

Comparison of Signal-to-Noise Ratios, Part 2

E. Voigtman

Department of Chemistry
University of Massachusetts - Amherst
710 N. Pleasant St.
Amherst, MA 01003-9336

e-mail: voigtman@chem.umass.edu

(Received November 19, 2007)

Abstract

It has been shown that previously published [1] probability density functions (PDFs) for several common signal-to-noise ratio (SNR) definitions are simply minor algebraic variants of the noncentral t distribution- based PDF results recently published by Nadarajah and Kotz [2]. The previously published, but unevaluated, integral expression for the PDF of quotients of SNRs has been shown to be in excellent quantitative agreement with Monte Carlo results. Furthermore, it has been shown that the same integral expression also yields the PDF for quotients of relative standard deviations (RSDs) and the PDF for quotients of simple detection limits. The latter was validated by comparison with detailed Monte Carlo simulations, with the result that accurate expectation values and detection limit 95% confidence intervals were obtained. As a consequence, a major step has been taken toward the goal of being able to compare simple detection limits on a fair basis and being able to perform a statistical test, precisely analogous to a standard F test, to determine whether a given pair of experimental detection limits are plausibly from the same chemical measurement system with the same measurement system parameters and measurement protocol.

Introduction

In 1997, I published a paper [1] in which the PDFs of three commonly used SNR definitions were derived, along with the PDF for the relative standard deviation (RSD). These PDFs were shown to be in excellent agreement with detailed Monte Carlo simulation results, and then an expression was derived for the quotient, defined as R , of two independent, identically distributed (*iid*) SNRs [1, eqn 12]. It was stated at the time that “Lack of a closed-form expression for the PDF for $\bar{x}/s$ effectively guarantees that quotients of two such ratios are cumbersome multiple integrals, as in eq 12, which are very time consuming to process numerically. Therefore, it was decided to bypass eq 12 until more computing power becomes available and instead use Monte Carlo techniques to generate accurate histographic approximations of the desired R PDF.”

Recently, Nadarajah and Kotz [2] have demonstrated the important result that the three SNR variant definitions considered previously, and that of the RSD as well, are all fundamentally based on the noncentral t distribution [3, 4]. Although it has been known in the statistics literature at least as far back as 1940 [5] that the coefficient of variation (*i.e.*, the RSD) was based on the noncentral t distribution, this connection was not known in analytical chemistry and Nadarajah and Kotz have done a service to the profession by explicating this matter. They go on to state “Often, in the chemistry literature, tables of critical values of quotients of experimental SNRs are obtained by Monte Carlo simulation, see *e.g.* Voigtman (1997). We feel that this is unnecessary because, as explained below, a better treatment could be provided by what is known in the statistics literature.” They then derived the PDF expressions for SNR , SNR' , SNR_e , and RSD (see below for definitions of these 4 variates), and a formidable expression [2, eq 20] for the PDF of two independent noncentral t variates. They did not present evidence to substantiate the latter expression, which is a double infinite summation of Gauss hypergeometric functions.

Given the central importance of SNRs and RSDs in analytical chemistry and related measurement sciences, and the obvious, but subtle, relationship between RSDs and the most commonly used simple limit of detection definitions, *i.e.*, those of the form ks_{blank}/b , it is of interest to know how the previous results compare with those of Nadarajah and Kotz. Specifically, how well do the previous PDFs agree with those based on the noncentral t distribution and, now that more computing power has become available, how well does the previous expression for the R PDF actually work? Answering these questions is important for another reason as well: since SNRs and RSDs are reciprocally related, quotients of RSDs

are governed by the same equation, with appropriate attention paid to degrees of freedom. Furthermore, quotients of detection limits (of the simple form given above) are also governed by the same equation as that for quotients of RSDs. Hence, all three problems fall if any one falls and this “hat trick” is what is demonstrated below.

Background

It is assumed that N independent samples are chosen from $N: \mu, \sigma$, i.e., from a Gaussian distributed population having population mean (μ) and population standard deviation (σ). Further, it is assumed that $\mu \ll \sigma$, for SNRs, and $\mu \ll 4\sigma$, for RSDs. The sample mean ($\bar{x}$), sample standard deviation (s) and sample standard error (s_e) are computed from the N replicates in the customary fashion, where $s_e = s/N^{1/2}$ and the population standard error (σ_e) is $\sigma/N^{1/2}$. The degrees of freedom (ν) are $N-1$ and the biased sample standard deviation (s') is $(\nu/N)^{1/2}s$.

With these assumptions, the experimental SNR and RSD definitions are as follows:

$$SNR \equiv \bar{x} / s \quad (1)$$

$$SNR' \equiv \bar{x} / s' \quad (2)$$

$$SNR_e \equiv \bar{x} / s_e \quad (3)$$

$$RSE \equiv s_e / \bar{x} \equiv 1 / SNR_e \quad (4)$$

and

$$RSD \equiv s / \bar{x} \equiv 1 / SNR \quad (5)$$

where RSE in eq 4 is defined as the relative standard error. The PDFs of these five variates are given in Table 1 and all are from [2], except for the PDF of RSE, which was trivially derived from that of SNR_e .

