIT		ISIT		ID	PM
Measurement times	1 s	30 s	1 s	30 s	1 s	30 s	1 s	1 s
Mode	CW		CW		CW		AM	WM
Detector-amplifier noise limit	0	1	3	4	4	5	3	3
Background noise limit (background modulated)§								
Shot	0	1	3	4	4	5	3	3
Flicker	0	0	2	2	3	3	2	2
Background noise Limit (background unmodulated)¶								
Shot	0	1	3	4	4	5	3	3
Flicker	0	0	2	2	2	2	3	4
Analyte noise limit								
Shot**	0	1	2	3	3	4	2	2
Flicker**	0	1	4	4	5	3	3	3

\* All optical, detective, and electronic components and measurement systems are identical except for the optical measurement approach, i.e. SLS (sequential linear scan), SSS (sequential slew scan), MC (multi-channel), and MX (multiplex) techniques. The same modulation mode is also assumed for each case. Finally the emission source in emission spectrometry and the excitation source-sample cell in luminescence spectrometry are also identical for the 4 approaches.

† The scale of ratings is 5 (best  $S/N$ ), 4 (next best  $S/N$ ), ..., 1 (poor  $S/N$ ), 0 (not analytically useful). Obviously, the ratings are not applicable to all possible situations where the general restrictions hold but do give good success for most experimental cases. Also it is not possible to compare  $S/N$  ratios of methods by comparing the ratings; the ratings are only given to give a *qualitative comparison*.

‡ Background implies cell or interferent emission background in emission spectrometry or emission background, molecular interferent background, or source scatter background in luminescence spectrometry.

§ Strong components are intense spectral lines or bands which are readily detectable above noise with an SLS method.

¶ Weak components are spectral lines or bands which are barely detectable above noise with the SLS method.

¶ Unmodulated background consists of flame emission background in AM flame atomic fluorescence spectrometry, of flame emission background, continuum scatter, and molecular fluorescence background in WM flame atomic fluorescence spectrometry, etc.

|| Analyte noise limit means the limiting noise is associated with the analyte signal.

\*\* The maximum  $S/N$  in the case of analyte noise limit is determined by analyte flicker noise, i.e. the  $S/N$  will increase with the square root of the measurement time until flicker noise dominates and  $S/N$  becomes constant. It is assumed here that for the SIT and ISIT devices flicker noise dominates for either the 1 s or 30 s measurement times but for the V, amplifier-detector noise completely dominates for the 1 s measurement time and partly dominates at the 30 s time.

integration of charges due to radiative signals in the target of the image device is apparent.

In Table 7, a comparison of the relative  $S/N$  ratios in emission and luminescence spectrometry for several image devices, an image dissector, and a good quality photomultiplier under several noise limiting conditions is given.

### III.C. SAMPLE MODULATION

Sample modulation, SM, was discussed above in Section III.A. However, this rather unique approach to analysis [9,10] requires some specific comments. In SM, the sample and blank are repetitively measured for  $n$  equal time periods each, and so unmodulated flicker noise sources, e.g. flame background in atomic fluorescence flame

[9] M. MARINKOVIĆ, and T. J. VICKERS, *Anal. Chem.* **42**, 1613 (1970).

[10] V. MOSSOTTI, F. N. ABERCROMBIE, and J. A. EAKIN, *Appl. Spectrosc.* **25**, 331 (1971).

spectrometry, continuum scatter or molecular band interferents in atomic fluorescence flame spectrometry, etc., will be reduced as the modulation frequency,  $f_{\text{mod}}$ , increases and the measurement system's noise bandwidth,  $\Delta f$ , decreases, i.e. the flicker factor,  $\xi_{ai}$  (see Part I) is related to  $\Delta f/f_{\text{mod}}$  by

$$\xi_{ai} \propto \sqrt{\frac{\Delta f}{f_{\text{mod}}}} = \sqrt{\frac{2t_0}{2nt_0}} = \sqrt{\frac{1}{n}} \quad (\text{III.C.1})$$

where  $t_0$  is the observation time of sample or blank per cycle and  $n$  is the number of sample-blank cycles. As the number of sample-blank cycles,  $n$ , increases,  $\xi_{ai}$  decreases inversely with  $\sqrt{n}$ . There is an upper limit for  $f_{\text{mod}}$  and therefore for  $\Delta f/f_{\text{mod}}$ , i.e. the time to change mechanically from sample to blank with no memory effects, and so  $f_{\text{mod}} \lesssim 10 \text{ Hz}$ . Thus SM may not be as effective in removing noise as WM modulation which requires twice the number of measurements (see Fig. 1). In addition in SM, an "ideal" blank, i.e. one containing everything in the sample except the analyte, must be prepared and used.

