

# Non-Poisson Distributions Observed during Counting of Certain Carbon-14-Labeled Organic (Sub)Monolayers<sup>1</sup>

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As shown by the index of dispersion statistic  $s^2/m$ , anomalous narrow statistical distributions have been consistently obtained from counts of  $\beta$  radiation emitted by adsorbed, high specific activity carbon-14-labeled organic (sub)monolayers (1) when first-order desorptions from metal oxide surfaces occur, (2) when adsorbed stearic acid-1-<sup>14</sup>C on certain nongrounded surfaces is counted, and (3) when aluminum foil containing such stearic acid-1-<sup>14</sup>C is charged at a positive potential (e.g., 90 V positive with respect to an adjacent, grounded aluminum "window") for sequential periods of up to 450 min. The markedly low variances, observed with external detectors, were in contrast to "normal" or Poisson-expected values which were invariably obtained using the same equipment when the surfaces had either nonadsorbed radiochemicals or nonevaporating radiochemicals under grounded or negative polarity conditions. Based on a number of individual experiments involving several different counting systems and detectors and representing several thousands of degrees of freedom, *the radioactive decay process observed under these certain conditions is not properly described by the Poisson distribution*. The inconsistency of this phenomenon with known and generally accepted theories of radioactive decay raises serious questions relative to the generality of the independence of radioactive decay events and/or the randomness of emissions.

## Introduction

A cornerstone of modern nuclear physics and fundamental to many uses of radioisotopes, the assumption that radioactive decay events within a given species are independent of each other was first phrased in 1905 when von Schweidler projected the thesis that radioactive decay processes are exponential.<sup>3</sup> The experimental testing of this assumption has invariably involved derivation of statistics of detected radioactive emissions and/or of times between detected emissions followed by comparison of such statistics with those expected for random events. The "proof" of the assumption has thus also involved the often tacit hypothesis that the statistical properties of emissions are directly and necessarily related to the decay process itself, a hypothesis which has proved difficult to verify experimentally but which is reasonable and is generally accepted.<sup>4</sup> [(1s)<sup>4</sup> A discussion of some of the factors relative to the use of external window detectors apropos of the hypothesis.]

If detected radioactive emissions are random and if there are sufficient events for statistical significance, then the statistical distribution of the counts (or of the recorded times-between-emissions) will be closely approximated by the Poisson distribution provided also that the events are rare (a low probability that any single event will occur) and that a single species of isotope is involved (all events have the same probability of occurrence).<sup>5</sup> [(2s)<sup>4</sup> A discussion of an exception (non-Poisson) which is not applicable in the present case. (3s)<sup>4</sup> A short discussion of mother-daughter deviations from the Poisson.]

The converse is also true. If, barring artifactuality, the distribution of detected emissions is statistically *not* of the same population as the Poisson, one or more of the cited conditions must be false.

Detection and counting of the single species carbon-14  $\beta$  particles involving  $1-6 \times 10^3$  counts/min arising from approximately  $3 \times 10^{14}$  carbon-14 atoms per specimen appear to limit the hereinafter detailed cases of low variance to questions involving only independence and randomness, particularly since the several types of equipment employed have invariably exhibited expected variances during reference and/or standard source counting (index of dispersion  $s^2/m = \sim 1.000$ ). [(4s)<sup>4</sup> The remote possibility that carbon-14 might not always be a single species isotope is discussed.]

## Background

Following the projections by von Schweidler that

(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., Mar 29, 1971.

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(3) E. von Schweidler, *Congres Internationale de Radiologie*, Liege, 1905.

(4) Listings of supplemental notes and material appearing in the microfilm edition of this volume of the journal are designated throughout the article with "s" notation, together with a brief comment on the nature of the supplemental material in brackets. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St. N.W., Washington, D. C. 20036, by referring to the code number JPC-72-3603. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche.

(5) R. D. Evans, "The Atomic Nucleus," McGraw-Hill, New York, N. Y., 1962, Chapters 26-28. The text includes references to a number of the prior studies which "verified" the generality of the Poisson.

natural radioactive decay processes are exponential, Rutherford and Geiger tested the distributions of observed  $\alpha$  particles and found them in good agreement with the expectation for random emissions. They therefore concluded that the evidence was in accord with the projection that the events were independent.<sup>6</sup> Many other workers, *e.g.*, Curtiss, subsequently confirmed these observations primarily using  $\alpha$  emitters.<sup>7</sup> Kovarik similarly reported that  $\beta$  emissions also appeared to exhibit random behavior.<sup>8</sup> As recently as 1966, Berkson reported a critical statistical study of times between detected  $\alpha$  emissions and observed no exception to the presumed universality of independent events. He carefully refrained, however, from concluding that his work *proved* the randomness concept pointing out that the particular statistical tests employed might have missed certain deviations from randomness.<sup>9</sup>

In 1924, Kutzner, while studying  $\alpha$  emissions from polonium, consistently observed low values of a variance index (Lexis divergence coefficient) and suggested his results were possibly due to nuclear-nuclear interactions.<sup>10</sup> Even though his findings were subsequently duplicated by Curtiss, the thesis was advanced by others—and apparently it has become firmly held—that the cause of the low values of the index was due to the phenomenon of aggregate recoil rather than to a lack of independence of the events.<sup>11,12</sup> At this time in view of the present work, the possibility that Kutzner did observe a manifestation of non-independence cannot be disregarded.

Despite the Kutzner reports, the independence of radioactive decay events and the resultant applicability of the Poisson distribution appear to be accepted almost universally, and determinations of probabilities in a variety of fields involving radioactive decay depends on the generality of this assumption. Evans<sup>5</sup> states unequivocally "Nuclear processes ... are random in ultimate character."