Table 1. Probability density functions for several SNR and RSD variates.

u	$p_u(u)$
$u \equiv SNR \equiv \bar{x} / s$	$N^{1/2} t(uN^{1/2} \nu, \delta)$
$u \equiv SNR' \equiv \bar{x} / s'$	$\nu^{1/2} t(u\nu^{1/2} \nu, \delta)$
$u \equiv SNR_e \equiv \bar{x} / s_e$	$t(u \nu, \delta)$
$u \equiv RSE \equiv s_e / \bar{x}$	$u^{-2} t(u^{-1} \nu, \delta)$
$u \equiv RSD \equiv s / \bar{x}$	$N^{1/2} u^{-2} t(N^{1/2} u^{-1} \nu, \delta)$

Table 2 gives the previously described PDFs [1], plus a newly derived analogous PDF for RSE. The α , K , β , γ and u expressions in Table 2 are substituted, as necessary, in the following master equation [1, eq 10]:

$$p_{\alpha}(\alpha) = K \int_0^{\infty} u^{\nu} e^{-\beta u^2 + \gamma u} du \quad (6)$$

Table 2. Previously published PDFs for several SNR and RSD variates.

α	K	β	γ	u
SNR	$\frac{1}{\sigma^{2\nu+1} 2^{(\nu-1)/2} \Gamma(\nu/2) \pi^{1/2}} e^{-(\nu+1)\mu^2/2\sigma^2}$	$\frac{\nu + (\nu+1)\alpha^2}{2\sigma^2}$	$\frac{(\nu+1)\mu\alpha}{\sigma^2}$	s
SNR'	$\frac{(\nu+1)^{(\nu+1)/2}}{\sigma^{\nu+1} 2^{(\nu-1)/2} \Gamma(\nu/2) \pi^{1/2}} e^{-(\nu+1)\mu^2/2\sigma^2}$	$\frac{(\nu+1)(1+\alpha^2)}{2\sigma^2}$	$\frac{(\nu+1)\mu\alpha}{\sigma^2}$	s'
SNR_e	$\frac{\nu^{1/2}(\nu+1)^{(\nu+1)/2}}{\sigma^{\nu+1} 2^{(\nu-1)/2} \Gamma(\nu/2) \pi^{1/2}} e^{-(\nu+1)\mu^2/2\sigma^2}$	$\frac{(\nu+1)(\nu+\alpha^2)}{2\sigma^2}$	$\frac{(\nu+1)\mu\alpha}{\sigma^2}$	s_e
RSE	$\frac{\nu^{1/2}\alpha^{\nu-1}}{\sigma_e^{\nu+1} 2^{(\nu-1)/2} \Gamma(\nu/2) \pi^{1/2}} e^{-\mu^2/2\sigma_e^2}$	$\frac{1 + \nu\alpha^2}{2\sigma_e^2}$	$\frac{\mu}{\sigma_e}$	$\bar{x}$
RSD	$\frac{\nu^{1/2}(\nu+1)^{1/2}\alpha^{\nu-1}}{\sigma^{\nu+1} 2^{(\nu-1)/2} \Gamma(\nu/2) \pi^{1/2}} e^{-(\nu+1)\mu^2/2\sigma^2}$	$\frac{\nu+1 + \nu\alpha^2}{2\sigma^2}$	$\frac{(\nu+1)\mu}{\sigma^2}$	$\bar{x}$

Comparison of the PDFs in Tables 1 and 2 requires numerical evaluation of the noncentral t distribution and numerical integration of eq 6. Likewise, for R defined as

$$R \equiv SNR_2 / SNR_1 = (\bar{x}_2 / s_2) / (\bar{x}_1 / s_1) \quad (7)$$

the previously given PDF for R [1, eq 12]

$$p_R(R) = \int_0^{\infty} SNR_1 \left[\int_0^{\infty} s_1 p_{s_1}(s_1) p_{\bar{x}_1}(s_1 \cdot SNR_1) ds_1 \right] \times \left[\int_0^{\infty} s_2 p_{s_2}(s_2) p_{\bar{x}_2}(s_2 \cdot R \cdot SNR_1) ds_2 \right] dSNR_1 \quad (8)$$

must also be numerically integrated (see below).

Experimental

Extensive Monte Carlo calculations were performed to test the PDFs in Tables 1 and 2 and eq 8. All simulations were performed using the author's *LightStone* simulation software libraries together with the *Extend* simulation program that runs it (*Imagine That, Inc., San Jose, CA, USA*, www.imaginathtatinc.com). The *LightStone* and *Extend* combination runs on both *Windows*-based PCs and on *Macintosh* computers. The present work was carried out on several *iMacs* (*Apple, Inc., Cupertino, CA, USA*). The *LightStone* software,

relevant information concerning *Extend*, and the simulation models described below, are available for free, with full, annotated source code, at the author's web site:

www.chem.umass.edu/~voigtman/LightStone/.

