CHAPTER 11

STATISTICAL INTERPRETATION OF RESULTS

When dealing with errors, distinction should be made between: (a) systematic errors, which determine the accuracy of a result; (b) random errors, which determine the reproducibility or precision.

By systematic errors the experimental results deviate from the true value, because of a bias. Statistics, on the other hand, only deal with random errors, which are a measure for the reliability of a procedure.

Systematic errors are described in Chapter 10. The present chapter illustrates how statistical methods may be applied to data obtained by activation analysis. Although the statistical method is a most important part in the evaluation assessment, no attempt is made to present a rigorous or complete treatment. Some typical examples will be given, which are frequently encountered when dealing with radioactivity measurements and with analytical results from activation analysis. Obviously, the statistical approach cannot obviate the need for common sense and sound analytical techniques, but unnecessary loss of operator time in the laboratory can often be eliminated and the reliability of the deductions increased by the use of statistical methods and of carefully designed experiments.

I. Application of Statistical Methods to Analytical Results

(A) Best Value for a Set of Observations

It generally makes no sense to define an error as the deviation of a measurement from the true value, as the latter is usually unknown. Thus, a definition of "error" can only be given after evaluation of the most probable value of the quantity measured. Experimental data are always associated with the inevitable errors of observation, i.e. they all can differ among themselves within some limits.

For a number n of observations $x_1, x_2, \ldots x_n$, made under the same conditions and all equally reliable, the "arithmetic mean" is the best representative value:

$$\bar{x} = \sum^{n} x_i/n \tag{11.1}$$

If all observations are not equally reliable (e.g. several "populati with the same form and mean), a statistical weight W_i can be introduced (data pooling). The most probable value is then the "weighted mean", sometimes called the "general or probable mean":

$$\bar{x} = \sum^{n} W_i x_i / \sum^{n} W_i \tag{11.2}$$

where $W_i = A/\sigma_i^2$ (equation 11.71). In section V of this chapter some examples are described showing how the statistical weights W_i are determined in practice.

(B) Precision – Standard Deviation

In some observation sets, the total spread can be so narrow that only a few measurements are needed to obtain a close approximation of the arithmetic mean, which should be found with a large population. In other cases, the measurements are widely scattered, necessitating a large amount of data. In the first case the results are said to be reproducible or precise, in the second case they are not. The degree of confidence can be expressed in terms of "probable error", "standard deviation", "nine-tenths error", etc. (Table 11.1).

The reproducibility of an analytical method in a given concentration range is usually expressed by the standard deviation $\sigma(x)$ on a single determination. This can be obtained from the statistical concept of variance, which for a single measurement is given by:

$$v = \frac{\sum^{n} (\bar{x} - x_i)^2}{n - 1} \tag{11.3}$$

where $n - 1$ indicates the degrees of freedom of the observation set. The applicability of (11.3) requires that all observations x_i are made under the same conditions and are all equally reliable. The standard deviation on a single observation is given by the square root of the variance, on condition that n is sufficiently large:

$$\sigma(x) = \sqrt{v} = \sqrt{\left\{\frac{\sum^{n} (\bar{x} - x_i)^2}{n - 1}\right\}} \tag{11.3 bis}$$

If a number of n analyses is made, a better estimate of the result is possible. The standard deviation which affects the whole series of results, $\sigma(\bar{x})$, [illegible] be calculated as follows:

$$\sigma(\bar{x}) = \sqrt{\left\{\frac{\sum^{n} (\bar{x} - x_i)^2}{n(n-1)}\right\}} = \frac{\sigma(x)}{\sqrt{n}} \qquad (11.4)$$

$\sigma(\bar{x})$ is an estimate for the standard deviation of the mean value $\bar{x}$.

If a precision $\sigma(\bar{x})$ is required for the result $\bar{x}$, the necessary number n of analyses can be computed from equation (11.4), if $\sigma(x)$ is known. Merely increasing the number of experiments, without varying the experimental conditions, decreases the influence of random errors, i.e. the precision improves. It is, however, useless to increase the number of observations beyond some limit, because of constant, systematic or individual errors (see I, G).

On the other hand, the greater the number and variety of the experiments (e.g. results obtained by different methods and/or different laboratories), the more the probability of occurrence of systematic errors will decrease, as they become of random nature.

The error on a single measurement can also be expressed as percentage standard deviation $\sigma_{\%}$, which is defined by the following relationship:

$$\sigma_{\%} = 100\sigma(x)/\bar{x} \qquad (11.5)$$

where $\bar{x}$ is given by equation (11.1) and $\sigma(x)$ by equation (11.3).

The exact standard deviation σ can be found from an infinite number of observations. For a limited number of observations, the symbol s is often used: $s(x)$ and $s(\bar{x})$.

(C) CONFIDENCE LIMITS

As the arithmetic mean for an infinite number of observations is usually not accessible, it is only possible to calculate the probability that this value is contained within the limits $\bar{x} \pm \Delta x$. The number Δx can be chosen arbitrarily small. It is common practice to express Δx in terms of the standard deviation, e.g. $\pm \Delta x = \pm t\sigma$, where t depends on the probability level and on the number of degrees of freedom. If the latter is large, $t \simeq u$ (see Table 11.1). For a normal distribution a result x_i will be obtained within the interval $\bar{x} \pm \sigma(\bar{x})$ with a probability $P = 0.683$ or 68.3%. This means that, in the average, two out of three results may be expected to deviate from the mean by less than one standard deviation. Hence, the interval $x_i \pm \sigma(x_i)$ will contain the arithmetic mean of an infinite number of observations with ca. 68% probability.

Obviously, the degree of confidence increases, as the "confidence interval" increases (Table 11.1).

For trace analysis, the 0.68 probability level is generally accepted. In other cases, e.g. minor constituent analysis, a more severe confidence limit may be required, for instance $\pm 2\sigma$ ($P \simeq 95\%$). The interval $\pm 3\sigma$ practically represents the maximum random error associated with a measurement ($P = 99.7\%$).

TABLE 11.1 Probability levels
P = probability that the error of an analysis $< u\sigma$
P' = probability that the error of an analysis $> u\sigma$ ($P' = 1 - P$)

Constant u	Probability P	P'	Error
0.6745	0.500	0.500	"Probable error"
1.000	0.683	0.317	"Standard deviation" (σ) (rms error)
1.177	0.761	0.239	
1.645	0.900	0.100	"nine-tenths error" or "reliable error"
1.960	0.950	0.050	"ninety-five hundredths error"
2.576	0.990	0.010	"ninety-nine hundredths error"
2.807	0.995	0.005	
3.000	0.9973	0.0027	3σ
3.291	0.999	0.001	
4.000	0.99994	0.00006	4σ

(D) OUTLIER REJECTION (CHAUVENET'S CRITERION)

There can be no question about the rejection of faulty observations, provided there is evidence for a mistake. Examples: (i) one notices that an irradiated sample was not etched before chemical separation of the element to be determined, so that contamination occurred; (ii) faulty determination of the chemical yield, e.g. incomplete development of a colour for spectrophotometric determination, due to wrong pH; (iii) during counting experiments outliers can occur by disturbances external to the nuclear process, such as amplifier noise, electrical line noise, shift of amplifier gain due to variation in temperature, etc. Other typical errors are: misreading the instrument, counting the wrong sample, counting the sample in the wrong counting position, failing to remove or insert an absorber, failure to remove a previous sample, failing to set proper discriminator levels, failing to record the data in legible form resulting in misreading of the written data, etc.

Sometimes an exhaustive search will fail to reveal any reason why some results diverge in an unusual and unexpected manner from the others. Several criteria have been suggested to guide the investigator in deciding whether doubtful observations shall be included in the mean. Chauvenet's criterion is perhaps the most convenient to use. It starts from the assumption that reliable observations will not deviate from the arithmetical mean beyond some limits (see end of foregoing paragraph).

In Table 11.2 the limiting value of the deviation from the mean of a single observation (in units of σ) is given as a function of the number of experiments performed. When this limiting value is exceeded, the measurement concerned may be rejected.

TABLE 11.2

Chauvenet's criterion for outlier rejection

Number of experiments	2	4	6	8	10	20	30	40
Limiting value of error (in units of σ)	1.15	1.55	1.73	1.88	1.98	2.25	2.40	2.50

Example: Determination of oxygen in steel by four different laboratories. Results (ppm).

		$(x_i - \bar{x})$	$(x_i - \bar{x})^2$
lab. 1	911	−18	324
	908	−21	441
lab. 2	947	+18	324
	938	+ 9	81
lab. 3	992	+63	3969
	944	+15	225
	919	−10	100
lab. 4	903	−26	676
	899	−30	900
average	929		

$$\sigma(x) = \sqrt{\left\{\frac{\sum (x_i - \bar{x})^2}{n-1}\right\}} = 30$$

Limiting value of error for nine experiments: $\pm 1.93\ \sigma(x) = \pm 58$ ppm (Table 11.2). This value is exceeded by the first determination of laboratory 3 ($992 - 929 = 63$), hence this measurement may be rejected. Then, the new average value becomes: 922 ppm; $\sigma(x) = \pm 19$ ppm; the limiting factor of error for the eight remaining experiments: $\pm 1.88\ \sigma(x) = \pm 36$ ppm. All the remaining results fall within 922 ± 36 ppm.

Conservation of moderate outliers is strongly suggested for the following reasons (1):

(a) Apparent patterns in sequences of random data are often startling. In the long run, averaging bunched results gives averages that deviate more from the "true values" than does the mean of all values.

(b) As the number of experiments increases, the number of outliers increases. Indeed, the rare occurrence of abnormal results is in accordance with the theory of errors.

(c) In a large group of measurements, omission of the outlier has little effect on the average.

The use of the above criterion is, therefore, permitted only if the number of observations is small. It is true that some good observations may be lost (it discards good observations in ~40% of the situations to which it is applied), but that is the price paid to get rid of serious deviations. It is perhaps needless to point out that a suspected observation may ultimately prove to be a real exception requiring further research.

(E) PROPAGATION OF ERRORS

Sometimes several results or measurements $x_1, x_2, \ldots$ affected with their corresponding errors, e.g. standard deviations $\sigma(x_1), \sigma(x_2), \ldots$ must be combined to give some new quantity $X = f(x_1, x_2, \ldots)$.

In Table 11.3, the error propagation in some common functions is summarized assuming normality. After computation of the standard deviation of X, the confidence limit of this quantity can be determined as $\pm t\sigma(X)$.

The expressions in Table 11.3 are valid if each $\sigma(x_i)/x_i$ is sufficiently small ($\leq 20\%$) and if all x_i's are statistically independent.

Several practical applications can be found in the course of this chapter.

TABLE 11.3

Error propagation in some common functions

Function	Standard deviation
(1) $X = x_1 \pm x_2$ (addition, subtraction)	$\sigma^2(X) = \sigma^2(x_1) + \sigma^2(x_2)$
(2) $X = \frac{x_1 x_2}{x_3}$ (multiplication, division)	$\frac{\sigma^2(X)}{X^2} \cong \frac{\sigma^2(x_1)}{x_1^2} + \frac{\sigma^2(x_2)}{x_2^2} + \frac{\sigma^2(x_3)}{x_3^2}$
(3) $X = ax_1 + b$	$\sigma^2(X) = a^2\sigma^2(x_1)$
(4) $X = x_1^r$	$\frac{\sigma^2(X)}{X^2} \cong r^2 \frac{\sigma^2(x_1)}{x_1^2}$
(5) $X = e^{cx_1}$	$\frac{\sigma^2(X)}{X^2} \cong c^2\sigma^2(x_1)$
(6) $X = \ln cx_1$	$\sigma^2(X) \cong \frac{\sigma^2(x_1)}{x_1^2}$
(7) $X = \ln(x_1 + x_2)$	$\sigma^2(X) \cong \frac{\sigma^2(x_1) + \sigma^2(x_2)}{(x_1 + x_2)^2}$
(8) $X = \ln \frac{x_1}{x_2}$.	$\sigma^2(X) \cong \frac{\sigma^2(x_1)}{x_1^2} + \frac{\sigma^2(x_2)}{x_2^2}$

(F) SYSTEMATIC AND RANDOM ERRORS – ACCURACY AND REPRODUCIBILITY OR PRECISION

The random errors hitherto discussed have this distinctive feature, that they are just as likely positive or negative. Some errors however do not have this character.

For a number of activation analyses using the comparator method, quite reproducible or precise determinations can be obtained, if, e.g. the standards are always prepared from the same stock solution. In the case of faulty preparation of this solution, the determinations will obviously be inaccurate. Inaccurate results will also be obtained if neutron shielding occurs in the sample or in the comparator or if interfering nuclear reactions occur. Such faulty analyses are said to be affected by constant or systematic errors. A number of important systematic errors are discussed in Chapter 10.

A major difficulty for an investigator is to detect and possibly eliminate constant errors. This is usually done by modifying the conditions under which the experiments are performed.

Examples: (a) Is the result of an iridium determination in a 1[illegible]g rhodium sample ($\sigma_{abs} \simeq 150$ barn for thermal neutrons) affected by neutron shielding in the sample (2)? Using the classical method (10 mg samples irradiated together with standards) one finds 17.0 ± 0.3 ppm Ir. If neutron shielding occurs in the rhodium samples and not in the iridium standards (1 μg of Ir spotted on filter paper), the result will be too low, as the specific activity of iridium in rhodium is lower than that in the standards. Indeed, a higher content (18.1 ± 0.5 ppm Ir) is found when using an addition method (see section V, C); the iridium standard solution is added to rhodium and the sample then dissolved in a closed quartz tube, prior to irradiation. One can conclude that neutron shielding occurs and an addition method is recommended.

(b) In the case of an iridium determination in osmium ($\sigma_{abs} \simeq 15$ barn for thermal neutrons) the following results were found (3): classical method (10 mg samples; standards 1 μg Ir on filter paper) 21 ± 2 ppm Ir; addition method (*cf.* example (a)) 19.5 ± 1.2 ppm Ir. As the mean value of each set of results differs by an amount to be expected from the standard deviations of the different sets measured under the same conditions, no error due to neutron shielding is detectable.

(c) Traces of iridium can directly be determined in palladium, after decay of the palladium activity and separation of ^{111}Ag (daughter of ^{111}Pd), using 72d ^{192}Ir. Counting of ^{192}Ir can be performed using the photopeaks at 317, 468 or 610 keV. For a given sample the following results were found: 0.20 ± 0.02 ppm (317 keV), 0.20 ± 0.02 ppm (468 keV), 0.26 ± 0.02 ppm (610 keV). By changing the counting conditions, some interfering impurity appears, which emits gamma-rays in the 610 keV region. Measuring the 610 keV photopeak could thus give rise to systematic errors.

