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# Fundamental noise in three chromatographic detectors<sup>☆</sup>

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## Abstract

Counting statistics are used to estimate the minimum theoretical noise of three chromatographic detectors, by assuming that the standard deviation of their baselines equals the square root of their primary chemical events. These primary events are taken to be the observed generation of photons in the flame photometric detector, the emission of  $\beta$  rays in the electron-capture detector, and the formation of ion pairs in the flame ionization detector. The theoretically estimated and the experimentally observed noise agree in every case. This suggests that baseline noise in the three particular detectors is due, predominantly if not exclusively, to random processes involving the atomic structure of matter: therefore, it cannot be further reduced.

## 1. Is there a minimal noise?

What causes chromatographic noise? The question has many answers; too many, in fact, to consider within a short manuscript. A more tractable question may be: What is the minimal detector noise? Or, differently put: What is the inherent, the unavoidable, the smallest possible part of the short-term baseline fluctuations we call noise? And: How does this fundamental noise compare with the experimentally measured one?

Good reasons exist for asking this question. Often, improvement in the signal-to-noise ratio ( $S/N$ ) is achieved by decreasing noise rather than by increasing signal. However, if the actual

noise is already close to the theoretical limit (and if it has already been smoothed to the maximum allowable extent), little is to be gained by attempting to suppress it further. Besides, knowing something about the nature of noise may turn out to be mechanistically interesting as well as analytically helpful.

In chromatographic detectors whose baselines derive from chemical reactions, these reactions must indeed contribute to noise—the question is only to what fraction of the total. The simplest unavoidable noise contribution is surely the one based on the atomic structure of matter. Detector reactions, as all chemical (or nuclear) events, are *random* at the molecular level. This implies that the standard deviation of their rate (and hence the noise of the baseline if no other source of variation is present) can be described as a square-root function of the time interval over which it is being observed. The generation of photons by chemiluminescence in the flame photometric detector (FPD), the emission of  $\beta$

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particles by the radioactive foil in the electron-capture detector (ECD), and the formation of ion pairs by chemiionization in the flame ionization detector (FID) would certainly qualify as such primary, random events.

The three detectors mentioned (FPD, ECD and FID) all play prominent roles in chromatography. Much has been, and continues to be published on and about them (e.g. [1]). Since we happened to have at our disposal representative models of all three detectors, we thought it interesting to take a look at their noise characteristics. This the more because we had previously used these three detectors in a study of root-mean-square (RMS) and peak-to-peak noise ( $N_{p-p}$ ) for possible interconversion of different types of detection limits [2].

In this study, we shall attempt to calculate the minimal noise levels of the FPD, ECD and FID as the square root of their (observed) fundamental events. If noise levels thus calculated should agree with experimentally measured ones, noise in the three detectors can be considered random and fundamental (i.e. non-reducible for a given measurement interval). Since various considerations, approximations and limitations are bound to become part and parcel of this attempt, we believe that the necessary equations are best developed and discussed with the help of actual cases and measurements. This will be done in a separate chapter for each detector. Following those chapters, an Appendix will condense the multi-step equation sets to single, compact and user-friendly (though perhaps not as easily ap-

praised) formulae. These formulae can facilitate the evaluation of noise from particular FPDs, ECDs and FIDs—and perhaps other detectors—in the chromatographic laboratory.

## 2. Fundamental noise in the FPD?

We recently attempted to increase the  $S/N$  of a multi-channel FPD [3] by increasing its light throughput. The success or failure of such an attempt depends on the nature of noise [4–6]: in the case of prevalently colored or correlated noise (e.g. flame flicker or chromatographic flow fluctuations) the attempt is likely to fail; in the case of prevalently white or random noise (e.g. photon shot noise) the attempt is likely to succeed. In the latter case, the  $S/N$  should increase with the square root of the light throughput (or the time span, or the number of repetitions).

Consequently, one of the simplest experiments for characterizing FPD noise is to decrease the light throughput from a (constant) flame, while measuring both the photomultiplier tube (PMT) current and the corresponding noise level right down to the dark current. The experiment can be extended to the high-input side by increasing the emissivity of the flame, i.e. by making it larger and hotter. (This also tests whether the flame starts to produce flicker noise at particular flow conditions.)

Fig. 1 shows the result of this experiment.