With the exception of the Kovarik reference,<sup>8</sup> a major portion of the earlier literature references involved studies of  $\alpha$  particle decay. Thus, historically, the development of the concept of the *general* validity of radioactive decay independence and randomness depended in large part on the additional hypothesis that all types of decay processes are alike with respect to the independence-of-events characteristic. This largely unphrased hypothesis does not appear to have been seriously tested in the literature at least with respect to solid experimental evidence.

### Statistical Method

To evaluate experimental data (such as counts resulting from radioactive emissions) for conformance with the Poisson expectation, a number of statistical tests may be used, each one of which tends to examine only particular characteristics of the observed dis-

tributions and none of which, if conformal with the expectation, guarantees that other tests will also be conformal. [(5s)<sup>4</sup> The close approximation of exponential behavior during determinations of exponential constants does not preclude nuclear interactions. (6s)<sup>4</sup> A discussion of the significance of single statistical tests.] The ones used in most of the work reported earlier were the  $\chi^2$  goodness-of-fit test which is a comparison of an observed frequency distribution to a theoretic one and the Lexis divergence coefficient cited earlier. The  $\chi^2$  test is primarily an overall or global test of the distribution, but, as Berkson has shown, the index of dispersion ( $s^2/m$ ) is oftentimes more sensitive.<sup>13</sup>

The index of dispersion statistic ( $s^2/m$ ) is the ratio of the observed variance ( $s^2$ ) to the expectation ( $m$ ) where  $m$  is the best estimate of  $\sigma^2$  for the Poisson; it has been employed in this paper to test the observed distributions of counts obtained from radioactive emissions. The index is calculated as

$$s^2/m = \sum_{i=1}^n (a_i - m)^2 / (DF \times m) \quad (1)$$

$$m = \sum_{i=1}^n a_i / n \quad (2)$$

where  $s^2$  is the variance,  $m$  the mean,  $n$  the number of observations,  $a_i$  the counts per unit time, and DF the degrees of freedom. When the mean does not sensibly change with time,  $DF = n - 1$ . When the "mean" is calculated for each point, as for example in a rapid exponential change,  $DF = n - 2$ .

Within a statistical set, several values of the index may be combined so as to determine an overall value of the index and thereby to determine an overall probability that the observed variance for a series of runs is due to chance alone, as

$$\overline{s^2/m} = [(s^2/m \times DF)_i + (s^2/m \times DF)_j + \dots] / (DF_i + DF_j + \dots) \quad (3)$$

The index is itself variable, a variability about 1.000 which is predictable theoretically as a function of the number of degrees of freedom. Standard tables showing the distribution are readily available.<sup>14</sup>

- (6) E. Rutherford and H. Geiger, *Phil. Mag.*, **20**, 698 (1910).
- (7) L. F. Curtiss, *J. Res. Nat. Bur. Stand., Sect. A*, **8**, 339 (1932).
- (8) A. F. Kovarik, *Phys. Rev.*, **13**, 272 (1919).
- (9) J. Berkson in "Research Papers in Statistics," F. N. David, Ed., Wiley, New York, N. Y., 1966, pp 37-54.
- (10) W. Kutzner, *Z. Phys.*, **21**, 281 (1924); *ibid.*, **44**, 655 (1927).
- (11) L. F. Curtiss, *J. Res. Nat. Bur. Stand., Sect. A*, **4**, 595 (1930).
- (12) Cf. R. W. Lawson, *Nature (London)*, **114**, 121 (1924).
- (13) J. Berkson, *J. Amer. Statist. Assoc.*, **33**, 526 (1938); *ibid.*, **35**, 362 (1940).
- (14) Cf. "Handbook of Tables for Probability and Statistics," 2nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, pp 295-298.

## Monolayers

In this work carbon-14-labeled organic (sub)monolayers adsorbed on activated metal (oxide) surfaces have been prepared by the evaporative deposition of suitably labeled organic compounds using the technique known as Evaporative Rate Analysis (ERA).<sup>15</sup> In this method chemisorption through functional group-surface site interaction is believed to take place at or near the retreating interface of an evaporating liquid cyclopentane solution containing approximately one monolayer equivalent of radiolabeled solute. [(7s)<sup>4</sup> A discussion of the number of molecules adsorbed per unit surface area.] The radiation emitted by the monolayers was then analyzed simply by observing the emissions using an adjacent "window" detector.

In particular, low variances of the detected radiation have been observed involving two types of monolayers, namely (1) desorbing monolayers in which the adsorbed species tends to desorb and to be swept out from under the detector by means of flowing gaseous nitrogen; thus the detected emissions arise almost exclusively from the adsorbed species; and (2) nondesorbing monolayers of stearic acid-1-<sup>14</sup>C under conditions that a positive or adventitious charge is permitted to build on the surface on which the radiochemical is adsorbed.

In each case of the restricted or narrow statistical distributions, the carbon-14 radioisotope was incorporated either within the adsorbed functional group or immediately adjacent to it.

In the case of the desorbing monolayers, the adsorbed material is essentially volatile under the conditions of test (ambient) and in the absence of adsorption evaporates virtually instantaneously. Thus, *e.g.*, 2-ethylbutyric acid-1-<sup>14</sup>C completely evaporates from non-adsorbent surfaces within a period of *ca.* 30 sec. Even when adsorbed on aluminum, it tends to desorb spontaneously. The observed radiation thus decreases with time as the molecules evaporate and as they are swept out from under the detector by the metered stream of nitrogen gas always employed. [(8s)<sup>4</sup> A discussion of the effect of the changing "mean" encountered in desorptions.]

Monolayer desorption phenomena are normally best described by simple first-order kinetics—that is,  $\log y$  vs.  $t$  plots are straight lines over extended periods. In the desorptions so far observed, no other method of data analysis—*e.g.*, linear-linear, log-log, Elovich, etc.—permits such general and extended straight line analysis from run to run or within runs. As a result, the changing values of  $y$  are derived from the equations

$$y = y_0 e^{-kt} \quad (4a)$$

or in  $\ln$  form

$$\ln y = \ln y_0 - kt \quad (4b)$$

by least-squares fitting of the  $\ln a_i$  values, and eq 1

therefore involves a series of  $y_i$  values rather than  $m$  calculated as a constant mean.