For evaluation of the noncentral t distribution, the version given by Keeping [4, eq 8.12.1] was programmed into a *LightStone* block, with one typographical error correction:

e^{-nk^2/t^2} should be $e^{-nk^2/2t^2}$. Four of the PDFs in Table 2 were already in *LightStone*, so all that was necessary was to add the PDF for RSE and program eq 8 into a *LightStone* block. All of the Monte Carlo histograms described below contained 10^7 independent results, in 400 bins.

Results

A. Comparing histograms with the PDFs in Tables 1 and 2

Figure 1 shows how the histograms were generated for each of the SNR and RSD variates in Tables 1 and 2. For each of 10^7 simulation steps, in ten simulations of 10^6 steps each, values of SNR and RSD were computed and binned into histograms. From the SNR variates, SNR' and SNR_e variates were computed, exactly as shown, and then binned. Similarly, RSE variates were computed from the SNR_e variates and binned. The time required to run the simulations was 195 seconds.

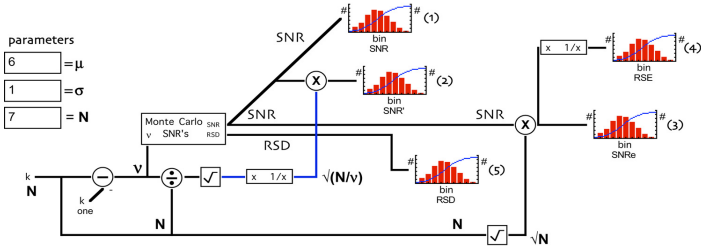


Fig 1: Monte Carlo simulation model for the generation of 10^7 event histograms for SNR, SNR' , SNR_e , RSD and RSE.

Figure 2 shows the histograms (markers only) for SNR, SNR' and SNR_e . Each histogram was overplotted with its PDF from Table 1 and also with its PDF from Table 2 and it is immediately apparent that the pairs of PDFs cannot be visually distinguished. By computing quotients of PDFs, of the form $\text{PDF}_{\text{Table1}} / \text{PDF}_{\text{Table2}}$, it was found that the maximum deviation from unity, for comparisons in the regions where the PDFs were visibly above the zero baseline, was less than 0.5 parts per billion (ppb). The cause of this excellent agreement is simple: Keeping's expression for the PDF of the noncentral t distribution is based on the Airy function $Hh(k)$ [4, eq 8.12.2]:

$$Hh(k) \equiv \int_0^{\infty} (u^{\nu} / \nu!) e^{-(u+k)^2/2} du \quad (9)$$

so the PDFs in Table 2 are simply algebraic variants of those based on Keeping's integral expression of the noncentral t distribution.

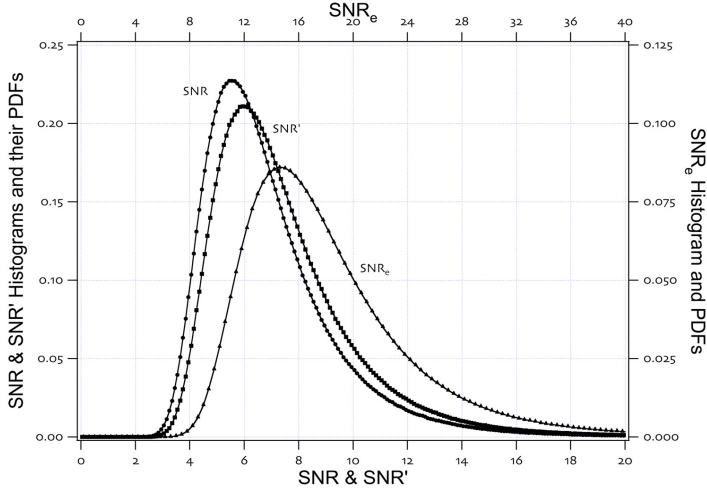


Fig. 2: Plots of the 10^7 event SNR , SNR' , SNR_e histograms produced by the simulation in Fig 1, each overplotted with both of its corresponding PDFs from Tables 1 and 2.

Figure 3 shows the results for the RSD and RSE histograms and, as for the SNRs, each histogram was overplotted with its PDF from Table 1 and also with its PDF from Table 2. For quotients of the form $PDF_{Table1} / PDF_{Table2}$, the maximum deviation from unity, for comparisons in the regions where the PDFs were visibly above the zero baseline, was less than 0.9 ppb .

Given the excellent agreement with the detailed Monte Carlo results, it is clear that Nadarajah and Kotz properly derived the PDFs for the SNR and RSD variates under consideration, as did the present author, though without having any idea that they were fundamentally related to the noncentral t distribution.