### III.D. WAVELENGTH MODULATION

Wavelength modulation, WM, was discussed above in Section III.A. but because of special advantages of this unique approach [11–13], several comments are needed. In WM, all flicker noise sources which are present "on" and "off" the analyte measurement wavelength are reduced, i.e.  $\xi_{ai} < \xi_{di}$ . If the samples and standards are identical in all respects, except for the analyte, then WM corrects the signal level for unmodulated signal components and reduces flicker noises due to these sources. Because WM can involve the mechanical movement of a small refractor plate or mirror in the optical train of a spectrometer, it is possible to obtain higher modulation frequencies, e.g. 100 Hz, than in SM (but lower than in AM); therefore, because  $\xi_{ai} \propto \sqrt{\Delta f/f_{\text{mod}}}$  as in equation III.C.1,  $\xi_{ai}$  can be made smaller than for the corresponding noise in SM. Of course, in luminescence spectrometry, any analyte emission signals must be corrected for by a separate "source off" measurement (see Fig. 1). If line interferents are present, WM will result in an erroneous analyte signal and increased noise, whereas in SM, assuming the line interferent is present in sample and blank, the analyte signal level will be correct but the noise is still degraded.

### III.E. PROCESSING OF SPECTRAL INFORMATION [6]

These are four major means of processing spectral data. These are: SLS—sequential linear scan, whereby a single slit spectrometer scans the wavelength region of interest at a linear rate; SSS—sequential slew scan, whereby the spectral components of interest are examined for any desired period of time with the time required to slew from one component to the next being negligible compared to the measurement time; MC—multichannel-detector systems, whereby the spectral information from more than one spectral component is acquired simultaneously and independently, although the spectral data may not be analyzed or readout simultaneously; and MX—multiplex methods, whereby the spectral information is encoded in the frequency domain. In the MX methods, more than one spectral component may strike the detector at any given time; in Fourier transform spectroscopy, FTS, optical signals are encoded, e.g. with a Michelson interferometer, to produce signals at different audio frequencies and a Fourier Transform (FT) is needed to decode the resulting interferogram; in Hadamard transform spectroscopy, HTS, a multislit cyclic mask is placed at a series of positions in front of the detector to allow certain combinations of spectral components to reach the

[11] R. C. ELSEY and J. D. WINEFORDNER, *Anal. Chem.* **44**, 698 (1972).

[12] W. SNELLEMAN, *Spectrochim. Acta* **23B**, 403 (1968).

[13] W. SNELLEMAN, W. C. RAINS, K. W. YEE, H. D. COOK, and O. MENIS, *Anal. Chem.* **42**, 394 (1970).

detector; a fast Hadamard Transform (HT) is needed to decode the complex signal array.

The  $S/N$  ratio for any MX method differs in two major ways from those for SLS, SSS, and MC: first each spectral component is measured effectively half the total (analysis) measurement time for all spectral components,  $t_M$ , i.e.  $t_M/2$  whether an FTS or an HTS system is used\*; second all spectral components within the measured wavelength interval  $\Delta\lambda$  contribute to the noise. For example, if two spectral lines are being measured, e.g. a weak Mn line and an intense Mg line, then shot and flicker noise due to the intense Mg line can greatly reduce the  $S/N$  due to the weak line. Because shot noises are independent, the background shot noise for an MX system is simply

$$N_{BS} = \sqrt{\sum_{l=1}^{l=p} \frac{t_M}{2} R_{BL}} \quad (\text{III.E.1})$$

where the summation is over all  $p$ -spectral components and  $R_{BL}$  is the emission background count rate at spectral component  $l$ . Similar equations apply to shot noise due to other sources of radiation within the spectral range of  $\Delta\lambda$ . Flicker noises are more complex because the addition of the noises with respect to wavelength and with respect to time depend upon the noises and add linearly (dependent) or quadratically (independent). Assuming that flicker noises of a given type, e.g. background emission in flame, background scatter in flames, molecular luminescence in flames, etc., are dependent with respect to wavelength and time, and assuming  $p$ -spectral intervals and  $p$ -time (measurement) intervals, then for emission or luminescence spectrometry

$$N_{XF} = \left(\frac{2^{x/2}}{2}\right) t_M \sqrt{\left(\sum_{l=1}^{l=p} \xi_{Xl} R_{Xl}\right)^2} \cong \frac{2^{x/2}}{2} t_M p \xi_{Xl} R_{Xl} \quad (\text{III.E.2})$$

where  $X$  is emission background in emission and luminescence spectrometry or continuum scatter or continuum interference in luminescence spectrometry, and where  $x = q, r, \text{ or } u$  for the cases of continuum background in emission or luminescence spectrometry, of continuum scatter in luminescence spectrometry, and of continuum luminescence interference in luminescence spectrometry. The right hand expression in equation III.E.2 occurs if all  $p$ -spectral components have approximately the same intensity. If the background flicker noises were temporally dependent but spectrally independent, e.g. lines of different elements in flame emission spectrometry, then

$$N_{XF} = \left(\frac{2^{x/2}}{2}\right) \frac{t_M}{p^2} \sqrt{\sum_{l=1}^{l=p} (\xi_{Xl} R_{Xl})^2}. \quad (\text{III.E.3})$$

There are no obvious cases of flicker noises which would be temporally and spectrally independent and so no expression will be given. For the case of line emission, luminescence, scatter, etc., the flicker noise is given by

$$N_{yF} = \frac{t_M}{2} \xi_y R_y \quad (\text{III.E.4})$$

where  $y$  represents the line radiative process.