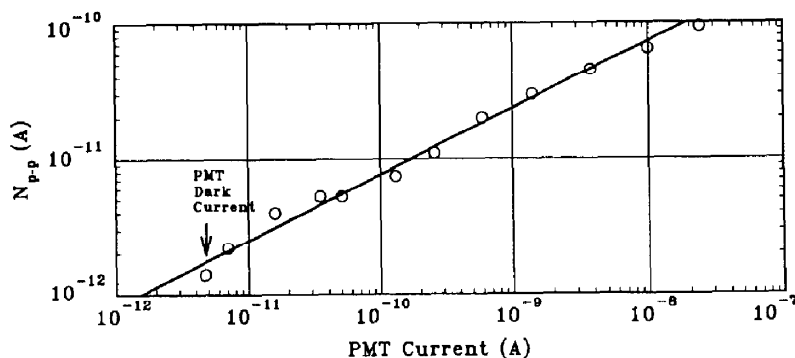


Fig. 1. Peak-to-peak noise vs. current in a Hamamatsu R-374 photomultiplier tube at  $-700$  V; with different light input from a typical FPD flame (see text for details).

About half of the data points were obtained by intercepting different fractions of the constant FPD light beam (with the opaque edge of a variable interference filter wheel that happened to be mounted on one side of the detector [3]); the other half were obtained by observing the light beam through a conventional, filterless FPD channel (mounted on the other side) and adding larger and larger amounts of air to the flame. All data points still fall on *one* line in the log–log plot of Fig. 1; and, as determined by least-squares linear regression, the line has a slope very close to one half. This indicates, as expected, a random process.

It does not, however, identify photon shot noise (really: the temporal randomness in the sequence of observed luminescent flame events) as the main culprit. Other effects could have been responsible for the observed square-root relationship [4–6]. Fortunately, though, circumstantial evidence and a back-of-the-envelope estimate can help to illuminate the case.

From the current and gain of the PMT, it is easy to estimate the number of photons that eject an electron from the photocathode during a given time interval. The square root of this number, as is well known from counting statistics, represents the standard deviation of the random, minimal noise. It can be translated back to current and, after conversion from RMS to  $N_{p-p}$ , can be compared to the experimentally measured noise of Fig. 1. (Note: The  $N_{p-p}$ /RMS ratio changes with the detector, its condition, and the extent of data smoothing [2]. It is possible to measure RMS noise directly but, for ease of experiment and chromatographic relevance, we prefer to measure  $N_{p-p}$ .)

There are also a number of assumptions or approximations hidden in this estimate. While they should not call into question the validity of a result that has only one significant digit, they should at least be mentioned.

The easiest overlooked of these may be the time constant. It hides the transfer function of the filter (or of the electrometer). Given the noise-equivalent-bandpass characteristics of integrating vs. low-pass resistor–capacitor (RC) circuits [4], and given our own, practical experience

in comparing non-weighted moving-window averaging with three-pole RC smoothing [2], we assume the effective integration time to equal roughly 1.7 times the RC constant of the filter. In the present case, the electrometer has a time constant of 0.22 s, hence the effective integration time is estimated to be 0.37 s.

The photon yield for the data points on the left side of Fig. 1 is about 20%, the typical value for the Hamamatsu R-374 PMT [7] receiving light from the leading edge of the variable interference filter (ca. 400 nm). The photon yield for the data points on the right side of Fig. 1 is an average that could, if necessary, be determined from the background spectrum and the sensitivity profile of the PMT; it drops strongly toward the red. The question is, however, whether the photon yield should be included in the noise calculation. While at least five photons strike the photocathode for each ejected electron, only photoelectrically effective ones count—and, therefore, only they need to be counted. *Non-effective* photons might as well have struck photoelectrically inert parts of the arrangement (as indeed the overwhelming majority of photons do). The noise-determining step in any multi-step process is obviously the one with the smallest rate of discrete events (here: the generation of electrons from the photocathode). The decision to exclude the photon yield from the calculation is further supported by the fact that Fig. 1 shows no discernable discontinuity in the mid-shift from mono- to polychromatic photons.

The gain of the R-374 PMT at  $-700$  V (the voltage used in the experiment) is estimated as  $2.0 \cdot 10^4$ . This estimate is based on the specified gain at  $-1000$  V ( $= 5.3 \cdot 10^5$  [7]) and our own measurement of the gain ratio between  $-1000$  and  $-700$  V ( $= 26$ ).