One immediate advantage of knowing that the SNR PDFs are based on the noncentral t distribution is that the moments of the noncentral t distribution are readily available [3, 6]. Thus Table 2 in [1] is supplanted by the following equation [3]:

$$E[\bar{x} / s] = \left(\frac{\mu}{\sigma} \right) \left(\frac{\nu}{2} \right)^{1/2} \frac{\Gamma((\nu-1)/2)}{\Gamma(\nu/2)} \quad \text{for } \nu > 1 \quad (10)$$

which corrects minor errors at $\nu = 2, 500$ and 700 , and a bigger one at $\nu = 1$, where the expectation value simply does not exist. More importantly, though, eq 8 makes it possible to entirely eliminate the previous SNR ratio tables and to directly compute risks, rather than having to settle for the limited risk values in the tables. This is demonstrated in the next section.

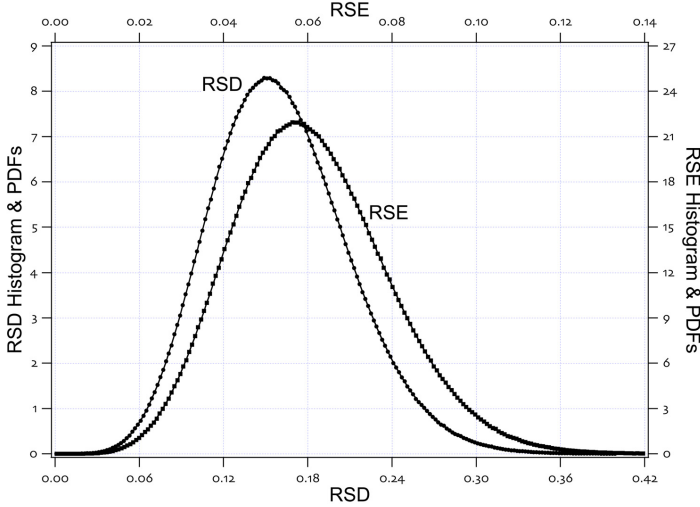


Fig. 3: Plots of the 10^7 event RSD and RSE histograms produced by the simulation in Fig 1, each overplotted with both of its corresponding PDFs from Tables 1 and 2.

B. Comparing SNR quotient histograms with eq 8

Figure 4A shows the Monte Carlo model used to generate quotients of SNRs of the form

$$R \equiv SNR_2 / SNR_1 \equiv (\bar{x}_2 / s_2) / (\bar{x}_1 / s_1) \quad (11)$$

Two representative situations are presented, denoted as Case 1 and 2. For Case 1, a single Gaussian distribution was used to obtain the requisite SNRs. Specifically, 7 replicates were chosen from $N:0.4,0.04$ and used to compute SNR_2 , another 7 replicates were chosen and used to compute SNR_1 , and then R was computed. This was done 10^7 times and the results were binned into a histogram block. This scenario is precisely analogous to the null hypothesis situation in a standard F test in that what is of interest is knowing how far from unity R can be before it becomes unlikely that only a single distribution has been sampled.

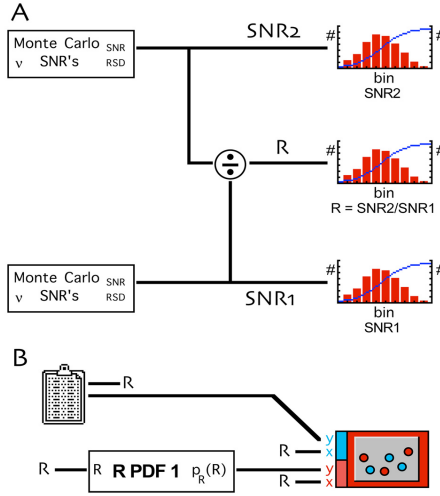


Fig 4: A) Monte Carlo simulation model for the generation of 10^7 event histograms for quotients of SNRs (as shown) or RSDs. B) Simulation model that computes the PDF for the quotient of SNRs (or RSDs) and overplots with SNR (or RSD) histogram results.

Case 2 was more complicated in that two different Gaussian distributions were used to obtain the requisite SNRs from which the 10^7 R variates were computed and binned. In this case, the distribution from which SNR_2 variates were computed was $N: \mu_2, \sigma_2$, with $\mu_2 = 1$, $\sigma_2 = 0.07$, and $N_2 = 3$ replicates, and the distribution from which SNR_1 variates were computed was $N: \mu_1, \sigma_1$, with $\mu_1 = 0.31$, $\sigma_1 = 0.04$, and $N_1 = 4$ replicates.

Figure 4B shows the block ("R PDF 1") that implemented eq 8. The required inputs for the block, aside from R values, were the four population parameters μ_2, σ_2, μ_1 , and σ_1 , and the numbers of replicates, N_2 and N_1 . Since eq 8 involved three integrals with infinite upper limits, the block also allowed for user-specification of the necessarily finite upper limits. These were simply multiples, typically by factors of 5 - 15, of $\mu_1/\sigma_1, \sigma_1$, and σ_2 , in left to right order in eq 8. This flexibility was important due to the long tails of the SNR distributions, particularly at low degrees of freedom. The integration itself was performed with a simple forward Euler algorithm.