(d) If some interfering threshold reaction can introduce a systematic error, e.g. ^{56}Fe(n, p)^{56}Mn when determining manganese in iron via the nuclear reaction ^{55}Mn(n, γ)^{56}Mn, one should choose irradiation positions in the reactor with different *k*-values (see Chapter 3, section VI, B, 3). If no interference occurs, the ratio ^{56}Mn/^{56}Fe should be constant. Hoste *et al.* (4) found, however, ratios varying from 13 in the reactor core, to practically zero in the reflector. Consequently, manganese determinations in iron must be performed in a well thermalized neutron spectrum.

Other examples of avoiding systematic errors are discussed in detail in Chapter 10.

s

1. $\sigma_{\%}$ *(sample)*

The percentage standard deviation of the sample is determined by the weight of the sample and even more by the homogeneous distribution of the element to be determined. Sample weights are usually maximized for the sake of sensitivity and counting statistics, taking however into account the induced matrix activity and possible shielding effects.

For sample weights over 1 mg the precision is better than 0.5%. From 0.1–1 mg the estimated error is ca. 1% (7). Weighing of a 100 mg aluminium sample can be done with high precision, but heterogeneity at this scale is not unlikely to occur, i.e. when repeating the analyses, the scatter of the results around a mean value can be much more important than expected.

If a non-destructive technique is applied, $\sigma_{\%}$ (chem) is zero. Assuming a sufficiently high activity and a reproducible counting geometry, $\sigma_{\%}$ (count) is small. Irradiation in reproducible conditions (small flux gradients and flux perturbations) makes $\sigma_{\%}$ (irrad) small too. If in these conditions large scatter is observed, this is most probably due to inhomogeneity of the samples, as $\sigma_{\%}(T)$ is practically determined by $\sigma_{\%}$ (sample). During a nondestructive determination of copper in bismuth by γ–γ-coincidence spectrometry, an unusually large scatter was observed for a given bismuth rod: from 0.04 to 0.4 ppm (8). Rearranging, however, the results according to their respective location along the axis of the rod indicated the existence of a concentration gradient of copper. (Figure 11.1.)

2. $\sigma_{\%}$ *(irrad)*

The percentage standard deviation of the irradiation is mainly produced by variations of the neutron flux and for short lived isotopes by inaccurate timing. The problem of flux gradients in different types of reactors is discussed in Chapter 10, section II, B, 2. In the case of a neutron generator, flux gradients are extremely important. Small variations in the positioning of a sample cause large variations in received flux. A displacement of 1 mm towards or away from the target gives rise to a flux variation of +12.5% or −11% for a sample of 9 mm thickness at a distance of 9 mm from the target (Figure 10.2).

At a distance of 18 mm, the change in flux is +7.4% and −8.5% respectively. For that reason the tolerance on the pneumatic tube

should be as small as possible (max. 0.5 mm), to reduce random deviations. Transversal displacement can also introduce considerable variations, but can reasonably be reduced by using a suitable bumper. In practice a reproducibility of ±2% can be obtained (9).

For very short irradiation times, when samples and standards are not irradiated simultaneously, $\sigma_{\%}$ (irrad) also depends on the reproducibility of the duration of the irradiation t_b, thus on the reproducibility of the timers, the pneumatic system, etc. Pneumatic systems always working under overpressure are often more reproducible than those where transportation is alternatively performed by over- and underpressure. The transport times obviously depend on the total

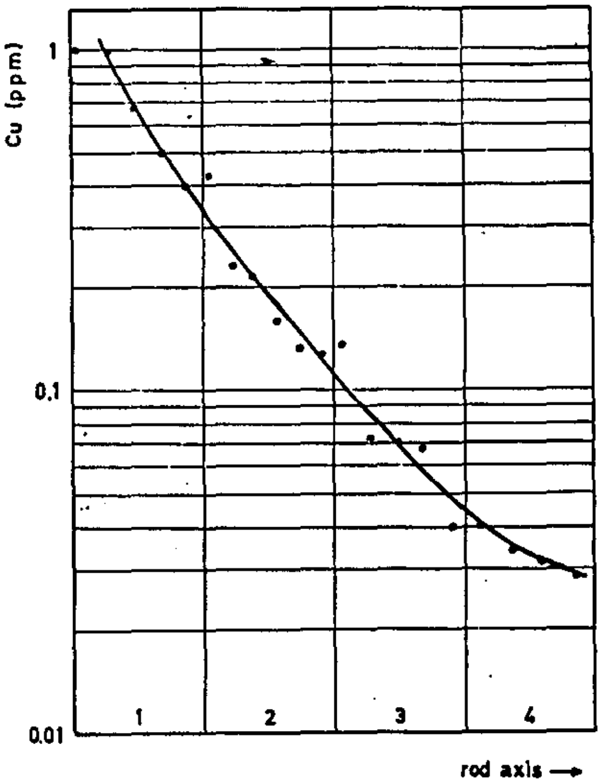

Fig. 11.1. Distribution of copper along bismuth rod (8).

length and inner diameter of the tubes and on the pressure, and, for a given system, on the sample weight (or weight of sample plus rabbit). For $t_b = 10$ s, the reproducibility is typically of the order of the percent.

3. $\sigma_{\%}$ (*chem*)

Obviously $\sigma_{\%}$ (chem) must only be considered when chemical separations are involved. Then it may further be resolved and contains: the dissolution of the sample and the different steps of the separation. Although the reproducibility depends on the method used, in the case of a standard procedure $\sigma_{\%}$ (chem) can be estimated to be ±2% or better.

When an element such as tin or zinc is too thoroughly etched after irradiation, so that its weight is reduced to 60–70% for instance, some of the dissolved trace elements, which are more electropositive than the matrix (Cu, Ag, Au, . . .) may again be deposited on the sample. Their concentration in the matrix will then be calculated with a wrong sample weight, thus giving positive errors.

During the dissolution, losses of the element of interest are possible by volatilization, by incomplete cleaning of the crucible after a fusion, etc. In general, some of the practically carrier-free material can be lost during the chemical treatment, e.g. by adsorption, if no carriers or hold-back carriers are added. But even then the problem of isotopic exchange remains and can cause random or even systematic errors. A typical example: osmium carrier, prepared by a sodium peroxide fusion of the metal sponge, was added to osmium tracer, prepared by dissolving the irradiated metal sponge in aqua regia.

After boiling in sulfuric acid and hydrogen peroxide, the carrier appeared to distill practically quantitatively, whereas the yield for the tracer was 85% only, even after repeated addition of carrier and repeated distillations. For that reason the chemical separation method must carefully be checked by suitable tracer experiments, particularly when dealing with elements forming a variety of complexes and (or) existing in a number of valency states. The radiochemical purity of the isolated fraction must obviously be checked by half-life measurement or gamma-ray spectrometry.

Other variables, such as manipulation errors, calibration errors in volumetric glassware, balances, weights, etc. can be neglected when adequate precautions are applied.

4. $\sigma_{\%}$ (*count*)

The percentage standard deviation of the counting is composed of the following factors:

(a) a geometrical factor;
(b) electronic drift;
(c) drift in gain and change in resolution as a function of counting rate;
(d) dead time corrections: these are more likely to introduce systematic errors and are discussed in Chapter 10, section II, E;
(e) counting statistics.

(a) Variations in geometry are usually smaller than ±1% when using a flat or well-type scintillator or semiconductor detector and standard counting vials. Unexpected errors can occur by evaporation of a liquid through plastic container walls or covers, or when counting solid samples of irregular shape. When counting volumes of 25–50 ml in a volumetric flask, placed directly on a flat detector, it is important to select flasks of the same form and fill them to the same height.

(b) Electronic drift and drift due to the temperature coefficient of the detector will usually not exceed ±0.3% if the temperature in the counting room is kept constant within ±0.5°C and the relative humidity within ±10%. If the temperature changes, the gain shift of the photomultiplier, the preamplifier, the amplifier and the pulse height analyzer can amount up to 1–2% per °C. Around room temperature sodium iodide and anthracene crystals exhibit a negative temperature coefficient of respectively 0.1% per °C and 0.5% per °C of the pulse height. When using a Compton-compensated spectrometer, this difference can result in a mismatch of the energy scale compensation, noticeable if the temperature in the neighbourhood of the detectors changes by ca. 5°C.

The gain shift characteristics of some multiplier phototubes (Dumont, RCA, EMI, CBS) have been examined by Covell and Euler (10). The stability of the photomultiplier gain also largely depends on the quality of the high voltage power supply. H.T. power supplies, stabilized with a Weston reference element, are recommended. Similar precautions must be taken with semiconductor detectors, although H.T. stabilization is less critical.

A drift control system, which corrects both for the overall drift due to gain changes and for the zero point drift, which is apparent in some multichannel analyzers, has been described by Fite *et al.* (11). In the decomposition of complex gamma spectra by weighted least squares analysis, the influence of electronic instabilities can be calculated with the χ^2 test (12).

(c) Drift in gain and change in resolution as a function of counting rate depend mainly on the quality of the photomultiplier tube (10) and the pulse shaping circuits. These factors also depend on the decay constant of the light pulses in the scintillator. Some typical data: NaI(Tl) 0.25 μs, CsI(Tl) 1.1 μs, KI(Tl) 1.0 μs, anthracene 0.032 μs, trans-stilbene 0.006 μs, plastic and liquid phosphors 0.002–0.008 μs.

The use of a selected photomultiplier tube is highly important to minimize changes in gain, whereas the bleeder chain and load resistor determine the pulse duration, thus affecting the resolution. The requirements of pulse height analyzers with respect to pulse duration vary from instrument to instrument, but pulse durations of one to several microseconds are most common. The linear amplifier transforms the detector signals into signals suitable for pulse height analysis (pulse shaping and amplification).

In the case of single-*RC* differentiation and single-delay-line differentiation the base line depends on the counting rate. At high counting rates the small but long undershoot departs appreciably from the normal level.

If the signal is measured with respect to an average reference base line, it is recorded as being smaller than at low counting rates. On the other hand, the probability for pile-up increases, since the signals can occur in statistical bursts: such signals will be recorded as being larger than at low counting rates. These effects result in a deterioration of the resolution; Figure 11.2 shows the effects for single-*RC*-clipping.

Base-line displacements are less important for double-*RC*-clipping (bipolar signals) but longer *RC* time constants are often necessary to keep the system linear. A longer time constant results however in a greater probability for pile-up. Hence, the upper limit of the counting rate at which spectral distortion is not excessive, may be similar for the three pulse shaping systems mentioned. The pulse lengthening can be avoided if the resistor in the second clip is parallelled by a D.C. restoring diode, which removes the undershoot (13) (Figure 11.3). The second clip is usually at the amplifier output and direct coupling between the second clip and the pulse height analyzer is used to keep the base-line location "independent" of the counting rate.

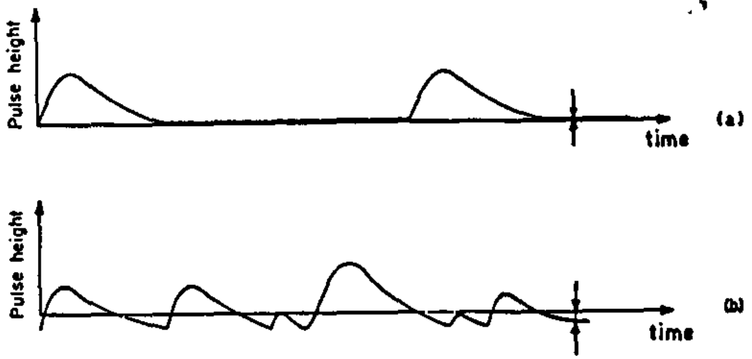

Fig. 11.2. Single-*RC*-differentiated signal, (a) at low counting rates, (b) at high counting rates (13).

Double-delay-line differentiation is less dependent on the counting rate and pile-up overloading can be minimized.

The preamplifier must be capable of driving the low impedance of the interconnecting circuit between preamplifier and amplifier over the full range of input signals without pile-up distortion due to statistical bursts. It must be noted that the largest signal from a radiation detector may frequently be more than a hundred times the smallest signal of interest. If the amplitude distribution of the latter is to be studied, distortion of the resolution can obtain, due to overload of the linear amplifier. Indeed, the larger signals give rise to extensive amplifier paralysis followed by a slow recovery. Smaller pulses occurring during the recovery interval will not be measured correctly and those occurring during the paralysis interval will be lost.

The change in resolution as a function of counting rate can easily be observed with semiconductor detectors. Even for relatively weak

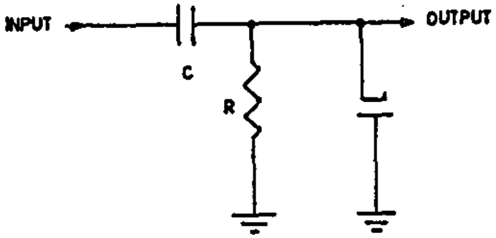

Fig. 11.3. *RC* circuit with restoring diode (13).