In a sense this type of desorption is thus somewhat similar, insofar as activity reaching the detector is concerned, to the decay process of a much shorter half-life radioisotope. For the desorptions described, the apparent half-lives vary downward from approximately 18 hr.

The calculation of the statistical distribution about each linear regression may be made on the basis of the real numbers (as in eq 1) or on the basis of  $\ln$  or  $\log$  values or in combination. In converting from real numbers into  $\log$  values for  $\log y$  vs.  $t$  plots and least-squares fitting, weighting is recommended primarily when orders of magnitude differences of  $y$  are encountered. With relatively small changes (10–20%) as are encountered herein, the differences are of no appreciable significance with respect to the derived "best" line and weighting has not been used herein. [(9s)<sup>4</sup> If any derived line is not the best possible line to describe the actual process, the derived variance statistic must be higher than would otherwise obtain.]

## Experimental Section

**Counting Systems.** Three counting systems based on completely independent design were employed in this work also involving four differing detector models.

System I (used primarily in the desorption experiments) is a commercially available solid state counting and control system marketed under the trade name MESERAN Model 720.<sup>16</sup> The total system comprises an electronic and control section with provision for accurately regulating the flow of gaseous nitrogen over the test surface and between the surface and the detector face, a thin end-window GM detector assembly which also provides for control of the evaporative environment and for reproducible positioning and maintenance of the test surfaces during counting, and a precision dispenser for depositing preformulated test solution (radiochemical and low-boiling cyclopentane solvent) onto the test surface. [(10s)<sup>4</sup> A description of the counting mechanism.]

The primary thin end-window GM tubes (diameter 2.9 cm, 1.4–2.0 mg/cm<sup>2</sup> grounded mica window, halogen quench) were those of Amperex Model 18526. An additional 0.0038 mm (0.15 mil) Mylar shield was provided to reduce system background arising from adsorption of vapor phase labeled molecules; the Mylar protected window was positioned 0.5 to 0.8 cm above the test surface in each case—in the "standard source" counting and in the low variance examples. No anticoincidence circuit was used. The shape of the

(15) Cf. J. L. Anderson, R. A. Baker, and J. F. Forbes, *J. Colloid Interface Sci.*, **31**, 372 (1969).

(16) The MESERAN Model 720 systems are produced and sold by AMETEK/Technical Products, a Division of AMETEK, Inc. Cf. J. L. Anderson, D. E. Root, Jr., and G. Greene, *J. Paint Technol.*, **40**, 320 (1968).

GM pulse appeared identical for both "normal" and narrow distributions. Overall counting efficiencies of 4–7% (including backscatter) of the emitted radiation obtained.

Several different units of this system were employed, and the four referees who carried out desorptions independently also used these systems.

The timing circuit utilizes a Cramer cyclic cam timer equipped with micro switches which were mechanically adjusted to provide the necessary on-off gates for the count totals. Each timer is based on a 60-Hz synchronous motor.

Not available commercially, System II is an integrated circuit advanced prototype of the MESERAN systems equipped with automatic data printout. It employs a timing circuit based on 60 Hz in which all switching is carried out electronically. It expressed all detected counts observed with an Amperex 18536 thin end-window GM tube whose experimentally determined resolution time was less than 100  $\mu$ sec. The detector-surface mechanical equipment was identical with that of System I.

System III is a Nuclear Data Model 1100 1024 multichannel analyzer which was used in the multiscale mode and was equipped with automatic data printout.<sup>17</sup> Count rates were maintained at a level low enough so that no observable loss was apparent. The timing circuit consisted of an external clock based on a crystal oscillator. The mechanical detector-surface setup approximated that used in the earlier experiments but was not identical due to a lack of the same equipment at time of confirmation. Two detectors were employed: a Tracerlab thin end-window organic quench GM tube of less than 100- $\mu$ sec resolution time (experimentally determined) and an anthracene crystal-photomultiplier tube assembly which was operated in the dark and which in one experiment had the Mylar shield removed. These detectors are designated in Table III as ND/GM and ND/A, respectively.

**Substrates.** The aluminum foil employed in this study was kindly supplied by Kaiser Aluminum and Chemical Corp., and consisted of two rolls of "smooth" 3003 aluminum foil of approximately 0.076 mm (3 mil) thickness which reportedly had triglyceride rolling oil residues left on the surfaces and which was in a "hard" or nonannealed condition. Approximately 10  $\times$  10 cm sections of the foil were removed and heated over thermostatically controlled, horizontally positioned cylindrical heaters (10 cm diameter) at 320° for at least 20 min to remove the rolling oil residues and to "activate" the surfaces. The sections were draped over the heater with their parallel, horizontal edges weighted to ensure intimate contact of the central portion with the heater surface. Only the top side (exposed to the laboratory atmosphere) was used for monolayer adsorptions. Following heating each specimen was removed, permitted to cool for a few seconds

to ambient, and then positioned on a vacuum-activated (from below) hold-down stage so that the now dead-soft foil formed a slight concavity into which the test solution was deposited. For the desorptions measurements, the specimens were then used in the hold-down stage following deposition and evaporation of low-boiling solvent cyclopentane by positioning the GM detector and initiating the counting sequence (which also started the gaseous nitrogen flow—ca. 600 ml/min). For the nondesorbing stearic acid-1-<sup>14</sup>C, each specimen was copiously rinsed with cyclopentane and/or trifluorotrichloroethane following evaporation of the deposition solvent. Then the portion of the specimen containing the monolayer (ca. 1.5  $\times$  1.5 cm) was cut out and positioned for counting.

The glass substrates (Table V) were prepared by sectioning the roughened portion of glass microscope slides, cleaning in hot sulfuric acid-dichromate (sample 2) or in hot sulfuric acid-nitric acid (sample 3) followed by copious rinsing with deionized water and drying in the atmosphere for 30 min.