Figure 5 shows the results for the two situations described above. For Case 1, with the taller histogram and overplotted R PDF, the agreement between the histogram results and the R PDF was excellent and it is evident that the mode is significantly below unity, *i.e.*, the ratio of population SNRs. From the histogram, the expectation value of R , $E[R]$, was 1.1059

and the central 95% confidence interval (95% CI) was $0.40 - 2.42$. Figure 6 shows how the R PDF was numerically integrated to obtain the cumulative distribution function (CDF), which resulted in a 95% CI of $0.42 - 2.44$, and how $E[R]$ was computed to be 1.1059 . The agreement between expectation values and CIs was excellent and, with the CDF in hand, it is immediately obvious that risks may be computed for any given experimental R value, *e.g.*, for this particular case, the probability that R exceeds 2 happens to be 6.0%. Thus the previously published tables are no longer necessary, exactly as Nadarajah and Kotz suggested was desirable [2].

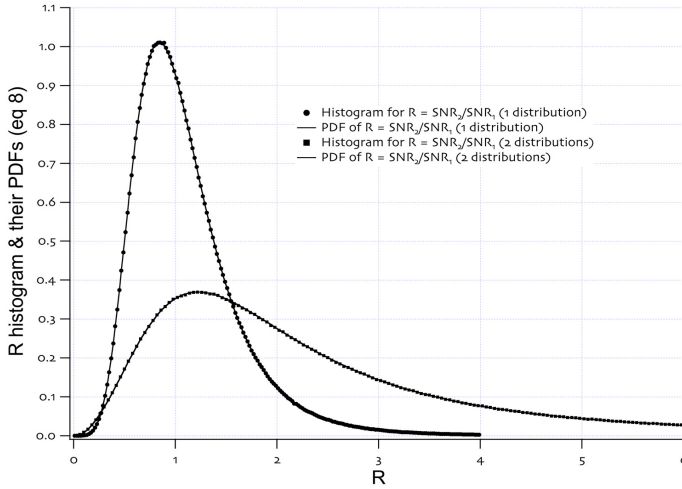


Fig. 5: Plot of two 10^7 event SNR ratio histograms produced by the simulation in Fig 4A, overplotted with their corresponding PDFs computed via the model in Fig 4B.

Figure 5 also shows the histogram results and the R PDF for Case 2 and again the agreement was excellent. As expected, the mode was clearly below 1.8433 , which is the ratio of population SNRs: $(1/0.07)/(0.31/0.04)$. For this case, $E[R]_{\text{histogram}} = 3.02$ and $E[R]_{\text{eq 8}} = 3.00$, so the expectation values differ by less than 1%. There is also a small difference in confidence intervals, since $95\% \text{ CI}_{\text{histogram}} = 0.44 - 11.6$ and $95\% \text{ CI}_{\text{eq 8}} = 0.48 - 11.7$.

C. Comparing RSD quotient histograms with eq 8

A difficulty that arises with RSDs is that they are not intrinsically censored, *i.e.*, nothing prevents a given experimental $\bar{x}$ from being arbitrarily close to zero, thereby causing the RSD to be unbounded. For this reason, expectation values of RSDs cannot exist, as is well known. Furthermore, as Koopmans *et al.* proved [7], neither can confidence intervals

exist unless some constraint is imposed on $\bar{x}$ relative to σ . Traditionally, this is done by assuming $\mu \geq 3\sigma$ [8], or $\mu \geq 4\sigma$ [3, p. 143], as assumed above. Nevertheless, it should be remembered that this does not afford absolute protection against small values of $\bar{x}$ and confidence intervals for RSDs can only be approximations [3].

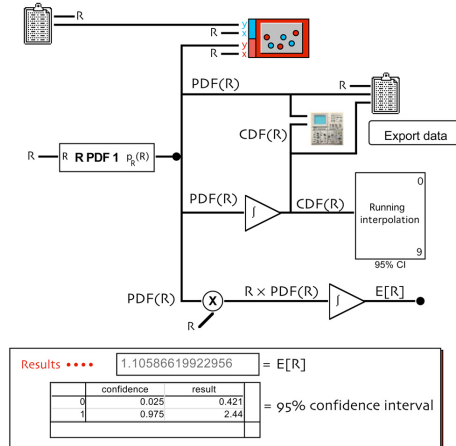


Fig. 6: Simulation model showing how expectation values and confidence intervals are computed for ratios of SNRs. This also applies for ratios of RSDs and simple detection limits.

From the reciprocal relationship between SNRs and RSDs, an immediate consequence is that

$$R \equiv \frac{SNR_2}{SNR_1} \equiv \frac{\bar{x}_2 / s_2}{\bar{x}_1 / s_1} = \frac{s_1 / \bar{x}_1}{s_2 / \bar{x}_2} \equiv \frac{RSD_1}{RSD_2} \quad (12)$$

so ratios of RSDs are fundamentally governed by the same equation as ratios of SNRs, *i.e.*, eq 8. Thus no separate testing was necessary. A much more important consequence, however, is the fact that ratios of simple detection limit variates, *i.e.*, of the general form ks_{blank}/b , where b is the ordinary least squares (OLS) slope of a linear calibration curve, must be distributed in the same fashion as ratios of RSDs. Accordingly, the next step was to generate 10^7 event histograms of quotients of simple detection limits and compare with the PDF computed via eq 8. This is demonstrated next.