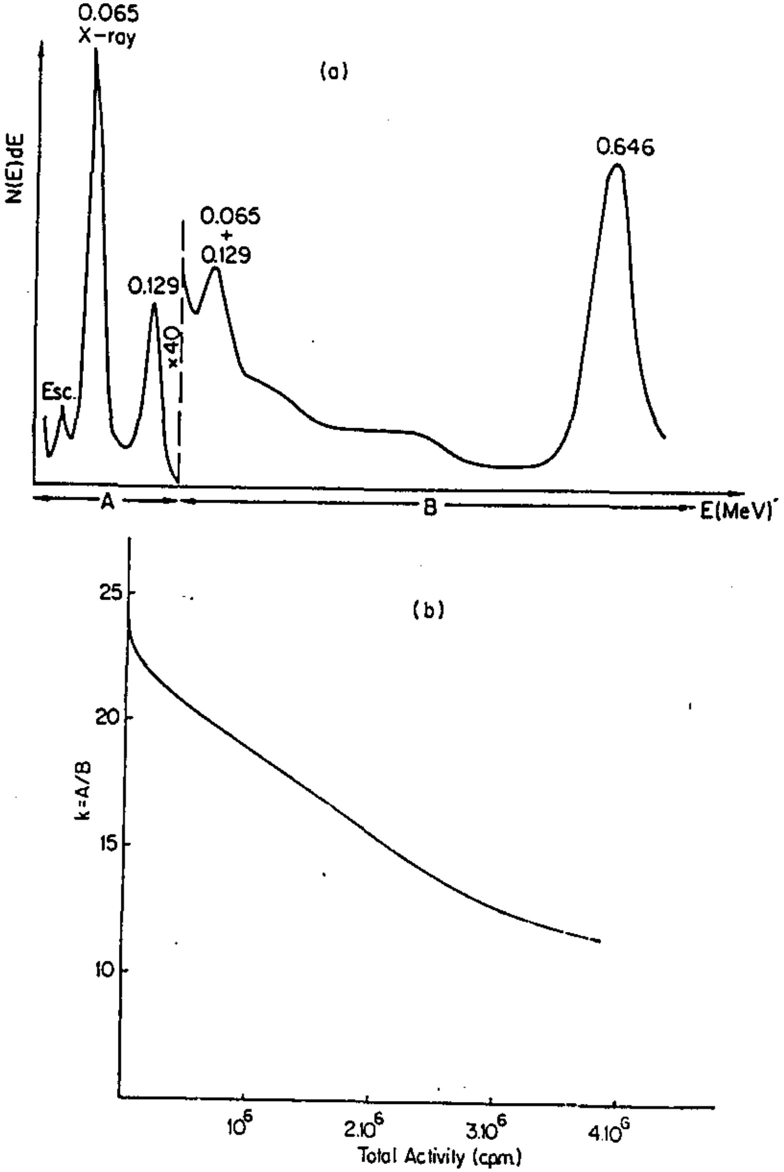

Fig. 11.5. Spectral distortion with counting rate; 7.5 cm × 7.5 cm NaI(Tl) detector, Fairstein amplifier (double-delay-line differentiation). (a) Spectrum of irradiated Os sample. (b) Activity ratio of region A over B.

such as ion-exchange, electrophoresis, electrodeposition, [illegible] The isolated fraction is then counted and if necessary, the chemical yield is determined. For each result, $\sigma^2_{\%}$ (sample) and $\sigma^2_{\%}$ (irrad) are, of course, identical. Hence, for the analysis of these sample aliquots, $\sigma^2_{\%}(T) = \sigma^2_{\%}$ (chem) + $\sigma^2_{\%}$ (count), where $\sigma^2_{\%}$ (count) can be found as described under (3). This allows the estimation of $\sigma^2_{\%}$ (chem). $\sigma^2_{\%}$ (chem) + $\sigma^2_{\%}$ (count) can also be estimated from tracer experiments in exactly the same experimental conditions and $\sigma^2_{\%}$ (chem) is deduced as described above.

(6) From (1), (2) – or (3) and (4) – and (5), $\sigma^2_{\%}$ (sample) can be estimated using equation (11.7).

(7) For short-lived radioisotopes, where no chemical treatment occurs, $\sigma^2_{\%}$ (chem) = 0; $\sigma^2_{\%}(T)$ is found as under (1): $\sigma^2_{\%}$ (irrad) + $\sigma^2_{\%}$ (count) follows from repeated analyses of the same sample. Since $\sigma^2_{\%}$ (count) can be estimated, $\sigma^2_{\%}$ (irrad) can be calculated. From equation (11.7) follows then $\sigma^2_{\%}$ (sample).

Obviously, the largest $\sigma^2_{\%}$ is the determining factor of the precision of the results and this stage should possibly be improved, if a better precision is required. It must be borne in mind that a similar $\sigma^2_{\%}(T)$ exists for the standard or comparator.

II. Counting Statistics

(A) BINOMIAL DISTRIBUTION

The radioactive decay has a statistical character. If a radionuclide is counted several times in identical experimental conditions, different counting rates (number of counts per unit time, R) will be observed, even for a very long lived species. These fluctuations follow statistical laws. It can be shown (15) that the probability $P(d)$ of obtaining d disintegrations in a time Δt from N_0 original radioactive atoms is given by the binomial distribution:

$$P(d) = \frac{N_0!}{(N_0-d)!\,d!}[1-\exp(-\lambda\Delta t)]^d[\exp(-\lambda\Delta t)]^{N_0-d} \qquad (11.8)$$

where $[1-\exp(-\lambda\Delta t)]$ is the probability of an atom disintegrating in a time Δt and $\exp(-\lambda\Delta t)$ the probability to survive the time Δt. The expected average number $\bar{N}$ of atoms disintegrating in the time Δt is

$$\bar{N} = N_0[1-\exp(-\lambda\Delta t)] \qquad (11.9)$$

The expected average number of observed counts with a detector is $c = \bar{N}z$, where z is the detection efficiency.

For small values of $\lambda\Delta t$, i.e. $\Delta t \ll T_{1/2}$, equation (11.9) is reduced to

$$\bar{N} = N_0\lambda\Delta t \tag{11.9a}$$

As the disintegration rate $D = -\mathrm{d}N/\mathrm{d}t = \lambda N_0$ (see equation (5.2)), equation (11.9a) can be written as

$$D = \bar{N}/\Delta t \simeq d/\Delta t \tag{11.10}$$

if a reasonably large number of counts has been obtained during the time Δt.

Note: When the decay of a radioactive sample is followed as a function of time, the counting rate $R = c/\Delta t$ is usually taken to represent the activity at the midpoint of the interval Δt, i.e. at a time $t_t = t_0 + 0.5\Delta t$. This approximation is only valid if $\Delta t \ll T_{1/2}$. If however $\Delta t \geq T_{1/2}$, the mean counting rate $R = c/\Delta t$ will represent the activity at a time $t_t = t_0 + f\Delta t$ where $0 < f \leq 0.5$. Indeed, from equation (11.9) and (11.10) follows that the average observed disintegration rate for the counting interval Δt is given by $N_0[1 - \exp(-\lambda\Delta t)]/\Delta t$. On the other hand, the true disintegration rate at a given moment $t_t = t_0 + f\Delta t$ is $-\mathrm{d}N/\mathrm{d}t = \lambda N_t = \lambda N_0 \exp(-\lambda f\Delta t)$. From this it appears that:

$$\exp(-\lambda f\Delta t) = [1 - \exp(-\lambda\Delta t)]/\lambda\Delta t$$

which allows us to calculate f, i.e. the moment at which the mean rate is equal to the true one:

$$-0.693\, f\Delta t/T_{1/2} = \ln\left[\frac{1 - \exp(-0.693\, \Delta t/T_{1/2})}{0.693\Delta t/T_{1/2}}\right]$$

or

$$f = \frac{3.322}{\Delta t/T_{1/2}} \log\left[\frac{0.693\, \Delta t/T_{1/2}}{1 - \exp(-0.693\, \Delta t/T_{1/2})}\right] \tag{11.11}$$

Some calculated values for f are given in Table 11.4. More numerical data are given by Hoffman (16).

TABLE 11.4
Correction factor f (equation 11.11)

$\Delta t/T_{1/2}$	0	1	2	3	4	5
f	0.500	0.472	0.443	0.416	0.390	0.368

Another approach is the introduction of a factor F, which allows the calculation of the true counting rate at the start of the counting. The true disintegration rate at t_0 is given by $-\mathrm{d}N/\mathrm{d}t = \lambda N_0$. The average observed disintegration rate is $N_0[1 - \exp(-\lambda\Delta t)]/\Delta t$, hence

$$\lambda N_0 = FN_0[1 - \exp(-\lambda\Delta t)]/\Delta t$$

or

$$F = \frac{0.693\, \Delta t}{T_{1/2}} \times \frac{1}{1 - \exp(-0.693\, \Delta t/T_{1/2})} \tag{11.12}$$

The larger $\Delta t/T_{1/2}$, the larger F. This correction factor is represented in Figure 11.6 (17).

It will be noted that if the observation time Δt is less than about 1.5% of $T_{1/2}$, the correction is less than 0.5%.

(B) EXPECTED STANDARD DEVIATION

In the case of radioactive disintegration it can be shown (15) that

$$\sigma = \sqrt{\{N_0[1 - \exp(-\lambda\Delta t)]\, z\, [1 - z + z \exp(-\lambda\Delta t)]\}} \tag{11.13}$$

where $[1 - \exp(-\lambda\Delta t)]$ is the probability of an atom disintegrating

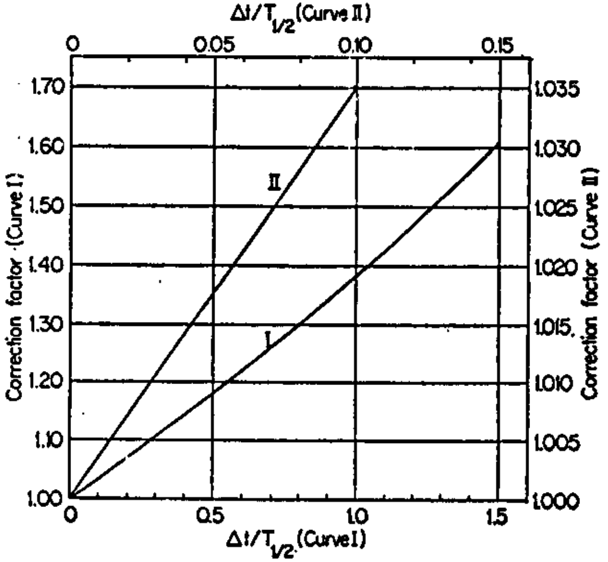

Fig. 11.6. Correction factor F as a function of $\Delta t/T_{1/2}$ (17).

in the time Δt; $[1 - \exp(-\lambda\Delta t)]\,z$ is the probability of a disintegration resulting in an observed count in the time Δt; $[1 - z + z\exp(-\lambda\Delta t)]$ or $1 - z[1 - \exp(-\lambda\Delta t)]$ is the probability of an atom not resulting in an observed count in the time Δt. Substituting equation (11.9) into equation (11.13) one obtains:

$$\sigma = \sqrt{\{\bar{N}z[1 - z + z\exp(-\lambda\Delta t)]\}} \qquad (11.14)$$

Usually $\Delta t \ll T_{1/2}$, thus $\lambda\Delta t \ll 1$ and $\exp(-\lambda\Delta t) \simeq 1 - \lambda\Delta t$, hence

$$\sigma = \sqrt{(\bar{N}z)} = \sqrt{(\text{number of counts})} \qquad (11.15)$$

Example: If 10^4 counts are recorded, $\sigma = 10^2$ or $\sigma_\% = 1\%$. The standard deviation for a given counting rate R (cpm or cps) is given by:

$$R = \frac{\bar{N}z}{\Delta t}, \text{ thus } \sigma_R = \frac{\sqrt{\bar{N}z}}{\Delta t} = \frac{\sqrt{R\Delta t}}{\Delta t} = \sqrt{\frac{R}{\Delta t}} \qquad (11.16)$$

If $\Delta t \gg T_{1/2}$, $\lambda\Delta t \gg 1$, $\exp(-\lambda\Delta t) \ll 1$, hence equation (11.14) is reduced to

$$\sigma = \sqrt{\bar{N}z(1 - z)} \qquad (11.17)$$

Thus, if Δt is long enough to allow all atoms to decay, and if the detection efficiency $z \approx 1$, the number of disintegrations is exactly known, and $\sigma = 0$.

If however $z \ll 1$, the above equation (11.17) becomes $\sigma \doteq \sqrt{\bar{N}z} = \sqrt{(\text{number of counts})}$.

When $\lambda\Delta t \sim 1$ and z is neither unity nor very small equation (11.13) must be used.

(C) Poisson Distribution and Normal or Gaussian Distribution

The binomial distribution may be replaced by the simpler Poisson distribution (15). The probability $P(d)$ of finding d disintegrations is then given by equation (11.18), where $\bar{N}$ is the average to be expected (equation (11.9))

$$P(d) = \frac{\bar{N}^d}{d!}\exp(-\bar{N}) \qquad (11.18)$$

on condition that $\lambda\Delta t \ll 1$ (≤ 0.01) and $N_0 \gg 1$ (≥ 100).

The above distribution law is also valid for very small disintegration rates, such as $D = \bar{N}/\Delta t = 10$ dpm. Note that, for small disintegration rates, the distribution is not completely symmetrical around $d = \bar{N}$.

For $\bar{N}$ (or d) > 100 and $\bar{N} \simeq d$, the Poisson distribution can be replaced by the normal or Gaussian distribution:

$$P(d) = \frac{1}{\sqrt{(2\pi\bar{N})}}\exp\left[-\frac{(\bar{N} - d)^2}{2\bar{N}}\right] \qquad (11.19)$$

The normal distribution is symmetrical around $d = \bar{N}$, as is the Poisson distribution for large $\bar{N}$.

For both the Poisson and Gaussian distribution it can be shown that for d large and $\lambda\Delta t \ll 1$:

$$\sigma_d = \sqrt{\bar{N}} \simeq \sqrt{d};\ \sigma_c = \sqrt{\bar{N}z} \simeq \sqrt{c};\ \sigma_D = \frac{\sqrt{d}}{\Delta t} = \sqrt{\frac{D}{\Delta t}};$$

$$\sigma_R = \frac{\sqrt{c}}{\Delta t} = \sqrt{\frac{R}{\Delta t}} \qquad (11.19a)$$

where c and d respectively represent a number of counts and disintegrations, and R and D indicate respectively a count rate and a disintegration rate.

The above discussion applies as well to the background activity as to the sample activity to be measured. If the number of counts of the background c_B is sufficiently large ($\sqrt{c_B} \gg 1$), the Poisson distribution of the background practically coincides with the normal distribution. Therefore the net count difference $c_S = c_C - c_B$ also obeys the latter (C refers to sample plus background, B to background alone, S to sample).

Note:

—For small values of c_B (≤ 4) this difference does not obey the Poisson distribution, but obeys a more complex distribution (18).

—If n observations are carried out, yielding $c_1, c_2 \ldots c_i$ counts, the standard deviation for one observation can obviously also be calculated by equation (11.3 bis):

$$\sigma = \left[\frac{\sum(c_i - \bar{c})^2}{n - 1}\right]^{1/2} \qquad (11.20)$$

where $\bar{c}$ represents the arithmetic mean of the n observations.

The statistical error given by this equation and that given by equation (11.15) should agree if the experimental data are truly statistical. If the equipment has produced counts (spurious counts, electrical noise, etc.) it would be noted that the positive and negative values of the residuals $c_i - \bar{c}$ would not occur with about equal frequency, and the standard deviations calculated in the two ways would not agree. If a small difference is found between the results of equations (11.20) and (11.15), a χ^2-test can be performed to find out whether the difference is significant or merely due to the finite number of observations.