At, say, 1 nA of baseline current (which is a fairly typical value for our operation of the FPD, and allows us to neglect the much lower dark current)

$$1.0 \cdot 10^{-9} \text{ A} \cdot \frac{0.37 \text{ s}}{1.6 \cdot 10^{-19} \text{ As/e}^-} \cdot \frac{1 \text{ } h\nu}{2 \cdot 10^4 \text{ e}^-} \\ = 1.2 \cdot 10^5 \text{ } h\nu$$

hence the RMS noise of photoelectrically effective photons ( $h\nu$ ) is  $(1.2 \cdot 10^5)^{1/2} = 3.4 \cdot 10^2 h\nu$  (for an integration time of 0.37 s). Changing back into current and converting RMS to  $N_{p-p}$  noise—with the conversion factor  $(N_{p-p}/\text{RMS})_{0.37\text{ s}} = 8$  derived from our own measurements [2]—yields

$$3.4 \cdot 10^2 h\nu \cdot \frac{2 \cdot 10^4 e^-}{1 h\nu} \cdot \frac{1.6 \cdot 10^{-19} \text{ As/e}^-}{0.37 \text{ s}} \cdot 8 \\ = N_{p-p} = 2 \cdot 10^{-11} \text{ A}$$

The result of the estimate is, of course, a one-significant-digit number, and it is deliberately written as one. This limitation being understood, the estimated noise compares well (almost too well) with the measured noise of about  $2.4 \cdot 10^{-11}$  A. The accuracy and credibility of both experiment and estimate could obviously be improved, e.g. by using photon counting, boxcar averaging, monochromatic photons (just in case), direct RMS evaluation, etc. However, even the present comparison suggests very strongly that the randomness of luminescent events (computationally: the counting statistic of photoelectrons) is responsible for the overwhelming part of the noise. In other words, this presumably typical FPD produces noise that is random and close to the fundamental minimum.

### 3. Fundamental noise in the ECD?

The chemistry of the ECD has been the object of much study and the subject of much discussion (e.g. [1,8–11]); yet much of it remains poorly understood. What is not in doubt, however, is that the reactions leading to the ECD's response involve  $\beta$  decay and ion-pair generation, followed by the capture of electrons by analyte molecules. There is also little doubt that ion-pair distributions, space charges, and various ion-molecule reactions all influence the detector's behavior. Again, the noise-determining step is the step with the lowest rate of observed discrete events. Since one  $\beta$  ray forms many ion pairs on its travel through the gas phase—i.e., since many more electrons are collected than  $\beta$

rays emitted—the minimal noise characteristics should depend primarily on the number of (effective) radioactive decays.

There exists, however, a problem unique to  $\beta$  decay:  $\beta$ 's are not monochromatic; they roughly conform to an exponential distribution in energy. A further complication is their backscattering from internal detector surfaces, particularly those of high atomic mass [12,13]. The exponential distribution of the ion pair yields from individual  $\beta$ 's must distort and broaden the initially Gaussian distribution of their counts (the intervals between sequential decays that translate into noise amplitudes). Relatively short intervals between  $\beta$ 's of relatively high energy must lead to the largest positive excursions of the baseline; relatively long intervals between  $\beta$ 's of relatively low energy to the largest negative ones.

On the other hand, the ECD may have a built-in damping system in its chemistry (reactions) and physics (space charges): for instance, the second-order ion pair recombination is much faster in regions or during episodes of high ionic density. The ECD thus represents a system far more complex than that of the FPD, in which (effective) photons produce electron avalanches of approximately the same magnitude; or that of the FID, in which unit charges are produced and (nigh immediately and exhaustively) collected.

A cursory simulation suggests that the RMS value of Gaussian noise increases by a factor of somewhere around 1.6 if randomly chosen Gaussian distribution values are multiplied by randomly chosen exponential distribution values within limits reasonable for a real-life  $^{63}\text{Ni}$  system [12]. Of the total specified foil activity (15 mCi), fewer than half of the  $\beta$ 's will have the correct direction for reaching the gas phase (neglecting isotopic purity as well as coating thickness, contamination, and curvature of the foil). We therefore arbitrarily assume one half of all  $\beta$ 's to be "effective" in generating gaseous ion pair trails. This is, admittedly, a very rough assumption.