D. Comparing LOD quotient histograms with eq 8

Although simple detection limits of the type given above are a variety of RSD, they have a major advantage over ordinary RSDs in that they have finite expectation values and confidence intervals, if b is the OLS slope of a linear calibration curve and the measurement noise is Gaussian. This has been explained in considerable detail elsewhere [9], so it suffices to say that, because the single-sided t test of the slope provides an intrinsic censorship of slopes that are small relative to their standard errors, simple detection limits must have finite upper and lower limits. This fact then guarantees that the moments and confidence intervals exist.

Figure 7A shows the Monte Carlo model used to generate 10^7 quotients of simple detection limits of the form

$$Q \equiv L_1 / L_2 \equiv (k_1 s_{blank,1} / b_1) / (k_2 s_{blank,2} / b_2) \quad (13)$$

where k_1 and k_2 are “coverage” factors, b_1 and b_2 are OLS calibration curve slopes, and $s_{blank,1}$ and $s_{blank,2}$ are sample standard deviations of the analytical blank. Two representative situations are presented, denoted by Case 1 and 2. For Case 1, the same chemical measurement system (CMS) was used to obtain the requisite detection limits in eq 13 above. Again this is analogous to the null hypothesis situation in a standard F test. For this case, the CMS was assumed to be linear, without systematic error, and had $\beta(\text{true slope}) = 2$, $\alpha(\text{true intercept}) = 1$, and homoscedastic, Gaussian noise with $\sigma = 0.1$. There were 6 evenly spaced standards ($X_i = 1, 2, \dots, 6$), $k_1 = 3 = k_2$, and $s_{blank,1}$ and $s_{blank,2}$ were separately computed from two independent sets of 5 blank replicates each, with new blank replicates for each of the 10^7 pairs of calibration curves. The simulation required 574 seconds on an *iMac 17*.

Case 2 was considerably more complicated in that two different linear CMSs were used to obtain the requisite detection limits from which the 10^7 quotients were computed and binned. In this case, the “numerator” CMS, giving L_1 detection limits, had the following parameters: $\beta_1 = 2$, $\alpha_1 = 1$, $\sigma_1 = 0.1$, $M_1 = 1$ (see below), $N_1 = 6$ standards ($X_i = 1, 2, \dots, 6$), $s_{blank,1}$ was estimated as the sample standard error about (OLS) regression, and $k_1 \equiv t_{0.05,4} \eta_1^{1/2}$, where $t_{0.05,4}$ was the critical t value for 95% confidence and 4 degrees of freedom (≈ 2.13185) and

$$\eta_1^{1/2} = [M_1^{-1} + N_1^{-1} + \bar{X}_1^2 / S_{xx,1}]^{1/2} \approx 1.36626 \quad (14)$$

Thus, $k_1 \approx 2.91266$. The “denominator” CMS, giving L_2 detection limits, had the following parameters: $\beta_2 = 3.3$, $\alpha_2 = 0.5$, $\sigma_2 = 0.23$, $M_2 = 1$ (see below), $N_2 = 8$ standards ($X_i = 1, 2, \dots$,

8), $s_{blank,2}$ was estimated as the sample standard error about (OLS) regression, and $k_2 \equiv t_{0.05,6} \eta_2^{1/2}$, where $t_{0.05,6}$ was the critical t value for 95% confidence and 6 degrees of freedom (≈ 1.94318) and

$$\eta_2^{1/2} = [M_2^{-1} + N_2^{-1} + \bar{X}_2^2 / S_{xx,2}]^{1/2} \approx 1.26773 \quad (15)$$

Therefore, $k_2 \approx 2.46343$ and $k_2 / k_1 \approx 0.845767$.

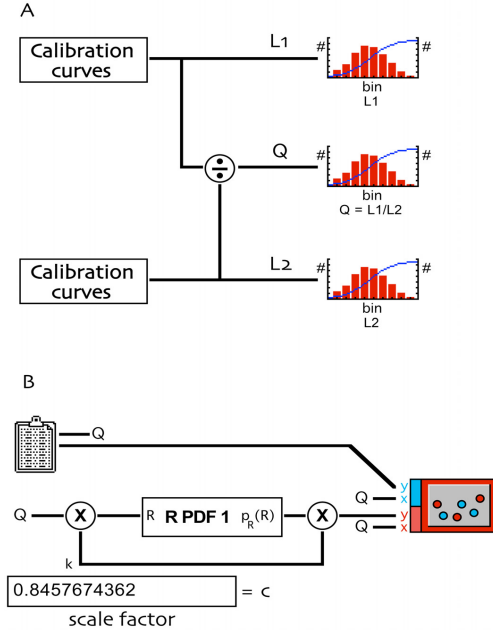


Fig. 7: A) Monte Carlo simulation model for the generation of 10^7 event histograms for quotients of simple detection limits of the form ks_{blank}/b . B) Simulation model that computes the PDF for the quotient of detection limits and overplots with LOD quotients histogram results.