(D) STANDARD DEVIATION FOR RATEMETERS AND IONIZATION CHAMBERS

According to Kip *et al.* (19) the standard deviation of the counting rate may be estimated from the relation:

$$\sigma = \sqrt{\bar{R}/2k(t)} = 0.71\sqrt{\bar{R}/k(t)} \qquad (11.21)$$

where $\bar{R}$ is the average pulse rate (in cps), and $k(t) = RC$, the time constant of the circuit (R in ohms, C in farads). The fractional standard deviation of a single reading is

$$\sigma/\bar{R} = (2\bar{R}k(t))^{-1/2} \qquad (11.22)$$

Hence, knowing $k(t)$ and determining $\bar{R}$ by calibration, the standard deviation may be assessed. If $k(t)$ is not known it may be estimated by observing the recorded activity as it falls to zero after an active source has been removed from the counter. $k(t)$ is equal to the time necessary for the observed reading to fall to $1/e$ (ca. 37%) of its original value. If $k(t)$ is determined in this way with a recording ratemeter, the pen drag should be reduced to a minimum.

III. Counters and Background

In practice, the activity of a source must be estimated by the difference between the observed activity, obtained with the source present, and the natural background activity in the absence of the source. Hence the rules for error propagation (see Table 11.3 (1)) must be applied. If the total number of counts obtained in a given period in the presence of the source is 400 and the natural background gives 64 counts during the same period, then the expected standard deviation σ of the net result, obtained by the difference $400 - 64 = 336$, is given by $[(400^{1/2})^2 + (64^{1/2})^2]^{1/2} = (464)^{1/2} = 21.5$. Hence the activity of the source is 336 ± 21.5 counts.

The final precision is thus determined not only by the activity of the source and by the background activity, but also by the counting times Δt_C and Δt_B.

If only a limited measuring time is available, e.g. because large series of samples must be counted, the choice of Δt_C and Δt_B becomes important (C refers to sample plus background; B to background alone). The choice of a detector with a suitable signal to background ratio is also of interest, particularly when the counting rates are low and when the counting rate of the sample $R_S = R_C - R_B$, is smaller than the background rate R_B. In the following discussion, the assumption $\Delta t_C < T_{1/2}$ is made.

(A) CHOICE OF $\Delta t_C/\Delta t_B$

According to Table 11.3 (1) and to equation (11.16) one can write:

$$v(S) = \sigma^2(S) = \sigma^2(C) + \sigma^2(B) = R_C/\Delta t_C + R_B/\Delta t_B \qquad (11.23)$$

The fractional standard deviation $\sigma_f = \sigma_{\%}/100$ of the measurement R_S is given by

$$\sigma_f^2 = \frac{\sigma^2(S)}{R_S^2} = \frac{R_C/\Delta t_C + R_B/\Delta t_B}{(R_C - R_B)^2} = \frac{r/\Delta t_C + 1/\Delta t_B}{R_B(r-1)^2} \qquad (11.24)$$

where $r = R_C/R_B$.

To use a counter efficiently one must choose either $\Delta t_C/T$ for a fixed total time $T = \Delta t_C + \Delta t_B$ so as to reduce σ_f to a minimum, or $\Delta t_C/T$ for a fixed σ_f to reduce T to a minimum. Both criteria are equivalent and lead to the same result. Using the first criterion for a given set of sample and background rates (i.e. R_B, R_C, r and T given), Δt_C must be chosen so as to reduce the nominator of equation (11.24),

$$r/\Delta t_C + 1/(T - \Delta t_C)$$

to a minimum. Thus the derivative of the nominator with respect to Δt_C must be zero:

$$-r/\Delta t_C^2 + 1/(T - \Delta t_C)^2 = 0$$

or

$$\Delta t_C/\Delta t_B = r^{1/2} = (R_C/R_B)^{1/2} \qquad (11.25)$$

and

$$\Delta t_C/(\Delta t_C + \Delta t_B) = \Delta t_C/T = r^{1/2}/(1 + r^{1/2}) \qquad (11.26)$$

The optimum $\Delta t_C/\Delta t_B$ ratio as a function of $R_S = R_C - R_B$ and of R_B can be read from the nomogram in Figure 11.7 (20).

Substituting for Δt_C and for Δt_B in equation (11.24), the minimal fractional standard deviation σ_f for a total counting time T becomes:

$$\sigma_f^2 = \frac{[r^{1/2}(1 + r^{1/2})]/T + [1 + r^{1/2}]/T}{R_B(r - 1)^2} = \frac{(r^{1/2} + 1)^2}{TR_B(r - 1)^2} \qquad (11.27)$$

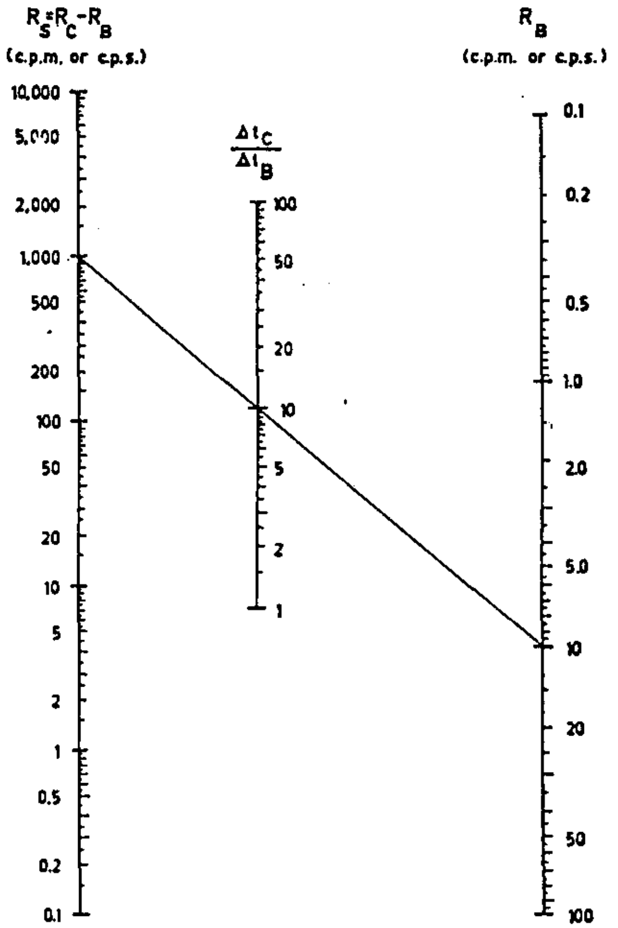

Fig. 11.7. Optimum $\Delta t_c/\Delta t_b$ as a function of background rate R_B and counting rate $R_s = R_C - R_B$ (20).

or

$$\sigma_f^2 = Q/T \qquad (11.28)$$

where

$$Q = \frac{(r^{1/2} + 1)^2}{R_B(r - 1)^2} = \frac{(r^{1/2} + 1)^2 R_B}{R_S^2} \qquad (11.29)$$

Equation (11.27) can also be written as follows:

$$\sigma_f = \frac{1}{(r^{1/2} - 1)\sqrt{TR_B}}$$

since $(r - 1) = (r_B^{1/2} + 1)\,(r^{1/2} - 1)$.

Hence,

$$R_C^{1/2} = (1 + \sigma_f\sqrt{TR_B})/\sigma_f\sqrt{T}$$

so that for the net count rate of the source ($R_S = R_C - R_B$):

$$R_S = (1 + 2\sigma_f\sqrt{TR_B})/\sigma_f^2 T \qquad (11.30)$$

Equation (11.30) expresses the minimum observable counting rate of the source which will have a fractional standard deviation σ_f, when recorded with a counter having a background R_B for a total time T, optimally divided between Δt_C and Δt_B.

Examples:

(a) $R_C = 176$ cpm, $R_B = 39$ cpm, $R_S = 137$ cpm, $r = R_C/R_B = 4.51$, $\Delta t_C/\Delta t_B = r^{1/2} = 2.12$, $\Delta t_C/T = 2.12/3.12 = 0.68$, $Q = 2 \times 10^{-2}$. If T is fixed at 100 m, σ_f^2 (min) $= 2.05 \times 10^{-4}$, $\sigma_f = 0.0142$ or $\sigma_{\%} = 1.42\%$, i.e. with optimal time division ($\Delta t_C = 68$ m, $\Delta t_B = 32$ m) the minimal possible percentage standard deviation is 1.42%.

(b) Requiring for the same sample a percentage standard deviation of only 3%, $\sigma_f = 0.03$, $\sigma_f^2 = 9 \times 10^{-4}$, $T_{(\text{min})} = Q/\sigma_f^2 \simeq 22$ m ($\Delta t_C = 15$ m, $\Delta t_B = 7$ m).

(c) When counting for a total time $T = 100$ m in optimum conditions the minimum counting rate R_S, which can be recorded by this counter with a standard deviation of 3% is $(1 + 0.06\sqrt{3900})/9 \times 10^{-4} \times 100 = 473.8/9 \simeq 53$ cpm.

The optimum time division in this case is $\Delta t_C \simeq 60$ m and $\Delta t_B \simeq 40$ m.

If the sample rate is much higher than the background rate ($R_S \gg R_B$), equation (11.29) can be simplified, as $r^{1/2} + 1 \simeq r^{1/2}$

$$Q \simeq rR_B/R_S^2 = R_C/R_S^2 \simeq R_S/R_S^2 = R_S^{-1} \qquad (11.31)$$

If however $R_S \ll R_B$, $r^{1/2} + 1 \simeq 1 + 1 = 2$; hence

$$Q = 4R_B/R_S^2 \quad \text{or} \quad 1/Q = R_S^2/4R_B = M^2 \tag{11.32}$$

M is called the figure (or factor) of merit of a counter in the region where the background is important (see further)

$$M = R_S/2\sqrt{R_B} \tag{11.32a}$$

From equation (11.28) follows that the condition for minimal σ_f (fixed T) or minimal T (fixed σ_f) is that Q be a minimum (1)).

(B) CHOICE OF COUNTER WITH MINIMAL-Q CRITERION

The minimal-Q criterion allows one to choose the best among several counters or among several operating conditions.

If the ratio of the counting efficiencies for sample and background is a constant while the sensitivity is changed ($r_1 = r_2$), it appears from equation (11.29) that

$$Q_2/Q_1 = R_{B2}R_{S1}^2/R_{B1}R_{S2}^2 = R_{S1}/R_{S2} = D_S z_1/D_S z_2 = z_1/z_2$$

since $R_{B1}/R_{S1} = R_{B2}/R_{S2}$. Only the efficiency determines the quality of the counter. If $z_2 > z_1$, then $Q_2 < Q_1$, so that on the basis of the minimal Q criterion one can conclude that counter 2 is the better one. In this case it is always advisable to increase the efficiency z as much as possible.

If the ratio of the efficiencies for sample and background is not constant with changing sensitivity ($r_1 \neq r_2$), both R_S^2/R_B and r depend on the counter.

If $R_S \gg R_B$ ($r \gg 1$) for both counters, equation (11.31) can directly be used:

$$\frac{Q_2}{Q_1} \simeq \frac{R_{S1}}{R_{S2}} = \frac{D_S z_1}{D_S z_2} = \frac{z_1}{z_2}$$

Under this condition the background is unimportant and, again, only the ratio z_1/z_2 determines which counter is superior. For high disintegration rates one should choose the instrument with the highest efficiency.

If $R_S \ll R_B$ ($r \simeq 1$) for both counters, equation (11.32) can directly be used. Counter 2 will be superior to counter 1, if $Q_2 < Q_1$, i.e. if $M_2 > M_1$. In that case M is a suitable figure of merit, consequently both R_S ($= D_S z$) and R_B must be considered to judge what counter should be chosen.

Use of the above expressions for comparing detector sensitivities generally involves the replacement of R_S by the product of the sample disintegration rate D_S and the detection efficiency z. Various detectors are then compared by examining their Q-values. Such a procedure suffers from a number of limitations (21):

(1) no allowance is made for short lived radioactivity;
(2) interference – especially "decaying" interference – is not considered;
(3) the formula may not be applicable to the comparison of critical levels or detection limits (see further), because type 1 and type 2 errors have not been included.
(4) the factor M can only be used on condition that $R_S \ll R_B$. This factor could lead to a wrong conclusion for w_D and w_Q (see further). This means that the exact equations of the form $w_D = \gamma L_D$ can lead to the conclusion that with one detection system the lower limit of detection is reached, but that with the other one the lower limit of determination is obtained.

IV. Limits for Qualitative Detection and Quantitative Determination Applied to Radiochemistry and Activation Analysis

(A) INTRODUCTION

Examination of the analytical and radiochemical literature for an appropriate definition of the "detection limit" reveals a plethora of mathematical expressions and widely varying terminology, as was pointed out by Currie (21). One encounters for example terms such as lower limit of detection (22–25), detection sensitivity (26), sensitivity (27), minimum detectable activity (or mass) (28) and limit of guarantee for purity (29) – all used with approximately equivalent meanings. The nomenclature problem is compounded, because other authors make use of the same or very similar terms to refer not to the minimum amount that may be detected, but rather to the minimum amount which may be determined with a given relative standard deviation. Still other expressions, such as the "detection limit at the 95% confidence level" are used without explicit mathematical definition, which leaves the meaning rather ambiguous. Moreover, various "nonstatistical" definitions appear in which the detection limit is equated to the background, 10% of the background, 100 dps (γ-radioactivity), or 1000 dpm (α-, β-, γ-radioactivity). In order to compare some of the more commonly used definitions, Currie (21) has calculated "detection limits" for a hypothetical experiment in which a long lived γ-emitter was counted for 10 minutes with an efficiency of 10%, using a detector with a background of 20 cpm. The results, plotted in increasing order in Figure 11.8, are unsatisfactory, for they encompass nearly three orders of magnitude!

In the subsequent discussion, a distinction will be made between

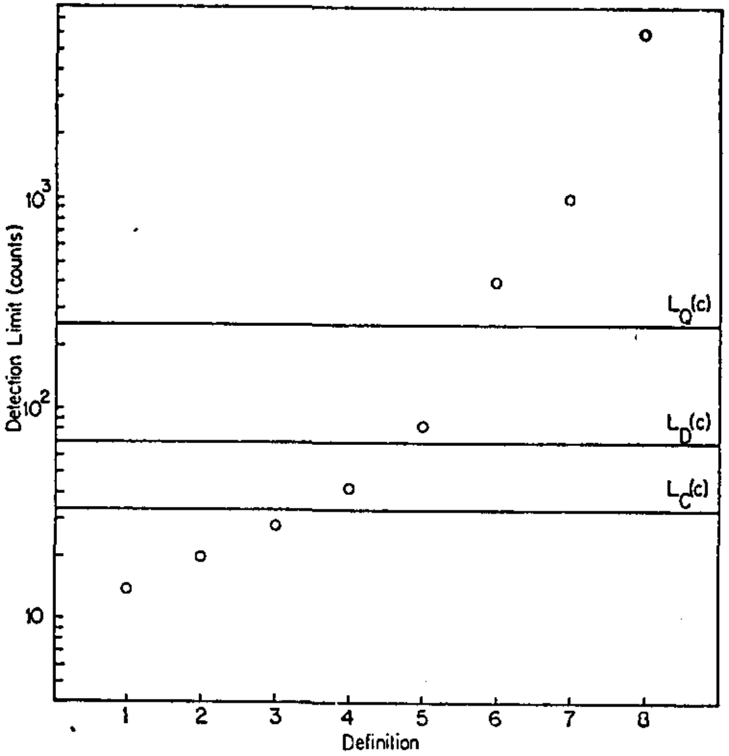

Fig. 11.8. Comparison of some commonly-used definitions of detection limit, when counting a long-lived γ-emitter for 10 m with an efficiency of 10%, using a detector having a background of 20 cpm. Definitions: 1. Background standard deviation σ_B; 2. 10% of the background; 3. $2\sigma_B$; 4. $3\sigma_B$; 5. $3\sigma_B + 3\sigma_D$ (σ_D = sample standard deviation); 6. Twice the background; 7. 1000 dpm.; 8. 100 dps. (21).

three specific levels, as proposed at the National Bureau of Standards (21). (i) a decision limit (critical level): L_C ($L_C(c)$ counts or $L_C(R)$ cpm); (ii) a detection limit: L_D ($L_D(c)$ counts or $L_D(R)$ cpm); (iii) a limit for quantitative determination: L_Q ($L_Q(c)$ counts or $L_Q(R)$ cpm).