One of our foils (in the Shimadzu ECD) is relatively new, but the other (in the Tracor

ECD) is beyond its teens —and its originally specified activity appears to have dropped from 15 to 11.9 mCi. (Of the drop, about 2 mCi is due to age, i.e. radioactive decay; the rest, we hope, is due to analytical contamination as opposed to annual clean-up. The apparent value of 11.9 mCi is derived from the ratio of maximal d.c. currents then vs. now, i.e. 3.0 vs. 2.37 nA). Not only is the Tracor ECD relatively old and the Shimadzu ECD relatively young, but the former is a two-chamber unit designed for d.c. and constant-frequency operation, the latter is a one-chamber unit designed for constant-current operation: the two thus provide ample opportunity for a wide-ranging comparison of duly representative measurements.

For the measurements, both ECDs are used in d.c. mode at their  $S/N$ -optimized potential; i.e. the way they would serve conventional d.c. ECD analysis. That means, however, that not all possible current is withdrawn (if it were, no electrons would be left for the analyte to capture, leaving the detector responseless). Yet, the electrons that are not withdrawn (34% in the Shimadzu, 38% in the Tracor) do kinetically and electrostatically influence the sampled system. Given our but rudimentary understanding of this system, such subtle and not-so-subtle effects are impossible to quantify.

It would have been interesting to produce for the ECD a graph similar to the one shown in Fig. 1 for the FPD. That would, however, have called for varying the random input itself, for instance by inserting a cylinder that would cover a variable fraction of the radioactive foil. For obvious reasons we did not want to do that. Although the following estimate of minimal noise must thus rely on a number only (as opposed to a number *and* a square-root relationship), it is at least based on mutually supportive data from two very differently constructed ECDs; ECDs that are, furthermore, monitored by different electrometers of different time constants.

The Shimadzu ECD has a 15 mCi  $^{63}\text{Ni}$  cylindrical foil; it is operated at  $-0.20$  V d.c., resulting in a 1.97 nA (of a maximum 3.0 nA) baseline current; and it makes use of a labora-

tory-made power supply and electrometer of RC time constant = 1.0 s (i.e. of an estimated 1.7 s integration time). Under these conditions, the  $(N_{\text{p-p}}/\text{RMS})_{1.7\text{ s}}$  ratio is close to 5.5 [2].

The “effective” number of disintegrations ( $d$ ) per second, i.e. the number of  $\beta$ 's likely to reach the gas phase, are

$$15 \cdot 10^{-3} \text{ Ci} \cdot 3.7 \cdot 10^{10} \frac{d}{\text{s} \cdot \text{Ci}} \cdot 0.5 = 2.8 \cdot 10^8 \frac{d}{\text{s}}$$

These  $\beta$ 's can produce a maximum current of 3 nA, hence

$$\frac{3 \cdot 10^{-9} \text{ A}}{1.6 \cdot 10^{-19} \text{ As/e}^-} = 1.9 \cdot 10^{10} \text{ e}^-/\text{s}$$

suggesting that, on average, 68 electrons are generated per one  $\beta$ . For an integration time of 1.7 s, the RMS noise, adjusted for the exponential ion-pair yield of  $\beta$ 's, is

$$N_{\text{RMS}} = \left( 2.8 \cdot 10^8 \frac{d}{\text{s}} \cdot 1.7 \text{ s} \right)^{1/2} \cdot 1.6 = 3.5 \cdot 10^4 d,$$

which, when converted to current, pared to the baseline of 1.97 nA, and finally changed to  $N_{\text{p-p}}$  noise, yields

$$\frac{3.5 \cdot 10^4 d}{1.7 \text{ s}} \cdot \frac{68 \text{ e}^-}{d} \cdot \frac{1.6 \cdot 10^{-19} \text{ As}}{\text{e}^-} \cdot \frac{1.97}{3.0} \cdot 5.5 = N_{\text{p-p}} = 8 \cdot 10^{-13} \text{ A}$$

This compares well with the experimental result of 0.6 pA. (Note: here as elsewhere, the calculations are carried out with a larger number of digits; however, only *two* digits are normally shown and the result, for obvious reasons, is represented by a *single* significant digit. If desired, additional digits can be easily obtained by repeating the simple calculation.)