Since eq 8 is directly applicable to quotients of SNRs, and since detection limits typically involve additional scale factors, *e.g.*, coverage factors, provision must be made for the situation in Case 2 above, where $k_1 \neq k_2$. This was done by dividing the independent variate (Q) by k_1/k_2 and also dividing the PDF by the same factor. This follows because, if x is a random variate with PDF $p_x(x)$, and $y = cx$, where c is a positive constant, then the PDF of y is $p_y(y) = (1/|c|) \times p_x(y/c)$ [10]. In the present case

$$p_Q(Q) = (k_1 / k_2)^{-1} p_R(Q / (k_1 / k_2)) = (k_2 / k_1) p_R(k_2 Q / k_1) \quad (16)$$

This equation is directly implemented in Fig 7B and the resulting $p_Q(Q)$ PDF is shown as being plotted with the histogram of Q variates.

A second consequence of eq 8 having been derived for quotients of SNRs is that the parameters necessary in eq 8 must be identified with corresponding parameters relevant to the CMSs. For the four population parameters, this is straightforward: $\mu_1 = \beta_1$, $\mu_2 = \beta_2$, $\sigma_1 = \sigma_{blank,1}$, and $\sigma_2 = \sigma_{blank,2}$. For calculation of $s_{blank,1}$ and $s_{blank,2}$ from direct replicate measurements of the analytical blank, the N_1 and N_2 values are simply the respective numbers of replicate blank measurements. However, if $s_{blank,1}$ and $s_{blank,2}$ are estimated by the sample standard error about regression (s_r) or by the standard error of the intercept (s_a), then equivalent values of N_1 and N_2 must be used. These are given by $N_{equivalent,1} = N_{standards,1} - I = \nu_1 + I$, and $N_{equivalent,2} = N_{standards,2} - I = \nu_2 + I$. For Case 2 above, $N_{equivalent,1} = 6 - I = 5$ and $N_{equivalent,2} = 8 - I = 7$.

Figure 8 shows the results for the two situations described above. For Case 1, with the shorter histogram and overplotted Q PDF, the agreement between the histogram results and the Q PDF was excellent and the mode was below unity, as expected.

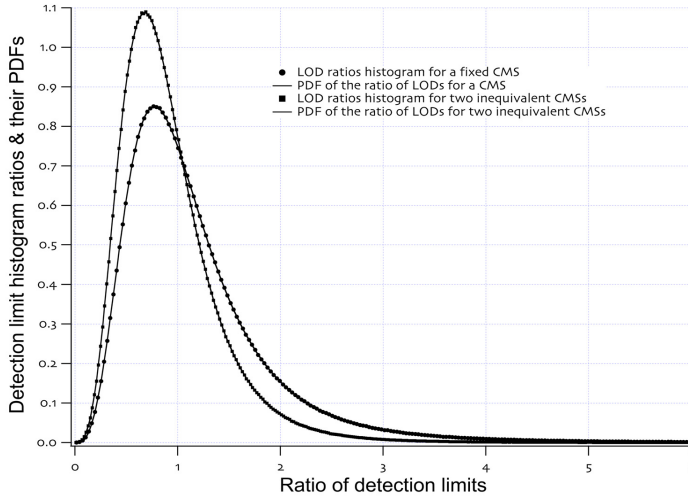


Fig. 8: Plot of two 10^7 event LOD ratio histograms produced by the simulation in Fig 7A, overplotted with their corresponding PDFs computed via the model in Fig 7B.

From the histogram, $E[Q] = 1.178$ and $95\% \text{ CI} = 0.31 - 3.08$. The Q PDF was numerically integrated as per Fig 6, yielding $E[Q] = 1.176$ and $95\% \text{ CI} = 0.34 - 3.12$. The agreement between expectation values and CIs was excellent. Figure 8 also shows the histogram results

and the Q PDF for Case 2 and again the agreement was excellent. As expected, the mode was clearly below 1.3939, which is simply $(\beta_1/\sigma_1)/(\beta_2/\sigma_2)$. For this case, $E[Q]_{\text{histogram}} = 0.918$ and $E[Q]_{\text{eq 8}} = 0.917$. Similarly, $95\% CI_{\text{histogram}} = 0.27 - 2.11$ and $95\% CI_{\text{eq 8}} = 0.29 - 2.13$. Again, the agreement between expectation values and CIs was excellent.

Discussion

Shortly after publishing a paper [11] on the statistical properties of several variant simple detection limit instantiations, Montville and Voigtman extended that work to the case of quotients of such detection limits. An expression other than eq 8 was derived and preliminary results, which included direct comparison of theory, Monte Carlo simulations and experimental detection limits obtained for thousands of calibration curves, was presented as a poster [12]. Further work, based on Montville's Ph.D. dissertation [13], is currently being written up for publication. However, there were computational difficulties with that work which were never fully resolved, although reasonably effective workarounds were found.