In the following paragraphs the nature of these quantities will be discussed in detail, taking into account the half-life of the radioisotope of interest, the detector background (in the energy region of interest), the optimum counting time in the case of short lived radioisotopes and the required confidence level. The results will also be applied to coincidence counting.

It is obvious that the statistics of decision, detection and determination apply directly to the observations (activity) rather than to the underlying quantity and therefore the following discussion will deal specifically with the observed signal and its associated random distribution. Statistical conclusions drawn in terms of the net signal may be extended to the related physical quantity by means of a calibration factor. In analytical practice it is convenient to express the "lower limit of detection", ... in terms of the mass w_D of the element to be detected under given irradiation and measuring conditions:

$$w_D = \gamma L_D(R) \quad \text{or} \quad w_D = \gamma L_D(c) \qquad (11.33)$$

If L_D is a counting rate, the calibration constant γ is expressed in gram (milligram, microgram) per cpm or per cps, and depends on the neutron flux, the isotopic abundance of the target nuclide, the atomic weight of the target element, the reaction cross section, the irradiation and waiting time, the disintegration scheme of the radionuclide formed, the counting geometry, the efficiency of the detector and the fraction of the pulses which are counted. The factor γ can thus be calculated from equation (10.1), if the parameters of interest are known.

If L_D is a number of counts, the calibration constant γ is expressed in gram per count.

Tables with calculated $1/\gamma$-values can be found in references (30,31). The count rate per minute per microgram of target element, obtained by 4π beta and alpha counting, single-gamma counting, gamma-gamma coincidence counting, beta-gamma coincidence counting and triple-coincidence counting were computed by Wing and Wahlgren (30) for irradiation times of 0.5; 5; 50; 500 and 5000 m at a thermal neutron flux of 10^{14} n cm^{-2} s^{-1}.

Induced activities (cpm/μg) as a function of irradiation time and of waiting time are also given by Girardi (31), taking into account the detection efficiency of a 7.5 × 7.5 cm NaI(Tl) detector for the geometry and the photopeak used. The data are given for thermal neutron fluxes of 5×10^{12}; 10^{13} and 2×10^{13} n cm^{-2} s^{-1}. Experimental results in cpm under the photopeak per gram element for single-gamma counting are given by Anders (32) for an irradiation time of 5 m at a flux of ca. 10^{8} moderated n cm^{-2} s^{-1} and by Yule (33) for an irradiation time of 1 h at a thermal neutron flux of ca. 4×10^{12} n cm^{-2} s^{-1}.

(B) Definitions – Signal Detection

If the observed number of counts from a sample + background and from the background alone, for an equal time of measurement Δt, are respectively c_{S+B} and c_B, then the count difference $c_S = c_{S+B} - c_B$ is a measure of the net activity of the sample. However, owing to the statistical fluctuations, this count difference at the averages of the background $\bar{c}_B$ and the sample $\bar{c}_S$ may obtain various values. At a relatively small value of c_S, the presence of the activity in the sample becomes doubtful. Therefore a so-called "critical value" L_C is introduced, that is often called in the literature the "minimum significant count difference" (22,25) or "decision limit" (21). For $c_S > L_C$ one assumes that the signal is present, for $c_S < L_C$ the decision "not detected" should be reported. The statistical character of the count rate means that such an assumption must always be connected with a probability of making a wrong decision. Two kinds of errors may occur:

(i) The measured value $c_S > L_C$; one concludes that the activity >0, when in fact the activity = 0 (type 1 error). The probability P_1 of making this error depends on the accepted value of $L_C = u_1\sigma(0)$ (Figure 11.9 curve a).

(ii) The measured value $c_S < L_C$; one concludes that the activity = 0, when in fact the activity >0 (type 2 error). Such a case is illustrated in Figure 11.9, curve b. Despite the fact that the signal >0, a relatively large probability P_2 exists, that the measured count difference $< L_C$. The probability P_2 of making this error depends on L_C and on the sample activity, i.e. on the position of the Gauss curve on the c_S-axis.

For $c_S = L_D$ (Figure 11.9 curve c), the probability of making the type 2 error is already so small, that the signal will practically always be detected. The smallest activity, corresponding to the value L_D, is called the "minimum detectable true activity" and will be identified with the "lower limit of detection" (22).

The foregoing discussion can be summarized as follows:

(i) if the result of a counting yields a count difference $c_S > L_C$, one can conclude (*a posteriori*) that the activity is present.

(ii) if an activity $c_S = L_D$ is present in the sample, one knows (*a priori*) that the analytical procedure may be relied upon to lead to its detection.

1. *The Critical Level or Decision Limit*

As appears from Figure 11.9, the critical level is mathematically given by

$$L_C = u_1\sigma(0) \tag{11.34}$$

The parameter u_1 is a multiple of the standard deviation, determining the probability of making the type 1 error. Usual accepted values for u_1 are 1.645; 1.960 or 3.000. Contrary to Table 11.1, this does not correspond to a confidence level of 90, 95 and 99.73% respectively, but to a confidence level of 95, 97.5 and 99.865% respectively. Indeed, the probability of making the type 1 error is respectively 10/2 = 5, 5/2 = 2.5 and 0.27/2 = 0.135% only (one side of the Gauss curve). For that reason, the symbol u has been replaced by u_1. The problem of the confidence intervals is discussed in detail by Currie (21).

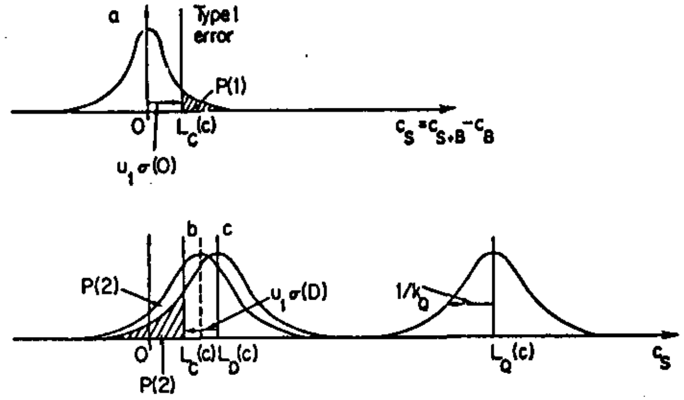

Fig. 11.9. Signal detection. Definition of critical level $L_C(c) = \mu_1\sigma(0)$ detection limit $L_D(c) = L_C(c) + \mu_1\sigma(D)$ and determination limit $L_Q(c) = k_Q\sigma_Q$ (21).

The variance for a count difference $c_S = c_{S+B} - c_B$ is given by $\sigma^2(S) = \sigma^2(S+B) + \sigma^2(B) = (c_S + 2c_B)$. If no activity is present, $c_S = 0 \pm \sigma(0)$ where $\sigma(0) = \sqrt{2c_B}$. Hence, the critical level is given by

$$L_C(c) = u_1\sqrt{2c_B} = u_1\sqrt{2R_B\Delta t} \qquad \text{(counts)} \qquad (11.35)$$

where c_B is the number of background counts and R_B the (average) background rate. When dealing with low activities, equation (11.25) is reduced to $\Delta t_C \approx \Delta t_B = \Delta t = 0.5\ T$. Equation (11.35) is valid for so called paired observations.

If the background is constant, and very well known by a long history of observations, one can state that $\sigma^2(S) \simeq \sigma^2(S+B) = c_S + c_B$. If no activity is present, $c_S = 0 \pm \sigma(0)$ where $\sigma(0) = \sqrt{c_B}$. Thus, by measuring the background during a long time ($\gg \Delta t$), one can decrease the critical level by a factor $\sqrt{2}$. Then

$$L'_C(c) = u_1\sqrt{c_B} = u_1\sqrt{R_B\Delta t} \qquad \text{(counts)} \qquad (11.35a)$$

where the prime serves as a reminder that the background is well known.

The corresponding "minimum significant counting rate differences" $L_C(R)$ and $L'_C(R)$ are thus given by

$$L_C(R) = L_C(c)/\Delta t = u_1\sqrt{(2R_B/\Delta t)} \text{ (cpm, cps) (paired observations)} \qquad (11.36)$$

and

$$L'_C(R) = L'_C(c)/\Delta t = u_1\sqrt{(R_B/\Delta t)} \text{ (cpm, cps) (well known background)} \qquad (11.36a)$$

For short lived isotopes $L_C(R)$ represents the average minimum significant counting rate difference (see further).

2. *The Lower Limit of Detection*

Mathematically, the "lower limit of detection", which is used to assess the *a priori* detectability, is given by

$$L_D = L_C + u_1\sigma(D) \qquad (11.37)$$

as appears from Figure 11.9. To simplify the discussion the same parameter u_1 will be used to determine both the probability of making a type 1 and a type 2 error. In the above equation, $\sigma(D)$ represents the standard deviation of a number of counts $c_S = L_D$:

$$\sigma^2(D) = \sigma^2(0) + L_D$$

Hence, equation (11.37) becomes:

$$L_D - L_C = u_1(\sigma^2(0) + L_D)^{1/2}$$

$$(L_D - L_C)^2 = u_1^2\sigma^2(0) + u_1^2 L_D$$

Remembering that $L_C = u_1\,\sigma\,(0)$ one obtains:

$$L_D(L_D - 2L_C - u_1^2) = 0$$

or

$$L_D = u_1^2 + 2L_C$$

Thus:

$$L_D(c) = u_1^2 + 2u_1\sqrt{2c_B} \qquad \text{(counts)} \quad \text{(paired observations)} \qquad (11.38)$$

$$L'_D(c) = u_1^2 + 2u_1\sqrt{c_B} \qquad \text{(counts)} \quad \text{(well known background)} \qquad (11.38a)$$

The corresponding counting rates are given by:

$$L_D(R) = u_1^2/\Delta t + 2u_1\sqrt{(2R_B/\Delta t)} \qquad \text{(cpm, cps)} \qquad (11.39)$$

$$L'_D(R) = u_1^2/\Delta t + 2u_1\sqrt{(R_B/\Delta t)} \qquad \text{(cpm, cps)} \qquad (11.39a)$$

For short lived radionuclides (and/or) background activities, $L_D(R)$ and/or R_B represent average counting rates (see further).

From these equations, the following conclusions can be drawn:

(i) The longer the counting time, the lower the limit of detection. Such long measuring times are obviously limited to long-lived isotopes and may be of interest in the case of long activation times (several hours or days), i.e. in the case of reactor activation analysis. Extremely high sensitivities can be obtained in this way.

(ii) The limit of detection depends on the accepted confidence level (u_1).

(iii) In many practical cases, $u_1^2 \ll 2u_1\sqrt{c_B}$, so that $L_D(c) \simeq 2L_C(c)$ and $L_D(R) \simeq 2L_C(R)$ (see example further).

(iv) In the case of zero background, it should be noted that $L_D(c)$ or $L'_D(c)$ is not zero, but u_1^2 (counts), and $L_D(R)$ or $L'_D(R) = u_1^2/\Delta t$ (cpm)

Using equation (11.30) and assuming $\Delta t = 0.5\ T$, it is possible to calculate the fractional standard deviation of $L_C(R)$ or $L_D(R)$. For $L_C(R)$ one finds

$$\frac{1 + 2\sigma_f\sqrt{(2R_B\Delta t)}}{2\sigma_f^2\Delta t} = u_1\sqrt{(2R_B/\Delta t)} \tag{11.40}$$

Solving for σ_f leads to

$$\sigma_f = \frac{1 + [1 + 2u_1/\sqrt{(2R_B\Delta t)}]^{1/2}}{2u_1} \tag{11.41}$$

If the background is not too small, i.e. $2u_1/\sqrt{(2R_B\Delta t)} \ll 1$, $\sigma_f \simeq 1/u_1$. At the 95% probability level $u_1 = 1.645$ (see above), so that $\sigma_\% \simeq 60\%$. For $L_D(R)$ one finds $\sigma_\% \simeq 30\%$ at the same confidence level.

3. *The Limit of Quantitative Determination*

The above data for $\sigma_\%(L_C)$ and $\sigma_\%(L_D)$ are not entirely satisfactory for a precise quantitative determination. It is obvious that one can calculate a "determination limit" for a desired percentage standard deviation (21). Such a definition is similar to that used by Adams *et al.* (34), who defined a "minimum working concentration" as that at which the percentage standard deviation is 10%, as far as counting statistics are involved. The term on the left of equation (11.40) expresses the minimum observable counting rate due to a radioactive source, which will have a given σ_f, when recorded by means of a counter with a background rate R_B, assuming paired observations. For $\sigma_\% = 10\%$, $\sigma_f = 0.1$ one finds:

$$L_Q(R) = \frac{1 + 0.2\sqrt{(2R_B\Delta t)}}{0.02\,\Delta t} \qquad \text{(cpm)}$$

and

$$L_Q(c) = L_Q(R)\Delta t = 50[1 + 0.2\sqrt{(2c_B)}] \quad \text{(counts)} \tag{11.42}$$

A different approach is given by Currie (21) for $\Delta t \neq 0.5T$. The results are however practically equal, if the background is not too small. Even for $R_B = 1$ cpm and $\Delta t = 16$ m, the results for L_Q differ by ca. 20% only.