The boehmite surface (Table IV) was prepared by immersing a specimen of the 3003 aluminum in boiling distilled water for 3 min followed by momentary drying at 168°. Then the surface was positioned and examined on the hold-down stage as above.

The nickel surface was prepared by heating a 0.125-mm section of nickel foil (kindly supplied by the General Electric Co.) in the same manner as was used for the aluminum surface (cf. Table IV).

The chromous oxide on steel surface (Table IV), kindly supplied by Kaiser Steel Co., was heated over a Bunsen burner for ca. 30 sec and cooled, and the surface away from the flame was employed for the desorption experiment.

**Radiochemical Test Solutions.** The 2-ethylbutyric acid-1-<sup>14</sup>C, the *N,N*-dimethyl-*N*-*n*-decylamine-1-<sup>14</sup>C, and the 2-cyclohexylethanol-1-<sup>14</sup>C were custom synthesized by Mallinckrodt/Nuclear and had, at time of receipt, no detected impurities, either radio or chemical. Each was dissolved upon receipt in a large volume of cyclopentane, having been dissolved in a smaller volume of the same solvent immediately following synthesis. At least double-distilled from an all-glass column (no greased joints), the cyclopentane had less than 0.5% volatile impurity by gc and nonvolatile residue of less than 1 part in 30 million by ERA.

The specific activities of the three above-mentioned radiochemicals were 60 mCi/mM (1 position essentially carrier-free <sup>14</sup>C) since they were synthesized without dilution from barium carbonate of similar activity. The overall rationale for using such high specific radiochemicals was based on the overall counting efficiencies involving thin end-window GM detectors.

(17) Located at the Special Training Division of Oak Ridge Associated Universities, Oak Ridge, Tenn.

Thus with approximately 5% efficiencies, ethylbutyric acid monolayers of  $6 \times 10^{14}$  molecules/cm<sup>2</sup> (roughness factor of *ca.* 2) emit sufficient  $\beta$  particles to give 8,000–10,000 cpm. Thus with coverages of 0.6 to 0.7 cm<sup>2</sup>, 5000–6000 cpm are customary.

The lower specific activity ethylbutyric acid-1-<sup>14</sup>C was obtained by diluting the previously prepared test solutions with appropriate concentrations of cold ethylbutyric acid (Aldrich) in similarly purified cyclopentane.

The stearic acid-1-<sup>14</sup>C was obtained in benzene solution from Chicago-Nuclear Corp. and had a specific activity of 48+ mCi/mM; following evaporation of the benzene, it was diluted in cyclopentane for the initial experiments but in cyclohexane for those confirmatory ones carried out at ORAU. (Note: The wettability of the stearic acid-1-<sup>14</sup>C–cyclopentane solution was considerably less than that of the corresponding cyclohexane one. Thus no assurance that a similarly deposited monolayer at time of confirmation is available.)

**Monolayer Preparation.** The monolayers of radioactive organic compounds were prepared simply by permitting the radioactive test solutions (*e.g.*, 20  $\mu$ l of ethylbutyric acid-1-<sup>14</sup>C–cyclopentane solution of *ca.* 1 part of radiochemical to 10<sup>5</sup> parts of solvent) to evaporate into the atmosphere following deposition of the liquid onto the suitably positioned heat-activated foil (or other) surfaces.

When less than 60 mCi/mM specific activity radio-material was employed, increased area coverages involving greater volumes of test solutions were used so that the *number* of retained molecules having carbon-14 incorporated in them would approximate those of high specific activity, the total number of retained molecules on a particular surface being a function of the area occupied by each molecule.

**Counting and Statistical Procedures.** The summaries as listed in the several tables include all the desorptions and nondesorbing experiments known to the author and in which statistical distributions have been calculated and in which the particular characteristics (such as the 42+ data point log *y* vs. *t* straight line condition in the desorptions) apply. In all the work so far carried out and reported herein, *no data point* (counts per unit time) has ever been eliminated from a statistical set regardless of the extent of the anomaly of any particular point.

In the cases of the desorptions, counting was invariably initiated by positioning the detector as soon as the solvent visibly disappeared by evaporation. In the cases of the nondesorbing stearic acid monolayers, an initial period of 50 min was routinely used to permit equilibration of conditions prior to the start of the counting sequences.

In the desorptions, end points of the log *y* vs. *t* straight lines were routinely first estimated by plotting

log *y* vs. *t* values on a greatly expanded scale (*e.g.*, 0.01000/5 cm on the log *y* axis) followed by sighting and placing of transparent straight edges to approximate the end points and intercepts. Such sightings were then routinely re-analyzed by at least one other person to reduce the possibility of adverse judgmental selectivity in such allocations. Secondly, the points within each line grouping were least-squares fitted by standard computer programs and the overall index by eq 3 computed so as to include the adjacent lines as well. In cases where the intercepts and/or end points were not completely obvious, one or two points at each end of the major line were then added to and subtracted from the adjacent lines and the statistics recalculated so that a minimal overall index was obtained. Then the *first* line of at least 42+ data points based on the minimum index criterion was used in the analysis. In general, reduced distributions in the lengthy lines (42+) were quite obvious as were the lines; intercepts were normally apparent to within one data point. [(11s)<sup>4</sup> The observed desorptions varied considerably in log *y* vs. *t* patterns from run to run. Illustrations are shown.]

In many cases the desorptions were continued beyond the limits cited in Table III. However the statistical summary includes only the *first* 42+ period lines so that the percentage of the monolayer involved would be relatively consistent.

While every effort was made to arrive at the proper and best line in each desorption by consensus of opinion as well as by computer-based analysis, ultimately the author takes the final responsibility in each case. Such decisions thus represent, to a degree, a judgment factor.