The analogous calculation for the Tracor ECD uses an estimated foil activity of 11.9 mCi and an estimated integration time of 0.17 s for the electrometer's 0.1 s RC time constant. The  $(N_{\text{p-p}}/\text{RMS})_{0.17\text{ s}}$  conversion factor is about 6 [2]. The detector is operated at  $-18$  V at a baseline current of 1.48 nA. Hence the RMS noise equals

$$\left(11.9 \cdot 10^{-3} \text{ Ci} \cdot 3.7 \cdot 10^{10} \frac{d}{\text{s} \cdot \text{Ci}} \cdot 0.5 \cdot 0.17 \text{ s}\right)^{1/2} \cdot 1.6$$

$$= N_{\text{RMS}} = 9.8 \cdot 10^3 d$$

and

$$\frac{9.8 \cdot 10^3 d}{0.17 \text{ s}} \cdot \frac{68 e^-}{d}$$

$$\cdot \frac{1.6 \cdot 10^{-19} \text{ As}}{e^-} \cdot \frac{1.48}{2.37} \cdot 6.0 = N_{\text{p-p}} = 2 \cdot 10^{-12} \text{ A}$$

This compares still reasonably well with the experimental result of 4.5 pA peak-to-peak noise.

No doubt experiments and estimates could both be improved, e.g. by measuring the foil count directly, by carrying out a more precise simulation of the roughly exponential  $\beta$  energy distribution, and by considering electron back-scattering effects in their influence on the root-mean-square calculation of noise, etc. Yet the twin experiments suggest—in unison and, in our opinion, with sufficient congruency—that (clean) ECD noise is predominantly caused by a fundamental process; and that this process is the decay of the radioisotope.

#### 4. Fundamental FID noise?

A pure hydrogen–air flame contains very few ions; the FID baseline current is therefore very low. Jentzsch and Otte [14] mention a value of “ $\leq 0.75 \cdot 10^{-11}$  A for an empty capillary replacing the column [and] obviously dependent on the cleanliness of the gases and the apparatus”. For “spectroscopic” types of flames, Alkemade et al. [15] summarize: “The ionization found is often due to metallic or organic impurities. In pure  $\text{H}_2$  flames some residual ionization close to thermal equilibrium may be found, involving  $\text{NO}^+$  and  $\text{H}_3\text{O}^+$  ions. The latter ion is formed by the recombination reaction  $\text{H} + \text{H} + \text{OH} \rightarrow \text{H}_3\text{O}^+ + e^-$  (see Hayhurst and Telford 1972, 1975)”.

In chromatographic practice, it is nigh impossible to exclude some contamination by carbon and silicon compounds (and occasionally by sodium or copper halides). However, the system may still behave in a fundamental, random

manner. Consequently, rather than maintain our minimalist approach and attempt to design and test the *cleanest* FID possible, we decided to use a just reasonably clean FID (in our case part of a three-detector ECD–FPD–FID combination available from a thesis project), and deliberately dope it with small amounts of typical contaminants: either directly by adding different levels of methane, or indirectly by adding different levels of bleed from a heated Carbowax 20M column to the hydrogen stream (the latter arrangement bypasses and thereby spares the Shimadzu ECD a possibly detrimental exposure to reactive oxygenates from the decomposing column [16]). This may simulate a high baseline; or it may simulate a —*continuously* introduced— analyte. (Note that —typically though not exclusively— the noise of importance to chromatography is the noise of the baseline; the noise of importance to spectroscopy is the noise of the signal.)

Fig. 2 shows the interesting result of this experiment. Increasing the rate of ionization over a decade from that of the “pure” hydrogen–air flame results, indeed, in a *square-root* increase of noise, thereby suggesting a random process. At still higher background levels —i.e. higher than a tenfold increase and thus perhaps beyond acceptable operating conditions of the FID— the noise increases *proportionally* with the current.

If this were a spectroscopic system, one would

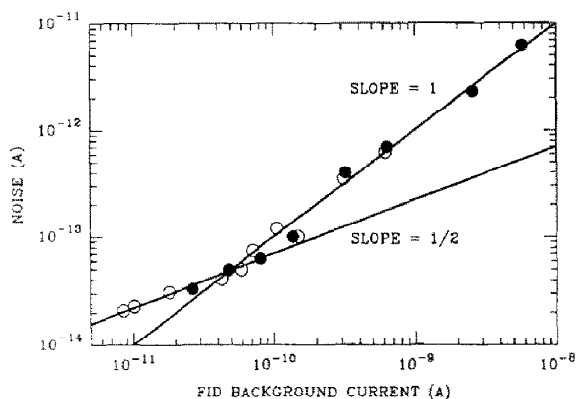


Fig. 2. Peak-to-peak noise vs. current in a flame ionization detector; with different levels of methane, or Carbowax 20M-derived bleed, added to the hydrogen flow. ● = Methane; ○ = Carbowax.

call the latter type of noise “multiplicative” and would typically attribute it to “analyte flicker” [17]. In spectroscopic systems it is indeed common to observe a change-over from additive to multiplicative noise (e.g. from photon shot noise to analyte fluctuation noise) as the signal level increases. A similar change-over appears to occur in the chemiionization system of the FID; a parallelism that could have been predicted.