The determination limit is defined as (see Figure 11.9a)

$$L_Q(c) = k_Q\sigma(Q) \tag{11.43}$$

where $L_Q(c)$ is the value of the net signal c_S with a standard deviat $\sigma(Q)$; $\sigma(Q)/L_Q(c) = 1/k_Q = \sigma_f(Q)$ is the fractional standard deviation; $\sigma(Q) = (L_Q(c) + \sigma^2(0))^{1/2}$, hence

$$L_Q^2(c) - k_Q^2L_Q(c) - k_Q^2\sigma^2(0) = 0$$

or

$$L_Q(c) = \frac{k_Q^2}{2}\left[1 + \left(1 + \frac{4\sigma^2(0)}{k_Q^2}\right)^{1/2}\right] \tag{11.44}$$

For paired observations, $\sigma^2(0) = 2c_B = 2R_B\Delta t$. Setting $\sigma_f(Q) = 0.1$:

$$L_Q(c) = 50\,[1 + (1 + 0.08\,c_B)^{1/2}] \quad \text{(counts)} \tag{11.45}$$

For a well-known background:

$$L'_Q(c) = 50\,[1 + (1 + 0.04\,c_B)^{1/2}] \quad \text{(counts)} \tag{11.45a}$$

The corresponding values for $L_Q(R)$ (long lived isotopes) are found by dividing by Δt. For short lived isotopes, $L_Q(R)$ represents the average counting rate.

Example:

For a counter with a background of 10 cpm, the values $L_C(c)$, $L_D(c)$ and $L_Q(c)$ will be calculated, assuming a counting time of 10 minutes and a confidence level of 95% ($u_1 = 1.645$)

$$L_C(c) = 2.33\sqrt{R_B\Delta t} = 23.3 \text{ counts (paired observations)}$$

or

$$L'_C(c) = 1.64\sqrt{R_B\Delta t} = 16.4 \text{ counts (well known background)}$$

This means, if the observed number of counts in 10 minutes for signal + background ≥ 123.3 (or 116.4), the decision "detected" should be reported.

Note that this count difference is known with a precision of ±66%:

$$L_C(c) = 123.3 - 100 = 23.3 \pm \sqrt{223.3} = 23.3 \pm 15.3 \text{ counts } (\pm 66\%)$$

$$L'_C(c) = 116.4 - 100 = 16.4 \pm \sqrt{116.4} = 16.4 \pm 10.8 \text{ counts } (\pm 66\%)$$

If one wants to be sure *a priori*, with a confidence level of 95%, that in the above conditions (R_B, Δt) an activity will be detected, the latter must be at least

$L_D(c) = 2.71 + 4.65\sqrt{R_B\Delta t} = 49.2$ counts (paired observations) or $L'_D(c) = 2.71 + 3.29\sqrt{R_B\Delta t} = 35.6$ counts (well known background), i.e. $c_{S+B} = 149.2$ (or 135.6) counts. Assuming long lived radioisotopes, $L_D(R) = 4.92$ cpm and $L'_D(R) = 3.56$ cpm.

If the detection efficiency of the counter is 20%, the limit of detection is a disintegration rate of 24.6 dpm, respectively 17.8 dpm.

Note that a number of counts $= L_D$ can be measured with a standard deviation of ±32%:

$$L_D(c) = 149.2 - 100 = 49.2 \pm \sqrt{249.2} = 49.2 \pm 15.8 \text{ counts } (\pm 32\%)$$

$$L'_D(c) = 135.6 - 100 = 35.6 \pm \sqrt{135.6} = 35.6 \pm 11.7 \text{ counts } (\pm 32\%)$$

The determination limit, assuming $\sigma_{\%} = 10\%$, in the above conditions

$$L_Q(c) = 50\,[1+(1+8)^{1/2}] = 200 \text{ counts} \quad \text{(paired observations)}$$

Indeed $c_S = c_{S+B} - c_B = 300 - 100 = 200 \pm \sqrt{400} = 200 \pm 20$ counts (±10%)

$$L'_Q(c) = 50\,[1 + (1+4)^{1/2}] = 162 \text{ counts (well known background)}$$

Indeed: $c_S = c_{S+B} - c_B = 262 - 100 = 162 \pm \sqrt{262} = 162 \pm 16.2$ counts (±10%), since the error in c_B is assumed to be negligible.

It is obvious that lower values for L_C, L_D and L_Q will be obtained when counting for a longer time Δt. This procedure is obviously limited to long lived isotopes.

It should be borne in mind that there exists a considerable difference between the lower limit of detection, the lower limit of determination (which both imply that the identity of the measured activity is known, i.e. that the combined procedure of chemical isolation and/or counting should be specific for the radioisotope of interest) and the lower limit of identification (21,22).

The lower limit of determination can be defined as a "minimum working concentration", at which the relative standard deviation is for instance 10%. When identification is required, the radiochemical purity must be checked by measuring the energy of the radiation and/or the half-life. For that purpose, the counting rate must often be higher than $L_D(R)$, e.g. one order of magnitude.

4. *Application to Short Lived Radioisotopes and Long Lived (Constant) Background* (simple counting method)

The same equations for L_C, L_D and L_Q are valid for short lived radionuclides, i.e. the same number of counts must be recorded for a given background, to obtain the critical level, the limit of dete[illegible] or the limit of determination. It can be shown however that an optimum counting time exists.

If at the beginning of the measuring time Δt the sample counting rate is R_0, the net number of counts recorded after the time Δt is given by

$$c_S = R_0 \int_0^{\Delta t} \exp(-\lambda t)\, dt = \frac{R_0}{\lambda}[1 - \exp(-\lambda \Delta t)] \qquad (11.46)$$

whereas the (constant) background yields $c_B = R_B \Delta t$ counts. During the decay of the radionuclide of interest, an increasing number of background pulses are counted. Consequently, there will exist an optimum measuring time, which allows the detection of the smallest starting rate R_0 in the presence of a constant background rate R_B.

According to equation (11.36) one can write for the "minimum significant counting rate difference" (critical level) at $t = 0$:

$$\frac{L_C(R)_0}{\lambda}[1 - \exp(-\lambda \Delta t)] = u_1 \sqrt{2 R_B \Delta t}$$

or

$$L_C(R)_0 = \frac{u_1 \lambda \sqrt{2 R_B \Delta t}}{1 - \exp(-\lambda \Delta t)} \quad \text{(paired observations)} \qquad (11.47)$$

$L_C(R)_0$ is a minimum if the derivative of this equation with respect to Δt is zero, i.e. $0.5\,[1 - \exp(-\lambda \Delta t)]\, u_1 \lambda \sqrt{(2R_B)} \Delta t^{-1/2} - u_1 \lambda^2 \sqrt{(2R_B)} \Delta t^{1/2} \exp(-\lambda \Delta t) = 0$, or $\exp(+\lambda \Delta t) = 1 + 2\lambda \Delta t$. The result is:

$$\Delta t = 1.81\, T_{1/2} \qquad (11.48)$$

The same solution will obviously be found for the "minimum detectable counting rate" (= lower limit of detection) $L_D(R)_0$ at $t = 0$.

It can be shown that the limit of detection reaches a minimum for $\Delta t = 1.81\, T_{1/2}$ if the condition $u_1 < \sqrt{(R_B T_{1/2})}$ is fulfilled (22). For small values of $R_B T_{1/2}$ (i.e. the background observed for $\Delta t = T_{1/2}$) the optimum measuring time is somewhat larger than 1.81 and depends on $R_B T_{1/2}$ (22) (Figure 11.10). A practical example using 5.7 h ^{134m}Cs has been described by Dybczyński (35).

Substitution of equation (11.48) in equations (11.35), (11.38) and

(11.45) yields:

$$L_C(c) = 1.9\, u_1\sqrt{(R_B T_{1/2})} \qquad L'_C(c) = 1.34\, u_1\sqrt{(R_B T_{1/2})} \tag{11.49}$$

$$L_D(c) = u_1^2 + 3.8\, u_1\sqrt{(R_B T_{1/2})} \qquad L'_D(c) = u_1^2 + 2.7\, u_1\sqrt{(R_B T_{1/2})} \tag{11.50}$$

$$L_Q(c) = 50\,[1 + (1 + 0.144\, R_B T_{1/2})^{1/2}]$$

$$L'_Q(c) = 50\,[1 + (1 + 0.072\, R_B T_{1/2})^{1/2}] \tag{11.51}$$

The ratio c_S/R_0 for $\Delta t = 1.81\, T_{1/2}$ follows from equation (11.46) and is $1.03\ T_{1/2}$. Hence:

$$L_C(R)_0 = L_C(c)/1.03\, T_{1/2} = 1.84\, u_1\sqrt{(R_B/T_{1/2})} \tag{11.52}$$

$$L_D(R)_0 = L_D(c)/1.03\, T_{1/2} = u_1^2/1.81\, T_{1/2} + 3.69\, u_1\sqrt{(R_B/T_{1/2})} \tag{11.53}$$

$$L_Q(R)_0 = L_Q(c)/1.03\, T_{1/2} = \frac{37.5}{T_{1/2}}[1 + (1 + 0.144\, R_B T_{1/2})^{1/2}] \tag{11.54}$$

The values for $L'_C(R)_0$, $L'_D(R)_0$ and $L'_Q(R)_0$ can be found as described above.

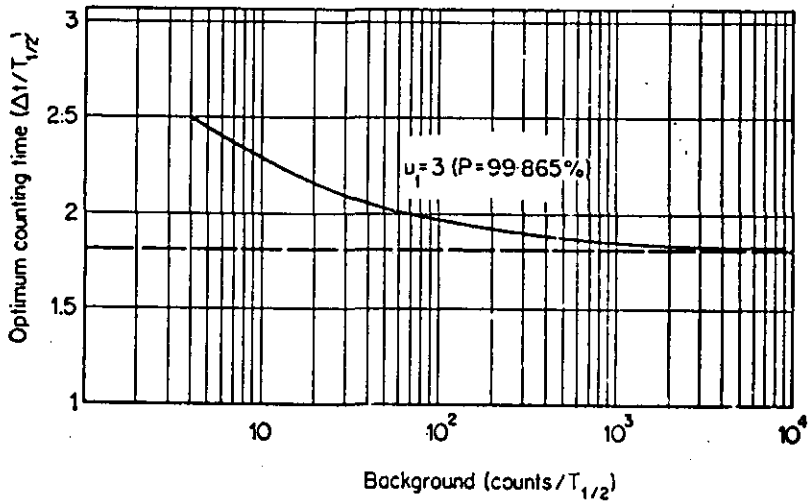

Fig. 11.10. Relationship of the optimum counting time $\Delta t/T_{1/2}$ and the observed number of counts of background in the time $T_{1/2}$ (22).

The "lower limit of detection" in terms of the mass w_D of the ele under given irradiation and measuring conditions is given by equation (11.33). Thus: $w_D = \gamma L_D(c)$, where $1/\gamma$ is expressed in counts per gram for a given counting time Δt.

One can also state $w_D = \gamma L_D(R)_0$ where $1/\gamma$ is expressed in cpm per gram at $t = 0$. Equation (11.47) has been derived, assuming $\Delta t_B = \Delta t_C$. By measuring the background during a longer time than the sample, one can obtain at most a decrease in the lower limit of detection and related quantities by a factor $\sqrt{2}$.

Example:

Assume that the 7.7 m positron-emitter ^{38}K is detected by means of the 0.511 MeV positron annihilation quanta using a sodium iodide crystal with a background of 20 cpm and a detection efficiency for ^{38}K of 32%. According to equation (11.48) a counting time of 14 m was chosen (21).

Using the general equations (11.35), (11.38) and (11.45) or (11.49), (11.50) and (11.51) one finds for $u_1 = 1.645$ (95% confidence level, paired observations):

$$L_C(c) = 2.33\sqrt{(R_B\Delta t)} = 2.33\sqrt{280} = 39 \text{ counts}$$

$$L_D(c) = 2.71 + 78 = 80.7 \text{ counts}$$

$$L_Q(c) = 50\ [1 + (1 + 0.08 \times 280)^{1/2}] = 292.5 \text{ counts } (\sigma_{\%} = \pm 10\%)$$

Suppose that an observation of sample + background gives a total of 310 counts. The net signal would then be $c_S = 310 - 280 = 30$ counts, with an estimated standard deviation of $\sqrt{(310 + 280)} = 24.3$ counts (paired observations). However $30 < L_C(c)$ and therefore such an observation would lead to the conclusion, "not detected".

The same result can be found using equations (11.52), (11.53) and (11.54):

$$L_C(R)_0 = 1.84 \times 1.645 \times \sqrt{(20/7.7)} = 4.9 \text{ cpm at } t = 0 \text{ (or 15.3 dpm)}$$

$$\begin{aligned} L_D(R)_0 &= (2.71/1.81 \times 7.7) + 3.69 \times 1.645\sqrt{(20/7.7)} \\ &= 0.194 + 9.8 \simeq 9.8 \text{ cpm at } t = 0 \text{ (or 30.6 dpm)} \end{aligned}$$

$$\begin{aligned} L_Q(R)_0 &= L_Q(c)/1.03 \times 7.7 = 292.5/7.95 \\ &= 37 \text{ cpm at } t = 0 \text{ (or 114 dpm).} \end{aligned}$$

Considering the same sample as above, the initial counting rate is given by 30/1.03 × 7.7 = 30/7.95 = 3.8 cpm. This value is <4.9 cpm and, again, such an observation leads to the conclusion "not detected".

A quantitative determination ($\sigma_{\%} \leq \pm 10\%$) is possible if the disintegration rate of ^{38}K at $t = 0$ is ≥ 114 dpm.

Until now, the assumption has been made that the background rate is constant. If however an element is determined without chemical separation, it must be counted in the presence of the matrix which can also be radioactive. This is mostly done using simple gamma ray spectrometry or coincidence methods. If both the activities from the impurity and the "background" are long lived, the problem is reduced to case 1.

If they are not long lived, but $\lambda \simeq \lambda_B$, the same conclusion is valid. It has however no sense to choose a $\Delta t >$ approximately 2.5 $T_{1/2}$, as more than 80% of the radioactive isotopes decay during that time.

If the half-life of the background activity is shorter than that of the radionuclide of interest, it is obviously recommended to start the counting after the decay of the matrix activity.

5. *Application to Short Lived Radioisotopes and Short Lived Background* (simple counting method)

If neither the counting rate of the activated impurity R_S nor the background rate R_B is constant, the number of counts recorded from the nuclide of interest is given by equation (11.46). The number of background counts is given by a similar equation:

$$c_B = R_{B,0}\,[1 - \exp(-\lambda_B \Delta t)]/\lambda_B$$

Substitution of this equation in equation (11.47) yields

$$L_C(R)_0 = u_1 \sqrt{\left(\frac{2R_{B,0}}{\Delta t}\right)} \frac{\sqrt{\left(\dfrac{1 - \exp(-\lambda_B \Delta t)}{\lambda_B \Delta t}\right)}}{\dfrac{1 - \exp(-\lambda \Delta t)}{\lambda \Delta t}} \qquad (11.55)$$

Again, the assumption $\Delta t_C = \Delta t_B = \Delta t$ has been made (paired observations).