In the results presented above, agreement between the Monte Carlo results and eq 8 has been shown to be excellent and, similarly, agreement between the respective confidence intervals and expectation values has generally been excellent or close to it. However, the integration routine employed (forward Euler) is the most primitive of all integration algorithms, having only the advantages of being trivially simple in both concept and implementation. The resulting inefficiencies are such that relatively large numbers of integration steps (e.g., hundreds or thousands) are required for each integral in eq 8, which, aside from being time consuming, can cause numerical problems, especially for small values of σ .

It is possible to work around this problem by suitable scaling of σ values and other standard tactics, but, ultimately, a better solution would be replacement of the integration algorithm with one that is more robust and time efficient and this is currently under investigation. Therefore, it is probably wisest to conclude that eq 8 provides the correct PDFs for quotients of SNRs, quotients of RSDs, and quotients of simple detection limits, but there is much room for improvement in the matter of accurately and efficiently obtaining numerical results from it. Another option is to investigate the performance of the equation derived by Nadarajah and Kotz (vide supra), and this, too, is currently under investigation.

Conclusions

It has been shown that previously published PDFs for several variant SNR definitions, plus that of the customary RSD [1], are simply minor algebraic variants of the elegant results recently published by Nadarajah and Kotz [2], who demonstrated that all of the PDFs were fundamentally based on the noncentral t distribution. The previously published, but unevaluated, integral expression for the quotient of two SNRs, eq 8 above, was shown to be in excellent quantitative agreement with quotients of SNRs obtained by detailed Monte Carlo simulations, even when the SNRs were computed from samples from different populations and with different degrees of freedom. It was shown that quotients of RSDs also have PDFs given by eq 8, and this immediately lead to recognition of the important result that quotients of simple detection limits must also have PDFs given by eq 8, with suitable identification of the relevant necessary parameters and degrees of freedom. This latter conclusion was also substantiated by detailed Monte Carlo simulations and both expectation values and 95% detection limit confidence intervals were given, with excellent agreement between the Monte Carlo results and the results obtained by numerical integration of eq 8.

As a consequence of eq 8 giving the PDFs for ratios of SNRs and also for ratios of RSDs, there is no need for tables of critical values for comparison purposes. In particular, the SNR ratio tables previously published [1] are now supplanted by use of eq 8, as has been demonstrated. With regard to ratios of detection limits, tables never would have been viable because of the large number of possible variations in calibration parameters. Thus, knowing that eq 8 gives the PDF for such ratios is a significant step toward the goal of being able to compare simple detection limits on a fair basis and being able to perform a statistical test, precisely analogous to a standard F test, to determine whether a given pair of experimental detection limits are plausibly from the same CMS. It is hoped that the above results will prove useful to the analytical community.

Acknowledgements

I thank S. Nadarajah and S. Kotz [2] for inspiration for the present work.

References

- [1] E. Voigtman, Comparison of Signal-to-Noise Ratios, *Anal. Chem.* **69** (1997) 226 - 234.
- [2] S. Nadarajah, S. Kotz, Computation of Signal-to-Noise Ratios, *MATCH Commun. Math. Comput. Chem.* **57** (2007) 105 - 110.
- [3] N. L. Johnson, S. Kotz, N. Balakrishnan, *Continuous Univariate Distributions, Volume 2*, second ed., John Wiley & Sons, New York, 1995, p. 513.
- [4] E. S. Keeping, *Introduction to Statistical Inference*, Dover, Mineola, NY, 1995, p. 190.
- [5] N. L. Johnson, B. L. Welch, Applications of the Non-central t-Distribution, *Biometrika* **31** (1940) 362 - 389.
- [6] D. B. Owen, A Survey of Properties and Applications of the Noncentral t-Distribution, *Technometrics* **10** (1968) 445-478.
- [7] L. H. Koopmans, D. B. Owen, J. I. Rosenblatt, Confidence Intervals for the Coefficient of Variation for the Normal and Log Normal Distributions, *Biometrika* **51** (1964) 25 - 32.
- [8] A. T. McKay, The Distribution of the Estimated Coefficient of Variation, *J. Royal Stat. Soc.* **94** (1931) 564 - 567.
- [9] E. Voigtman, Limits of Detection and Decision, Part 4, *Spectrochimica Acta Part B*, accepted for publication November 12, 2007 (to be published in a special honor issue dedicated to J. D. Winefordner). DOI: 10.1016/j.sab.2007.11.014
- [10] A. Papoulis, Probability, *Random Variables, and Stochastic Processes*, second ed., McGraw-Hill, New York, 1984.
- [11] D. Montville, E. Voigtman, Statistical Properties of Limit of Detection Test Statistics, *Talanta* **59** (2003) 461-476.
- [12] D. Montville, E. Voigtman, Comparison of Limits of Detection and Associated Statistics, *2006 Winter Conference on Plasma Spectrochemistry*, Tucson, AZ, January 8-14, 2006.
- [13] D. J. Montville, Statistical Properties of Limits of Detection and their Quotients, Ph.D. Dissertation, University of Massachusetts - Amherst, 2007.