The analytical usefulness of MX methods in the u.v. visible-near i.r. regions where photon detectors are used is minimal because of radiative flicker noises and background shot noises which result in a serious reduction of  $S/N$  from all but the strongest spectral components, i.e. a *multiplex disadvantage* exists, and  $S/N$  with the MX method will be less than  $S/N$  with the SLS method. In the i.r. region where detection noise predominates, a significant  $S/N$  advantage exists for MX over SLS, which is called a

\* The  $t_M/2$  factor has been used by other (see references in Ref. [5]) and will be used here. However, for a fairer comparison, the factor should be  $t_M/8$  for FTS and  $t_M/4$  for HTS [14].

[14] R. TREFFERR, *Appl. Opt.* **16**, 3103 (1977).

Table 8. Relative signal-to-noise ratios with optical measurement systems in emission and luminescence spectrometry\*†

Condition	SLS	SSS	MC	MX
1. Quantitative analysis				
a. Few (5 or less) spectral components				
(1) Strong (or weak) components‡ (detector noise limit)	2 (or 1)**	4 (or 3)	5 (or 5)	5 (or 5)
(2) Strong (or weak) components‡ (background§ shot noise limit)	2 (or 1)	4 (or 3)	5 (or 5)	1 (or 0)
(3) Strong (or weak)‡ components (background§ flicker noise limit)	2 (or 1)	2 (or 1)	2 (or 1)	0 (or 0)
(4) Strong (or weak) components‡ in presence of strong components (component shot noise limit)	2 (or 1)	4 (or 3)	5 (or 5)	3 (or 0)
(5) Strong (or weak) components‡ in presence of strong components (component flicker noise limit)	5 (or 5)	5 (or 5)	5 (or 5)	2 (or 0)
b. Many (6 or more) spectral components				
(1) Same as a(1)	2 (or 1)	3 (or 2)	5 (or 5)	5 (or 5)
(2) Same as a(2)	2 (or 1)	3 (or 2)	5 (or 5)	1 (or 0)
(3) Same as a(3)	2 (or 1)	2 (or 1)	5 (or 5)	0 (or 0)
(4) Same as a(4)	2 (or 1)	3 (or 2)	5 (or 5)	2 (or 0)
(5) Same as a(5)	5 (or 5)	5 (or 5)	5 (or 5)	1 (or 0)
2. Qualitative analysis (measurement of spectra)	5	3¶	3¶	5

\* All optical components are assumed to be identical. The emission source in emission spectrometry and the excitation source-sample cell in luminescence spectrometry are also identical. The image devices: vidicon, V, silicon intensified target vidicon, SIT, and intensified silicon intensified target vidicon, ISIT are assumed to be "state of the art" devices, i.e. similar to those used by Princeton Applied Research, Princeton, NJ, in their Optical Multichannel Analyzer. The photomultipliers: conventional photomultiplier and image dissector, ID, photomultiplier are also assumed to be "state of the art" devices, e.g. similar to the EMI 6256B photomultiplier and the EMR 658 (EMR Photoelectric, Princeton, NJ). The image devices, V, SIT, and ISIT are assumed to be used in essentially the CW mode (except for AM of the device with respect to the upper and lower halves of the target). The ID and PM devices are assumed to be used in the AM or WM modulation modes.

† The rating is 5 (highest  $S/N$ ), 4 (next highest  $S/N$ ), ... 1 (poor  $S/N$ ), 0 (not analytically useful  $S/N$ ). Ratings have only qualitative meaning; quantitative comparisons between ratings have no absolute meaning but rather are useful only in relative terms.

‡ Modulated background consists of flame background in AM flame emission spectrometry, of luminescence background due to impurities, solvents, etc. in AM molecular luminescence spectrometry, and of source induced background (scatter, molecular fluorescence) in atomic fluorescence flame spectrometry. Image devices can be used for qualitative analysis but are limited in atomic spectrometry because of the need for about 500 channels/25 nm whereas in molecular spectrometry of species in the condensed phase can be covered with about 500 channels/100 nm.