If $\lambda > \lambda_B$ there exists also an optimum measuring time, which depends on λ and on λ_B. This time can be estimated from Figure 11.11 (23) which can be compared with Figure 11.10.

Again the general equations (11.35), (11.38) and (11.45) for L_C, L_D and L_Q are valid, where c_B is the number of background counts recorded in the optimum counting time = $k \times T_{1/2}$. Equation (11.55) can be used to calculate the critical initial counting rate $L_C(R)_0$ if $R_{B,0}$ is given.

For a nondestructive analysis, R_B depends on the matrix. Schulze (23) calculates the matrix (background) counting rate R_B for simple gamma ray spectrometry, taking into account the specific activity per milligram of matrix element, the decay scheme, the geometry factor, the total efficiency of a 7.5 cm × 7.5 cm NaI(Tl) crystal and the relative distribution of pulses in gamma ray spectra up to 2.7 MeV.

A nomographic estimation of the detection limits of an element in complex media is described by Haerdi (36).

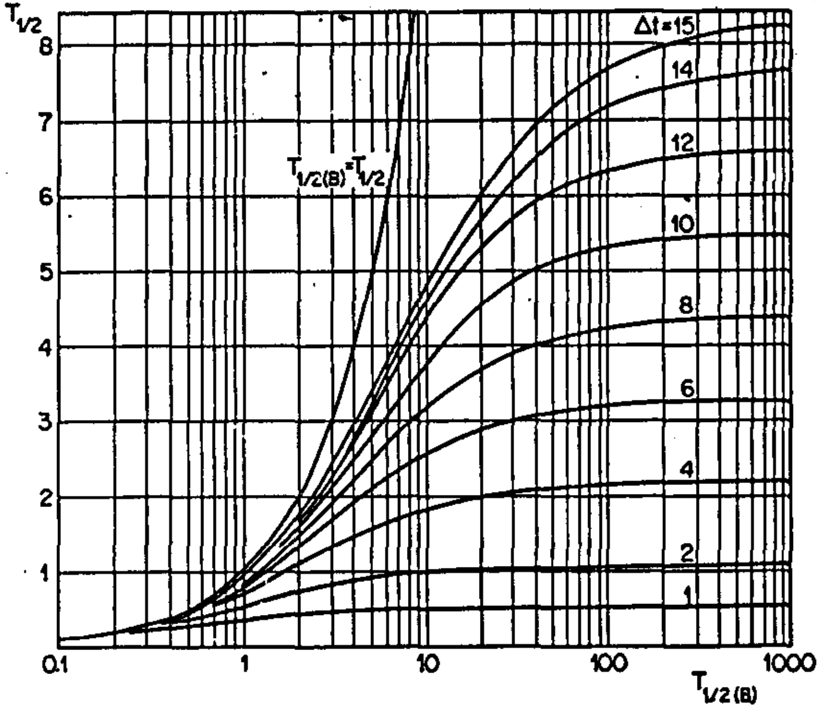

Fig. 11.11. Optimum counting time in the case of different half lives for signal and background ($\lambda > \lambda_B$). Example: if $T_{1/2}$ = 2.6 m (s, . . .) and $T_{1/2}(B)$ = 10 m (s, . . .), the optimum counting time is 6 m (s, . . .) (23).

This problem is also theoretically discussed by Currie (21).

The determination of optimum schedule and sensitivity for nondestructive activation analysis in the presence of interfering activities is given by Quittner *et al.* (37,38).

(C) THE LOWER LIMIT OF DETECTION AND OF QUANTITATIVE DETERMINATION FOR COINCIDENCE COUNTING

1. *Definitions and General Equations*

Consider a radionuclide in the decay of which time correlated cascades occur, which can be detected with a suitable coincidence system (see chapter 10, Section III, E, 1). Assume that this activity is to be counted in the presence of a relatively high "interfering" activity, such as the matrix activity in the case of a neutron activated sample. The assumption will be made here that in the decay of the latter radionuclides no time correlations occur which can be detected with the coincidence set-up; random coincidences are, however, possible and these are assumed to be more important than the random coincidences caused by the natural background.

If the two detectors of the coincidence system record c_1 and c_2 counts respectively during a time Δt, then the number of coincidence counts recorded during that time is given by:

$$c_C = c_S + c_{B'}$$

where C refers to the composite count rate $S + B'$, S to the true coincidences and B' to the random or chance coincidences (+natural background). Due to the statistical character of c_1 and c_2 the number of random coincidences $c_{B'}$ can be written as follows (13):

$$c_{B'} = 2\tau c_1 c_2/\Delta t \tag{11.56}$$

where τ is the resolving time of the coincidence circuit. $C_{B'}$ can be determined experimentally by counting the source after "mismatching" the two channels, e.g. by introducing in one channel some fixed delay time which is $\gg \tau$. At a relatively small count difference $c_S = c_C - c_{B'}$ the presence of the activity in the sample becomes doubtful. Mathematically, the critical level has been defined as $L_C = u_1\sigma(0)$ (see equation 11.34). The variance of a true coincidence count difference $c_S = c_C - c_{B'} = c_{S+B'} - c_{B'}$ is given by $\sigma^2(c_S) = \sigma^2(c_C) + \sigma^2(c_{B'})$.

If no activity is present $c_C = c_{B'}$ and $c_S = 0 \pm \sigma(0)$, where

$$\sigma(0) = \sigma(c_{B'})\sqrt{2} \text{ (paired observations) or } \sigma(0) = \sigma(c_{B'}) \text{ (well known background)}$$

In the case of coincidence measurements, it must be borne in mind that $c_{D'}$ is not directly subjected to the statistical laws of radioactivity, as is the case for c_1, c_2 and c_S:

$$\sigma(c_1) = \sqrt{c_1}; \quad \sigma(c_2) = \sqrt{c_2}; \quad \sigma(c_S) = \sqrt{c_S}$$

Hence, it is not allowed to substitute $\sigma(c_{B'})$ by $\sqrt{c_{B'}}$. Using the laws of error propagation (Table 11.3), $\sigma(c_{B'})$ can be calculated from equation (11.56)

$$[\sigma(c_{B'})/c_{B'}]^2 \cong [\sigma(c_1)/c_1]^2 + [\sigma(c_2)/c_2]^2$$

or

$$\sigma^2(c_{B'}) \cong c_{B'}^2\left(\frac{1}{c_1} + \frac{1}{c_2}\right) \tag{11.57}$$

Hence, the critical level or decision limit is given by:

$$L_C(c) = u_1\sigma(0) = u_1 c_{B'}\sqrt{2}\left(\frac{1}{c_1} + \frac{1}{c_2}\right)^{1/2} \text{ (paired observations)} \tag{11.58}$$

$$L'_C(c) = u_1 c_{B'}\left(\frac{1}{c_1} + \frac{1}{c_2}\right)^{1/2} \text{ (well known random coincidence rate + natural background)} \tag{11.58a}$$

and the lower limit of detection:

$$L_D(c) = u_1^2 + 2L_C(c) = u_1^2 + 2\,u_1 c_{B'}\sqrt{2}\left(\frac{1}{c_1} + \frac{1}{c_2}\right)^{1/2} \text{ (paired observations)} \tag{11.59}$$

$$L'_D(c) = u_1^2 + 2u_1 c_{B'}\left(\frac{1}{c_1} + \frac{1}{c_2}\right)^{1/2} \text{ (well known random coincidence rate + natural background)} \tag{11.59a}$$

After introduction of the counting rates $R_1 = c_1/\Delta t$ (first channel) $R_2 = c_2/\Delta t$ (second channel), $R_{B'} = c_{B'}/\Delta t = 2\tau c_1 c_2/\Delta t^2$ and $L_C(R) = L_C(c)/\Delta t$, $L_D(R) = L_D(c)/\Delta t$ (assuming long lived radioisotopes), the above equations can be written as follows:

$$L_C(R) = 2u_1\tau\sqrt{2}\,[R_1R_2(R_1 + R_2)/\Delta t]^{1/2} \tag{11.60}$$

$$L'_C(R) = 2u_1\tau\,[R_1R_2(R_1 + R_2)/\Delta t]^{1/2} \tag{11.60a}$$

and

$$L_D(R) = u_1^2/\Delta t + 4u_1\tau\sqrt{2}\,[R_1R_2(R_1 + R_2)/\Delta t]^{1/2} \qquad (11.61)$$

$$L'_D(R) = u_1^2/\Delta t + 4u_1\tau\,[R_1R_2(R_1 + R_2)/\Delta t]^{1/2} \qquad (11.61a)$$

Equations (11.59a) and (11.61a) correspond to N_C and C in ref. (24) assuming $u_1 = 3$.

The limit of quantitative determination $L_Q(c)$ is found, starting from equation (11.44) and substituting $\sigma^2(0)$ by $2c_{B'}^2[1/(c_1) + 1/(c_2)]$; $k_Q = 1/0.1 = 10$.

$$L_Q(c) = \frac{k_Q^2}{2}\left\{1 + \left[1 + \frac{8c_{B'}^2}{k_Q^2}\left(\frac{1}{c_1} + \frac{1}{c_2}\right)\right]^{1/2}\right\}$$

or

$$L_Q(c) = 50\left\{1 + \left[1 + \frac{0.32\,\tau^2}{\Delta t^2}\,c_1c_2\,(c_1 + c_2)\right]^{1/2}\right\} \qquad (11.62)$$

Similar equations can be calculated for $L'_Q(c)$, $L_Q(R)$ and $L'_Q(R)$.

Some interesting conclusions can be drawn from the above equations (24):

(a) Assuming a counting time of 900 s, a resolving time $\tau = 10^{-6}$ s, a confidence level of 95% ($u_1 = 1.645$), channel rates $R_1 = R_2 = R = 10^4$ cps and paired observations, the limit of detection $L_D(R) = 0.44$ cps although $R_{B'} = 2\tau R_1R_2 = 200$ cps! This means that an activity of 0.44 cps can be detected even if the random rate is higher by several orders of magnitude (200 cps). High channel rates R are often encountered in nondestructive activation analysis. The effect can be explained by the entirely different relationships, defining the statistical variations of the quantities $c_{B'}$ and c_S, and is easily demonstrated by introducing numerical values.

For the above example, one finds:

$c_S = L_D(c) = 396$ counts
$c_{B'} = 180{,}000$ counts; $\sigma(c_{B'}) = (180{,}000)\,(2/9 \times 10^6)^{1/2} = 85$ counts
$c_C \simeq 180{,}396 \pm 85$ counts.

Note that the standard deviation of $c_{B'}$ and c_C is ca. 0.05% only. The difference $180{,}396 - 180{,}000 = 396 \pm \sqrt{(85^2 + 85^2 + 396)} = 396 \pm 122$ counts is thus quite significant. The percentage standard deviation is ca. 31%, as expected (equation 11.41).

In this example it is assumed that the electronic circuit is working perfectly. In the case of pulse height dependent jitter, for instance, broadening of the resolving time occurs which might lead to a less ideal situation.

(b) From the above equations it appears that at an established level of confidence (given u_1), the lower limit of detection will improve if the "background" rate $R_{B'} = 2\tau R_1R_2$ is low and if the counting time Δt is long (assuming long lived radioisotopes).

(c) In Figure 11.12 (24) the value of $L'_D(R)$ is plotted versus $R(= R_1 = R_2)$, assuming a counting time $\Delta t = 900$ s, a resolving time $\tau = 1\ \mu$s and a confidence level of 95% ($u_1 = 1.645$). For low channel rates (in the case of Figure 11.12, $\leq 10^2$ cps), $L'_D(R)$ is constant, nl. $u_1^2/\Delta t$, i.e. the first term of equation (11.61a). Thus, if the sample size or the neutron flux is increased by a factor of 10, the concentration limit is improved by a factor of 10. For higher channel rates ($> 10^3$ cps), the value of $L'_D(R)$ increases more rapidly than R since the slope of the

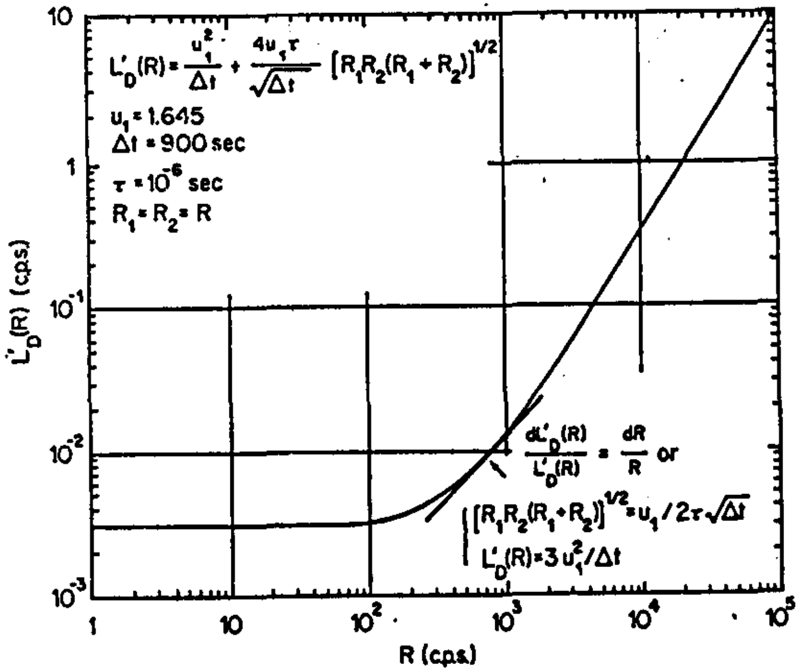

Fig. 11.12. $L'_D(R)$ as a function of channel rates $R_1 = R_2 = R$, allows to choose optimal sample activity, i.e. optimal sample size and/or optimal neutron dose (24).

straight line >1, i.e. further increasing the sample weight and/or the neutron flux worsens the lower concentration limit. Moreover, the detectors and the coincidence circuit may be overloaded. Thus for coincidence measurements there exists an optimal neutron flux (for a given sample weight) or an optimal sample size (for a given neutron flux). Optimalization is obtained (24) if $\mathrm{d}L'_D(R)/L'_D(R) = \mathrm{d}R/R$ or

$$\sqrt{\{R_1R_2(R_1 + R_2)\}} = u_1/2\tau\sqrt{\Delta t} \qquad (11.63)$$

Then, the lowest value of $L'_D(R)$ (well known random coincidence rate + optimum sample activity) is given by

$$L_D(R) = 3\,u_1^2/\Delta t \text{ cps} \quad (\Delta t \text{ in seconds}) \qquad (11.64)$$

From this equation it appears again that long counting times will appreciably improve the lower limit of detection.