In the nondesorbing experiments, most of the incidental charge and deliberate charge runs were halted after approximately 8 hr although in two much longer times were observed. However to ensure that the summary included only relatively homogeneous conditions, an arbitrary limit *ca.* the first 500 data points in each case has been used. In those shorter runs listed, the runs were interrupted at the end points listed.

## Results

**"Standard Source" Counting.** As a criterion of "normal" equipment performance and using the very same experimental setup in each case as was used later to observe the statistical abnormalities, the three equipment systems were each qualified with respect to the statistical index of dispersion (*s*<sup>2</sup>/*m*) using so-called "standard sources" and/or adsorbed stearic acid-1-<sup>14</sup>C on *grounded* aluminum surfaces. [(12s)<sup>4</sup> A description of the New England Nuclear Corp. "standard sources." ] As shown in Table I not only did the overall statistical index approximate 1.000 with each system but also the variance of the statistic itself was that expected. It is apparent from even a casual inspection of the derived statistics that the values vary above and below 1.000.

Table II (whose values were taken from ref 14 cited above) illustrates the theoretically expected probabilities for these two degrees of freedom (49 and 53) and also the marked tendency to approach a very limited variance as the number of degrees of freedom increases.

Table I

System	Degrees of freedom (DF)	Index $(s^2/m)$	Sources
A. "Standard Source" Counting			
I	1063	1.030	Stearic acid, NENC
II	2546	0.990	Stearic acid, NENC
III <sup>a</sup>	741	0.985	Stearic acid
B. "Standard Source" Distributions of $s^2/m$			
1. System I: NENC Source; DF = 53 <sup>b</sup>			
1.243	1.434	1.056	0.727 1.208 1.415 1.154 1.422
1.022	0.831	1.126	0.893 1.129 1.010 0.890 1.216
0.730	1.024	0.965	1.137 1.122 0.781 0.854 1.210
Mean = 3733		$\frac{s^2}{m} = 1.067$	
2. System II: Stearic Acid on Aluminum (Grounded) DF = 49 <sup>c</sup>			
1.411	0.969	0.916	1.136 0.944 1.052 0.843
1.049	1.030	0.984	1.306 0.685 0.998 0.835
Mean = 5399		$\frac{s^2}{m} = 1.011$	

<sup>a</sup> Including both GM and anthracene-PMT detectors. <sup>b</sup> Based on eight 54-period groups of each of three 200-data period sets and involving three different units of System I. <sup>c</sup> Based on 14 sequential groups of 50-data periods each during 700 min of counting employing System II.

Table II: Expected Variability of the Index of Dispersion<sup>a</sup>

Degrees of freedom	Probability (P), %					
	0.1	1.0	2.5	97.5	99.0	99.9
49	0.4894	0.5906	0.6440	1.4331	1.5290	1.7418
53	0.5050	0.6041	0.6562	1.4151	1.5065	1.7089
100	0.6192	0.7007	0.7422	1.2956	1.3581	1.4945
1000	0.8675	0.8989	0.9143	1.0895	1.1070	1.1440
3000	0.9221	0.9409	0.9500	1.0513	1.0611	1.0817

<sup>a</sup> Data taken from ref 14, pp 297, 298.

**Desorptions.** Table III lists the values of the variance index obtained from the desorptions involving (sub)monolayers of 2-ethylbutyric acid-1-<sup>14</sup>C and encompassing all the desorptions so far examined having at least a 42+ data point log  $y$  vs.  $t$  straight line. Only the statistics of the first such line in each desorption are listed although only in a very few such cases was a second such lengthy line observed within the first 150 data points. The statistics are listed with increasing values of the slope,  $k$ , of the log  $y$  vs.  $t$  line. There appears to be no general relationship of statistical index with slope except for the possibility that at the higher

values ( $k$  greater than 0.00200) the index may approach a more normal index.

In none of the 22 desorptions was an index as high as 1.000 observed. (Note: Of a total of 33 desorptions so far observed and analyzed, 11 did not have a line of at least 42+ data points in length.)

As noted, the referee-run desorptions are listed by the names of the referees. The desorptions employing less than 60 mCi/mM specific activity radiomaterial are noted and do not appear to have as low a statistical index as the others; more work needs to be carried out before definitive conclusions can be drawn in this regard.

Table IV lists the results obtained from three other "desorptions" involving other substrates and/or radiochemicals. These data seem to indicate that the phenomenon of narrow statistical distributions is general for a variety of surfaces and monolayers. No data are available to the author involving these or other materials than those listed. [(13s)<sup>4</sup> Table I (S) includes all the data points obtained for four of the desorptions which are illustrative of the patterns of desorption.]

**Nondesorbing Monolayers.** Adsorbed monolayers of stearic acid-1-<sup>14</sup>C on heat-activated aluminum foil (grounded) have been shown to emit radiation which follows very closely to Poisson expectations (cf. Table I). On the other hand, nongrounded substrates having adsorbed monolayers of stearic acid-1-<sup>14</sup>C exhibit restricted or narrow distributions as are shown in Table V. The identical sample that was described in Table IB and also listed as sample 1a in Table V was further counted using System II after placing the sample on a piece of polyethylene film and thereby effectively isolating it electrically from ground, as listed in sample 1b. The generation of charge was presumably due both to the continuous flow of extremely dry nitrogen gas over the surface during counting as well as the net emission of  $\beta$  particles. The ground on the adjacent end-window of the GM tube was that provided by the metallic flash with which all such tubes are constructed. The observed mean was essentially that observed in the grounded configuration recognizing that differences in geometry presumably occurred as a result of a small change in positioning of the sample relative to the detector.

The same sample was then recounted a second time for 500 min except in this case an additional electrically grounded aluminum foil absorber (ca. 0.0125 mm thick) was placed between the monolayer emitter and the detector window; the mean detected count decreased approximately 60% which is that expected for the absorber. In both cases of nongrounding, the  $s^2/m$  statistic was considerably low over the first 500 min of counting, and in each case during a 300-min sequence (of the 500) the statistic was markedly lower. The similarities are striking.