It would be interesting, nevertheless, to find out what causes this excess noise—spatial or temporal heterogeneity in analyte concentration, perhaps, or influence of the analyte on the geometry or chemistry of the flame—and whether the square-root range can vary among different FID models and/or can be expanded for analytical ends by a change in conditions. However, in the particular context of this study (and, we presume, in the practical context of most chromatographic techniques), this question is of minor importance.

The experiment used the Tracor electrometer of  $RC = 0.10$  s time constant, i.e. of an assumed 0.17 s integration time. The  $(N_{p-p}/RMS)_{0.17\text{ s}}$  ratio equals approximately 6 in this newly constructed FID (which, compared to older conventional FIDs in our possession, is still remarkably free of spikes). The baseline current in the absence of deliberately added column bleed or constantly bled-in analyte is  $8.6 \cdot 10^{-12}$  A; the p-p noise at this point (the lowest data point of Fig. 2) is  $2 \cdot 10^{-14}$  A. (This compares favorably with the noise level mentioned by Jentzsch and Otte, i.e.,  $\leq \pm 5 \cdot 10^{-14}$  A [14]; however, this comparison must remain highly approximate in the absence of any literature information on time constants.)

The number of ion pairs generated within the integration interval is then

$$8.6 \cdot 10^{-12} \text{ A} \cdot \frac{0.17 \text{ s}}{1.6 \cdot 10^{-19} \text{ As/e}^-} = 9.1 \cdot 10^6 \text{ e}^-$$

and  $N_{p-p}$  equals

$$(9.1 \cdot 10^6)^{1/2} \cdot \frac{1.6 \cdot 10^{-19} \text{ As/e}^-}{0.17 \text{ s}} \cdot 6 = 2 \cdot 10^{-14} \text{ A}$$

The estimated magnitude of noise that originates from the randomness of ion-generating

events is thus essentially identical with the value measured in a “clean” FID flame. Although—as in the ECD and FPD cases—experimental accuracy could no doubt be improved, the data are good enough to allow us to presume that most if not all of the FID’s baseline noise is fundamental in character; i.e. that it is due to the atomic nature of matter and that, consequently, it is determined by, and cannot be reduced below, counting statistics.

The fact that this statement applies not only to the FID but also to the ECD and the FPD—i.e. to every one of the detectors tested—is welcome indeed. For one, it highlights a fundamental property that these three (and perhaps more) otherwise disparate chromatographic detectors have in common. Also, this fundamental property quantitatively defines the theoretical noise level. That can prove a practical advantage: it may help the analyst evaluate how well an actual detector is performing, or how clean it is, or how (or whether) the fluctuations of its baseline could be further reduced.

### Acknowledgement

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### Appendix

To facilitate such practical assessments, we have condensed the developed equation sets into single, simple and general formulas. The fundamental noise levels for the three detectors thus are

$$RMS_{\text{FPD}} = \sqrt{\frac{I \cdot e \cdot g}{t}}$$

$$RMS_{\text{ECD}} = I \cdot f_e \cdot \sqrt{\frac{1}{A_{\text{eff}} \cdot Ci \cdot t}}$$

$$RMS_{\text{FID}} = \sqrt{\frac{I \cdot e}{t}}$$

where, again, RMS is the root-mean-square (the

standard deviation  $\sigma$  in case of a Gaussian distribution) of the baseline fluctuations in A;  $I$  is the baseline current in A;  $e$  is the charge of the electron ( $1.6 \cdot 10^{-19}$  As);  $t$  is the integration time of the measurement (the counting time or effective time constant of the acquisition/filter system);  $g$  is the PMT gain at the voltage of the experiment;  $A_{\text{eff}}$  is the effective activity of the ECD foil in Curies (for this study assumed to be roughly one half of the total remaining activity—a number in definite need of refinement);  $C_i$  is the number of disintegrations per second of one Curie ( $3.7 \cdot 10^{10}$ ); and  $f_e$  is a factor that mainly describes the widening of the random-emission RMS noise band by the exponential  $\beta$  energy distribution. (Note: for this study,  $f_e$  is assumed to be roughly 1.6. This number has been confirmed—though only for the ideal mixing of Gaussian and exponential distributions—by a Dalhousie student project in chemometrics [18], which was carried out while this manuscript was under review.

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