§ The relative  $S/N$  for the integration type image devices, i.e. V, SIT, and ISIT are given for 1 s and 30 s measurement times whereas the relative  $S/N$  for non-integration type devices, PM and ID are given for 1 s integration times (integration is via a photon counter) only.

¶ An SSS system approaches an SLS system if one programs the SSS to stop at each spectral interval. This is not an analytically useful case of an SSS system, however.

|| A MC device can be either a direct reader or an image device. A direct reader can *not* be used for measurement of molecular spectra except for discrete components but can be used for predetermined atomic lines.

\*\* Values in parentheses refer to weak components.

*multiplex advantage.* No multiplex advantage would ever result for MX over MC assuming equivalent optical and detection systems are used. The SSS method would be expected to approach the MC method as long as few spectral components are measured and to approach the SLS method for many spectral components.

The SLS, SSS, and MC methods differ only in the time available for measuring each spectral component assuming that a given time of measurement exists for the measurement of all spectral components in both the blank and sample and assuming identical instrumentation in all other respects. The  $S/N$  expressions in Table 1 apply here except that the measurement times vary. For example, assuming a total measurement time of all spectral components of  $t_M$  is available for the sample and blank, then  $t_M/2$  is available for the sample and a corresponding time  $t_M/2$  is available for the blank. Thus, if there are a total of  $p$ -spectral components in the wavelength range of interest, i.e.  $\Delta\lambda = \lambda_u - \lambda_l = p\Delta\lambda_m$  where  $\Delta\lambda_m$  is the spectrometer bandpass, then the total measurement times for each spectral components in the SLS, SSS, and MC methods are

$$t_m = \frac{t_M}{p} \quad \text{for SLS,} \quad (\text{III.E.5})$$

$$t_m = \frac{t_M}{r} \quad \text{for SSS,} \quad (\text{III.E.6})$$

where  $r$  is the number of spectral components to be measured, where  $r < p$ , and

$$t_m = t_M \quad \text{for MC.} \quad (\text{III.E.7})$$

For the MX case,

$$t_m = t_M/2. \quad (\text{III.E.8})$$

Table 9. Examples of real experimental cases where expressions in Table 3 apply

Emission spectrometry (excitation via collisions, chemical reactions*, and other non-radiational means)
Flame† atomic spectrometry
Plasma† atomic spectrometry (Plasma = d.c.-arc, a.c.-spark, RF-ICP, MW-CCP, etc.)
Flame† molecular spectrometry (e.g. C <sub>2</sub> , OH, CH, PO, CaOH, SrOH, BaCl, etc.)
Luminescence spectrometry (excitation via radiation)
Flame† atomic fluorescence (luminescence) spectrometry
Flame† molecular fluorescence (luminescence) spectrometry
Furnace† atomic fluorescence (luminescence) spectrometry
Gas phase atomic‡ luminescence spectrometry
Gas phase molecular‡ luminescence spectrometry
Condensed phase‡ molecular luminescence § spectrometry

\* Chemical reactions resulting in excitation-emission result in chemi-luminescence.

† These cases involve an emission background typical of the cell itself.

‡ These cases do *not* contain an emission background and so all  $R_B$  terms in the  $S/N$  expressions can be omitted. Typically, these systems are measured at room temperature or lower. However, these systems or the other luminescence systems, do contain source induced background, such as scatter and molecular luminescence of the cell environment.

§ Typically this method is called fluorimetry if it involves fluorescence radiation and phosphorimetry if it involves phosphorescence radiation. The other cases could also be so named. Fluorescence involves spin allowed transitions and phosphorescence involves spin forbidden transitions.



In Table 8, a comparison of the relative  $S/N$  ratios in emission and luminescence spectrometry for the four optical measurement systems (SLS, SSS, MC, and MX) for several limiting noise conditions is given.

### III.F. USE OF SIGNAL-TO-NOISE EXPRESSIONS IN ANALYTICAL EMISSION AND LUMINESCENCE SPECTROMETRY

The  $S/N$  expressions in Table 1 with definitions of terms in Table 1, 3, 4, and 5 (also Table 2, Part I) allow estimates of  $S/N$  ratios for the most important situations in analytical emission and luminescence spectrometry. No attempt will be made here to do this as it would increase overwhelmingly the length of this manuscript, and, in addition, such information is or will be available in publications [5–7]. In Tables 2, 6, 7, and 8 general comparisons are given with respect to the effect of modulation, source pulsing and detector gating, image detectors vs photomultiplier detectors, and optical measurement methods upon noises and signal-to-noise ratios. These tables allow the reader to compare on a general basis the influence of various major parameters on the signal-to-noise ratio. Combination of parameters and small changes of parameters are often more subtle and can only be evaluated by careful calculations. In order for the reader to apply more readily the expressions and parameters in the above tables to real experimental situations in analytical emission and luminescence spectrometry, refer to Table 9 for typical real cases.