Samples 2 and 3 of Table V consisted of stearic acid-

Table III: Values of Variance Index for Desorptions

Sample	Limits	Length, min	Av $\Delta C/\text{min}$	Means $y_\alpha, y_\omega$	$k$ in $\log y =$ $\log y_0 - kt$	Index $s^2/m$
Sok	58-147	90	4.5	6797, 6389	0.00030	0.444
1421	34-97	64	3.7	5282, 5047	0.00031	0.695
0814	1-74	74	4.5	5427, 5095	0.00037	0.796
5119	37-89	53	5.1	5850, 5580	0.00039	0.766
0750 <sup>a</sup>	19-64	46	1.8	1656, 1574	0.00048	0.860
0999 <sup>a</sup>	20-97	78	4.9	4442, 4068	0.00049	0.817
0997 <sup>a</sup>	15-58	44	5.6	4960, 4715	0.00050	0.701
0617	46-107	62	5.9	4511, 4146	0.00059	0.732
ND/A1	61-122	62	7.5	4690, 4225	0.00064	0.786
0861 <sup>a</sup>	24-65	42	9.1	6035, 5652	0.00068	0.642
Miranda	7-64	58	8.1	3848, 3381	0.00097	0.915
0734	23-96	74	10.4	4667, 3895	0.00106	0.870
0732	51-118	68	10.5	4730, 4019	0.00108	0.659
0454	1-65	65	11.7	5096, 4335	0.00108	0.638
ND/GM1	1-52	52	14.4	4910, 4163	0.00137	0.457
0299	23-74	52	14.6	4863, 4102	0.00142	0.466
ND/A2 <sup>b</sup>	9-102	94	9.2	3240, 2380	0.00151	0.722
Jennings	34-83	50	10.1	2451, 1947	0.00200	0.624
Pietras	26-70	45	5.0	1042, 817	0.00234	0.658
1429 <sup>a</sup>	40-96	57	14.1	3026, 2222	0.00236	0.972
ND/GM2	55-108	54	11.6	2165, 1533	0.00278	0.766
0453 <sup>c</sup>	9-60	52	34.6	3248-1451	0.00673	0.819

For 1292 degrees of freedom, overall  $\overline{s^2/m} = 0.717$

<sup>a</sup> Low specific activity runs (ca. 6.7-7.5 mCi/mM). <sup>b</sup> 30-sec accumulations; when 9,10; 11,12; etc., were summed and the index recalculated on the basis of 47-min periods,  $s^2/m = 0.709$ . <sup>c</sup> Nitrogen gas saturated with respect to water vapor.

Table IV: Other Substrate Desorptions

Surface	Adsorbate	$s^2/m$	Remarks
(1) Boehmite on 3003 Al (AlOOH)	$\beta$ -Cyclohexylethanol-1- <sup>14</sup> C	0.644 ( $N = 47$ )	200 30-sec accumulations (data points); six slopes: three more-or-less horizontal ones—separated by much more rapid ones—had low index values; the lowest is shown
(2) Nickel (oxide)	<i>N,N</i> -Dimethyl- <i>N-n</i> -decylamine-1- <sup>14</sup> C	0.666 ( $N = 48$ )	The cited low index was for a slope positioned between two others of 1.000 ( $N = 39$ ) and 1.049 ( $N = 43$ ); total $N = 149$
(3) Chromous oxide on mild steel ("tin-free steel")	2-Ethylbutyric acid-1- <sup>14</sup> C	0.515 ( $N = 32$ )	First "lengthy" $\log y$ vs. $t$ straight line

1-<sup>14</sup>C as monolayers on freshly cleaned glass surfaces which had been placed on polyethylene film (2) and on cast sulfur (3) to electrically isolate from the environment. In keeping with the observations of Perkins and MacDonald, 170 min was required before the "mean" settled down to a constant value in (2) and 30 min in (3).<sup>18</sup> [(14s)<sup>4</sup> A short description of the observations.] In both cases the variance about the initial regressions (varying means) appeared low but was not calculated.

Figure 1 is a scatter diagram of counts obtained using System II in the same configuration (with the aluminum absorber in place) as described above in which the identical monolayer on aluminum (Table V, samples

1a-1c) was positioned on polyethylene film and was attached by a thin silver wire (crimped along one side of the specimen) to an external battery pair (two 45-V dry cells in series) and held for 436 min at 90 V + (the first 20 min of which were used for equilibration and counts for which have not been included in the figure or in the statistical summary), then at 90 V - for 580 min and then at 90 V + for a final 60 min. The changes in polarity were accomplished externally without altering the surface-detector relationship. The marked change in the statistical index as a function of the applied potential from 0.846 (90 V +) to 1.088

(18) H. J. Perkins and M. D. MacDonald, *Science*, **138**, 1259 (1962).



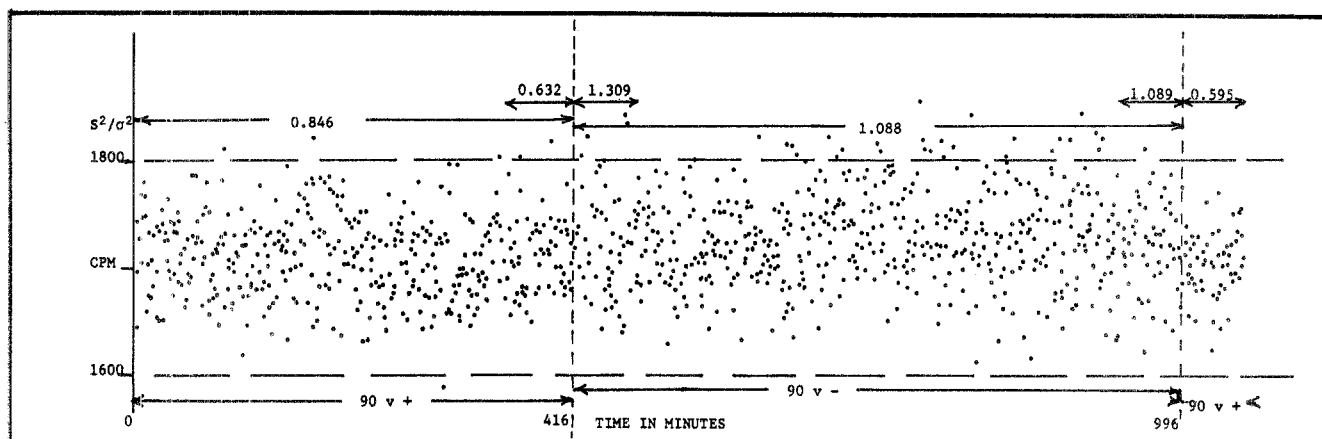


Figure 1. Scatter diagram.

**Table V:** Effect of Adventitious Surface Charge Involving Stearic Acid-<sup>14</sup>C Monolayers

Sam- ple	Mean	Number of data points	$s^2/m$	Remarks
1a	5399	700	1.011	Aluminum surface, grounded
1b	5164	500	0.893	Sample 1a on polyethylene
		300	0.793	A 300 data point sequence of sample 1b
1c	1865	500	0.871	Same as sample 1b; Al ab- sorber
		300	0.818	A 300 data point sequence of sample 1c
2	4080	530	0.862	Glass surface, on polyethylene
3	2326	230	0.854	Glass surface, on cast sulfur

(90 V -) and to 0.595 (90 V +) are indicated on the diagram together with the 60-min statistics just prior to and just following each change in polarity.

The initial mean at 90 V + was 1713 over 416 periods, followed by 1728 at 90 V -, and then by 1707 at 90 V +. In the absence of an artifact, the change in mean from 1713 to 1728 and back to 1707 is statistically extremely unlikely. The standard deviation of the mean for Poisson distributions is defined as

$$\sigma_y = \frac{\sigma}{(n)^{1/2}} \quad (5)$$

Thus, assuming the mean during the negative charge (90 V -) is "normal,"  $\sigma_y = (1728)^{1/2}/(580)^{1/2} = 1.73$ . The mean during the 90 V + conditions is therefore more than nine standard deviations lower than was observed at 90 V -. The extent of this shift is, statistically, even more remarkable than that of the shift of the index of dispersion, but since the detected emissions are  $\beta$  particles, the mean shift is more difficultly separated from the artifactual possibility. No data were observed at zero voltage.

A similar experiment was carried out using the ND/A System III (ORAU) in which the initial 90 V + index

was 0.929 (400 min) and the second 90 V + index was 0.911 (350 min). The change from 90 V + to 90 V - was not as dramatic as is shown in Figure 1 since the "normal" index at 90 V - (450 min) was somewhat less than 1.000, *i.e.*, 0.962. The means changed just as dramatically—from 12,885 to 12,994 and back to 12,828 ( $\sigma = 5.4$ ). The similarity of the initial increase and then larger decrease is, percentage-wise, striking. [(15s)<sup>4</sup> Figures 2 (S) and 3 (S) are histograms of the ( $a_i - m$ ) distributions for the two cases. A marked skewness at + voltage is apparent.]

Table VI lists the statistics ( $s^2/m$ ) showing the effect of positive charge and of incidental charge buildup (believed to be positive in each case) and the total or overall variance index for the group as a whole. To keep the conditions of counting as uniform as possible, only the first series for each run is included. An overall index for a number of runs at 90 V - is also listed for comparison purposes.

**Table VI:** Effect of Adventitious or Positive Charge

Number of of periods	Charge	$s^2/m$	Remarks
1-416	90 V +	0.846	See Figure 2 (scatter diagram)
1-450	90 V +	0.912	
1-350	160 V +	0.877	
1-400	90 V +	0.929	ND/A system
1-500	+ !	0.893	See Table V, sample 1b
1-500	+ !	0.871	See Table V, sample 1c
1-530	+ !	0.862	See Table V, sample 2
1-230	+ !	0.854	See Table V, sample 3
Overall $s^2/m$		0.881	DF = 3339 (+)
		0.989	DF = 2914 (-)

Assuming the absence of all artifactuality, the overall probabilities that the two examples (desorptions and positive charge buildup) are of the same population as that of the Poisson expectation are less than  $10^{-12}$  and  $10^{-8}$ , respectively.



## Discussion

*"Standard Source" Counting.* As listed in Table I, the "standard sources" always appear to exhibit the expected Poisson distributions when counted in bulk (the NENC benzoic acid-7-<sup>14</sup>C reference sources) or when held grounded or at negative potential. Not only are the overall values of the index those which are expected, but the variability of the statistical index of dispersion is also quite similar to that shown in the theoretic probability tables (Table II).

The "normal" or expected statistical behavior of the several "standard sources" is believed to be an excellent test of the proper operation of the equipment used for counting at least with respect to the particular statistical test employed; such a criterion has been adopted.

*Monolayer Desorptions.* The ultimate validity of the log  $y$  vs.  $t$  straight lines with respect to the assumption of first-order behavior—and to the end points of the straight lines in each case—obviously determines the variance statistics from such lines. As mentioned above, many other models were examined including log-log, Elovich, and even linear-linear ones. With the variety of desorptive patterns (*cf.* 11s),<sup>4</sup> only the log  $y$  vs.  $t$  consistently yielded lengthy (*e.g.*, 42+ data point) straight line constructions in a substantial majority of the cases (two-thirds). When the limit is reduced to 35+ data points, more than 90% of the desorptions possess such lines. The assumption of first-order behavior in each case is certainly strengthened by the lengths of the lines and even by the "too good" fit of the data points. The straight line patterns illustrated cannot be improved by the other types of constructions; to use one and only one method for data analysis, the overall generality of the first-order process was thus assumed.

With an average length of straight line of 60 data points, the assumption of the first-order model certainly is not unreasonable. Adding or subtracting a point or two from the ends of any lines does not materially alter the value of the overall index. While the values given in Table III comprise 70% of the total data points, in no case does the major line comprise fewer than 50% of the points listed. [(16s)<sup>4</sup> A discussion of some of the other factors influencing desorptive behavior.]

Since it early became apparent that the restricted statistical distributions (low values of  $s^2/m$ ) constituted an unexplained phenomenon at considerable variance with accepted theories of radioactive decay, four scientists (see acknowledgments) in other parts of the United States were asked to perform similar desorptive measurements using the same type of equipment (System I) and using similar radiochemical and foil as those employed earlier by the author. These referees observed desorptions which were just as restricted and low as those seen earlier. Since the referees did not have the benefit of the cylindrical, thermostatically controlled heaters, flame or oven heating was substituted

to drive off the prior adsorbents and to prepare the surfaces.

*Nondesorbing Monolayers.* The several studies involving monolayers of stearic acid-1-<sup>14</sup>C on surfaces held at electrical potentials above ground (positive charge) illustrate a marked alteration of the statistical behavior caused by a single environmental parameter although in no single case did the anomalous statistical variance approach the extremely low level found in the desorptions.

In many respects the use of the nondesorbing species has significant advantages over the necessarily dynamic conditions of the desorbing monolayers. The identical sample was used time and again in observing the condition of low variance whereas no single specimen was used more than once in the desorption experiments.

Though insufficient statistical evidence is available for definitive assessment, the characteristic low variance did not appear to exist at 1.4 V +, at 30 V +, or even at 800 V +. Whether the phenomenon of non-Poisson character is a function of certain more or less specific voltages—and perhaps of the precise geometry employed, a factor which might affect the electrical force field—is as yet unknown.

In only two cases was the experimental setup of such a nature to permit direct comparison of the means during the 90 V +/90 V – conditions and, in both cases, the means and the statistical index changed significantly. While the change in the means might have been due to simply pushing the  $\beta$  particles into or out of the subtended cone, the possibility that the variance ratio was also affected by the same more or less trivial effect appears most improbable. Obviously if such an effect can be observed employing other than  $\beta$  emitters, the question of the triviality of the mean shift can be largely resolved at the same time.

There is no obvious or even known reason why the mean and the index of dispersion should vary simply as a result of the applied potential.

*Potential Errors.* A number of potential errors such as equipment related errors, possible double pulsing of the GM tubes, resolution time errors, potential back scatter errors, and even a possible correlation between decay and desorption have been considered and analyzed; they are discussed in detail in the appended or supplemental notes. None appears to be causal in any degree with respect to the anomalous values of the index of dispersion. [(17s) A discussion of possible errors and a discussion of the effect of possible judgmental selectivity.]

*General.* The necessary and sufficient assumption on which the applicability of the Poisson distribution depends—that radioactive decay events are independent of each other—does not require that the events are necessarily independent of the environment. As has been pointed out by Kandel, a body of evidence now exists that, at least for so-called  $k$ -capture radio-

activity or radioactivity which involves internal conversion processes, significant differences in half-lives of  $^{99}\text{Tc}$  and  $^7\text{Be}$  have been observed as a function of chemical composition.<sup>19</sup> No hint of an exception to the generality of the Poisson distribution was made in the cited references although conceivably such a phenomenon might exist unrecognized.

One may well postulate that the effect of environment could be of at least two quite different types: (1) an effect in which the rate of decay changes but which does not involve cooperation or mutuality of the decaying nuclei, and (2) an effect which does involve, or at least permits, such cooperation or mutuality.

The cited references in footnote 19 are presumably examples of type 1 while the abnormal statistics cited herein—in the absence of artifactuality—appear to be manifestations of type 2.

Throughout this work, opinions of a large number of independent scientists encompassing many and diverse disciplines have been sought to criticize the work and to comment on it. Listed in the acknowledgments, these men have generously given of their time and have suggested many of the avenues of verification employed. Where suggested experiments have been performed, the results have invariably confirmed and extended the phenomenon of non-Poisson character. At this writing, the author is unaware of any substantive arguments, other than disbelief, which are germane to the experiments, the statistics, or even the more-or-less obvious implications.

**Conclusions.** Assuming the absence of artifactuality, at least under the two cited conditions of measurement—the desorbing monolayers and the (positively) charged monolayer-surface systems, the  $\beta$  emissions detected by external counters positioned adjacent to the adsorbed carbon-14-labeled monolayers are not properly described by the Poisson distribution. The further pronounced change in the means, as a result of change in the polarity of the applied surface potential alone, probably independently substantiates the inapplicability of the Poisson.

**Unanswered Questions.** (1) What possible mechanisms are operating to cause the restricted statistical distributions and the changes in means? (1a) Are there unsuspected nuclear-nuclear interactions? (1b) Does the surface charge couple, or permit coupling of, such interactions? (2) Is it possible that radiation following emission is so altered in random behavior that the distribution is altered? (2a) If so, are the decay events themselves independent of the emissions at least insofar as the statistics of emissions are concerned? (3)

In some manner is the backscatter effect responsible for the anomaly? (4) Are the factors causing narrow or low distributions different in the case of desorbing monolayers and the case of nongrounded surfaces? (5) Does the orientation of the molecules at the interface relate to the effect? (5a) If so, are the nuclei also oriented? (5b) If the nuclei are oriented with respect to the surface, are they also oriented with respect to each other? (5c) If nuclei are oriented with respect to each other, can they cooperate in the decay process? (6) Does the rate of decay change more than incidentally from mutuality in the decay process?

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(19) R. J. Kandel, U. S. Atomic Energy Commission, personal communication; cf. *Phys. Rev.*, **90**, 430 (1953); *Phys. Rev. C*, **2**, 1616 (1970).