2. *Application to Short Lived Radioisotopes and Long Lived (Constant) Background* (coincidence counting)

The same equations (11.58), (11.59) and (11.62) for $L_C(c)$, $L_D(c)$ and $L_Q(c)$ are valid, as for coincidence counting of long lived radioisotopes. It can be shown that there exists an optimum counting time, given by $\Delta t = 1.81\ T_{1/2}$ on condition that $R' = 2u_1\tau\sqrt{\{R_1R_2(R_1 + R_2)\}}$ is sufficiently high, e.g. >10. For smaller values of R', the optimum counting time $\Delta t > 1.81\ T_{1/2}$, nl. ca. 2.2 for $R' = 1$ and ca. 4 for $R' = 0.1$ (Figure 11.13 (24)).

Assuming $\Delta t = 1.81\ T_{1/2}$, $L_C(c)$, $L_D(c)$ and $L_Q(c)$ can be calculated from equations (11.58), (11.59) and (11.62) by substituting $c_1 = R_1\Delta t = 1.81\ R_1\ T_{1/2}$ and $c_2 = R_2\Delta t = 1.81\ R_2\ T_{1/2}$. The corresponding counting rates $L_C(R)_0$, $L_D(R)_0$ and $L_Q(R)_0$ at time $t = 0$ are then

$$L_C(R)_0 = L_C(c)/1.03\ T_{1/2};\quad L_D(R)_0 = L_D(c)/1.03\ T_{1/2};$$

$$L_Q(R)_0 = L_Q(c)/1.03\ T_{1/2}$$

as in section IV, B, 4 of this chapter.

Again, there exists an optimum neutron flux and/or sample weight which allows one to reach the lowest concentration limit. Then, the lowest $L'_D(R)_0$ value is given by (24)

$$L'_D(R)_0 = 3\,u_1^2\lambda/[1 - \exp(-\lambda\Delta t)] \qquad (11.65)$$

If both the sample activity and the counting time Δt are optimally chosen, then (24):

$$L'_D(R)_0 \simeq 2.5\,u_1^2/T_{1/2} \text{ cps } (T_{1/2} \text{ in seconds}) \qquad (11.66)$$

Optimal counting time Δt and optimal R'-value can be read from Figure 11.13 for a given $T_{1/2}$ (dashed line).

Example: (see Figure 11.13)

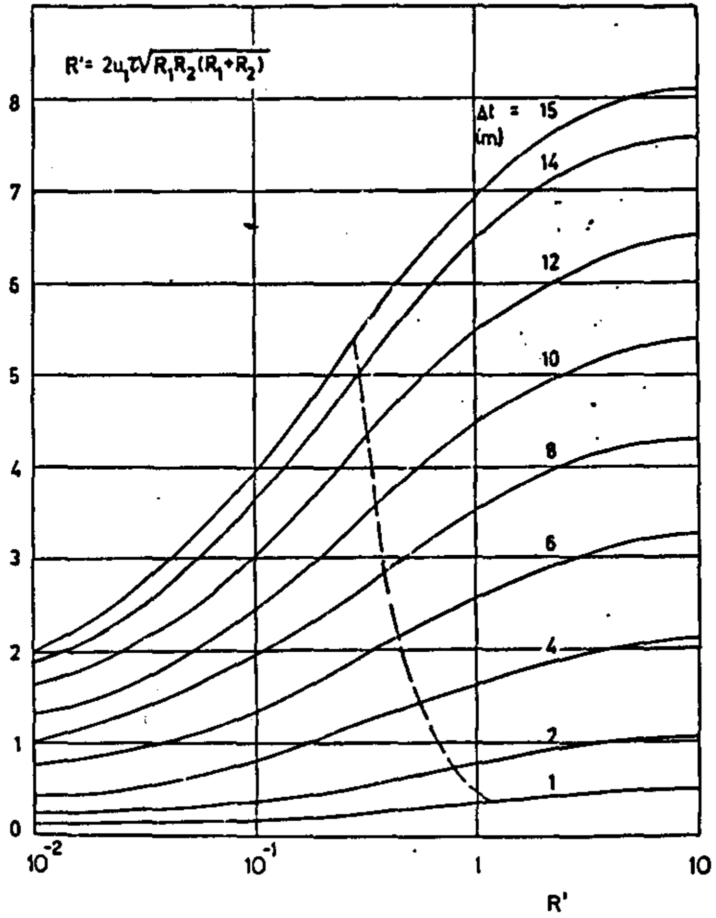

Fig. 11.13. Optimal counting time for short lived coincidences and constant background. The dashed line represents the points with optimal Δt and R' values (24). Ordinate: $T_{1/2}(m)$; abscissa: $R'(s^{-1/2})$.

If $T_{1/2} = 5$ m, the optimum counting time is ca. 14 m and the optimum sample activity is reached for $R' \simeq 0.3$.

Assuming $\tau = 10^{-6}$ s, $u_1 = 1.645$ and $R_1 = R_2 = R$, this means: $0.3 = 2 \times 1.645 \times 10^{-6}\sqrt{(2R^3)}$ or $R = 1420$ cps.

3. *Application to Short Lived Radioisotopes and Short Lived Background* (coincidence counting)

Similar expressions can be derived if both the true coincidence rate and the background (random coincidence rate) are short lived. They are, however, more complex and will not be derived here. Reference is made to Schulze (24). The confidence level is assumed to be 99.865% ($u_1 = 3$).

It can be shown that distinction should be made between two cases:

(a) If $T_{1/2}(B')/T_{1/2} > 5.6$ there exists an optimum counting time, which depends on the ratio $T_{1/2}(B')/T_{1/2}$. $\Delta t/T_{1/2}$ is approximately 3 to 5 (see Table 11.5). There also exists an optimum sample weight (or neutron flux) which allows one to detect the lowest concentration limit. Indeed, $R_0' = 6\tau\sqrt{\{R_{1,0}R_{2,0}(R_{1,0} + R_{2,0})\}}$ ($s^{-1/2}$) is also function of $T_{1/2}(B')/T_{1/2}$ (Table 11.5). $R_{1,0}$ and $R_{2,0}$ are the channel rates at the beginning of the counting time.

TABLE 11.5

Optimum counting time and sample activity if both true and random coincidence rates are short lived for $T_{1/2}(B')/T_{1/2} > 5.6$

$T_{1/2}(B')/T_{1/2}$	$\Delta t/T_{1/2}$	$R_0'\sqrt{T_{1/2}}$
>25	3	5.45
10	3.6	5.65
6	4.9	5.85

Example:

$T_{1/2} = 1$ m, $T_{1/2}(B') = 16$ m, $T_{1/2}(B')/T_{1/2} = 16 > 5.6$. According to Table 11.5, $\Delta t/T_{1/2} \simeq 3.2$ or $\Delta t \simeq 3.2$ m, whereas $R_0'\sqrt{T_{1/2}} \simeq 5.55$, thus $R_0' = 5.55/\sqrt{60}\ s^{-1/2} = 0.72\ s^{-1/2}$. Assuming $R_{1,0} = R_{2,0} = R_0$ and $\tau = 1\ \mu s$: $6 \times 10^{-6}\sqrt{(2R_0^3)} = 0.72$ or $R_0 \simeq 1930$ cps. This allows one to choose the optimum sample activity at the beginning of the counting.

(b) If $T_{1/2}(B')/T_{1/2} < 5.6$ it is also possible to calculate the optimum sample weight (and/or neutron flux) for a given Δt, as appears from Table 11.6. The counting time Δt must however be chosen arbitrarily, as there is no optimum value. A counting time $\Delta t = 2.5\ T_{1/2}$ allows one to detect more than 80% of the total number of true coincidences.

Example:

$T_{1/2} = 1$ m, $T_{1/2}(B') = 3$ m, then $T_{1/2}(B')/T_{1/2} = 3 < 5.6$. Choosing $\Delta t = 2.5\ T_{1/2} = 2.5$ m $= 150$ s, then $\Delta t/T_{1/2}(B') = 2.5/3 = 0.83$ and $R_0'\sqrt{\Delta t} = R_0'\sqrt{150} = 13.5$; $R_0' = 1.1\ s^{-1/2} = 6 \times 10^{-6}\sqrt{\{R_{1,0}R_{2,0}(R_{1,0} + R_{2,0})\}}$ (if $\tau = 1\ \mu s$). Assuming $R_{1,0} = R_{2,0} = R_0$, one finds $3\ R_0^3 = 33 \times 10^9$ or $R_0 = 2500$ cps.

TABLE 11.6

Optimum sample activity as a function of counting time, if both time and random coincidence rates are short lived for $T_{1/2}(B')/T_{1/2} < 5.6$

$\Delta t/T_{1/2}(B')$	0	1	2	3	4	5
$R_0'\sqrt{\Delta t}$	8	14	19	24.5	29	33

V. Linear Equations

(A) GENERAL CONSIDERATIONS

In analytical methods, one often needs to determine the parameters a and b of a linear equation

$$Y = a + bx \tag{11.67}$$

with associated statistical errors $\pm u\sigma(a)$ and $\pm u\sigma(b)$. The least squares method for fitting a straight line to a series of experimental points is well known, on condition that the experimental errors in x are small compared with those in y and that the x-values cover an adequate range. The former requirement is met in the examples given below, nl (i) study of a decay curve, $x = t$, the times at which the activities are observed; (ii) addition method of analysis, x = weights added to the sample, which are only affected by small weighing and/or diluting errors. The y quantities however have all the procedure steps as a source of variation (case (ii)) or are at least affected by the statistical character of the activity counting (mostly $\geq 1\%$, case (i)).

For a set of n measurements, the best estimates of b and a are

$$\text{slope: } b = \frac{\sum W_i \sum W_i x_i y_i - \sum W_i x_i \sum W_i y_i}{D}$$

$$= \frac{\sum W_i x_i y_i - \bar{x}\bar{y} \sum W_i}{\sum W_i x_i^2 - \bar{x}^2 \sum W_i} \qquad (11.68)$$

intercept with ordinate:

$$a = \frac{\sum W_i x_i^2 \sum W_i y_i - \sum W_i x_i \sum W_i x_i y_i}{D} = \bar{y} - b\bar{x} \qquad (11.69)$$

where

$$\bar{y} = \frac{\sum W_i y_i}{\sum W_i}; \quad \bar{x} = \frac{\sum W_i x_i}{\sum W_i} \quad (cf.\ \text{equation } 11.2)$$

and

$$D = \sum W_i \sum W_i x_i^2 - (\sum W_i x_i)^2 \qquad (11.70)$$

W_i is the "statistical weight", which is inversely proportional to the variance of the corresponding measurement i (definition):

$$W_i = A/\sigma_i^2 \qquad (11.71)$$

where A is a constant, arbitrarily chosen to make the values of the weight convenient for computation, e.g. $A = 1$. It can be shown that A cancels out and does not influence the results. For data that are only subjected to counting statistics, W is determined by the number of counts. For other data, weights are determined from the scatter of the data (see section V, C).

The above formulas make the sum of the squares of the residuals $\sum Z_i^2 = \sum W_i (Y_i - y_i)^2$ a minimum. Y_i is the value calculated for a given x_i using the best estimates of b and a (equations 11.68) and (11.69)); y_i is the corresponding experimental value of y at $x = x_i$.

Standard deviations can be calculated from the following formulas:

$$\sigma^2(b) = A \sum W_i / D \qquad (11.72)$$

$$\sigma^2(a) = A \sum W_i x_i^2 / D \qquad (11.73)$$

Confidence limits are $\pm u\sigma(b)$ and $\pm u\sigma(a)$ in agreement with previous definitions (see Table 11.1).

Two practical examples will be given below.

(B) Decay Curve (single component)

1. *Background Negligible*

The equation $R_t = R_0 \exp(-\lambda t)$ must be made linear by the logarithmical form: $\ln R_t = \ln R_0 - \lambda t$. In terms of equation (11.67) this becomes $y = \ln R_t$, $x = t$, $a = \ln R_0$ and $b = -\lambda$.

If at a time t_i, c_i counts are recorded during a counting time Δt_i, the counting rate is $R_i = c_i/\Delta t_i$ at the time $t_i + 0.5\ \Delta t_i$ (assuming $\Delta t_i \ll T_{1/2}$, see section II, A) and the transform is $y_i = \ln R_i$. According to equation (11.16) one can write:

$$\sigma^2(R_i) = c_i/\Delta t_i^2 = R_i \Delta t_i/\Delta t_i^2 = R_i/\Delta t_i$$

An estimate of $\sigma^2(y_i)$ is possible using the laws of error propagation (see Table 11.3, item 6).

$$\sigma^2(y_i) \simeq \sigma^2(R_i)/R_i^2 = 1/R_i \Delta t_i = 1/c_i \qquad (11.74)$$

From equation (11.71) it follows

$$W_i = A/\sigma^2(R_i) = Ac_i \qquad (11.75)$$

The simplest method of determining a half-life with calculable statistical precision (= accuracy if the sample is radiochemically pure so that the exponential decay of a single radioactive species is the only factor causing the change of the counting rate) is to measure the time necessary to obtain a preset number of counts during each of the n observations ("preset count" mode of counting). Then all $c_i = c =$ constant and all observations have the same weight. If this weight is arbitrarily set $= 1$, then $A = 1/c$ (from equations (11.71) and (11.75)) and $\sum W_i = n$. Equations (11.68), (11.69) and (11.70) are then reduced to:

$$b = -\lambda = (n \sum t_i \ln R_i - \sum t_i \sum \ln R_i)/D' \qquad (11.76)$$

$$a = \ln R_0 = (\sum t_i^2 \sum \ln R_i - \sum t_i \sum t_i \ln R_i)/D' \qquad (11.77)$$

$$D' = n \sum t_i^2 - (\sum t_i)^2 \qquad (11.78)$$

The variances are respectively:

$$\sigma^2(b) = \sigma^2(\lambda) = n/cD' \qquad (11.79)$$

$$\sigma^2(a) = \sigma^2(\ln R_0) = \sum t_i^2/cD' \qquad (11.80)$$

The standard deviation of the half-life can be calculated using items 3 and 4 in Table 11.3 ($r = -1$ and $a = 0.693$):

$$T_{1/2} = 0.693/\lambda$$

Thus

$$\frac{\sigma(T_{1/2})}{T_{1/2}} \simeq \frac{\sigma(\lambda)}{\lambda} \quad \text{or} \quad \sigma(T_{1/2}) = 0.693\,\sigma(\lambda)/\lambda^2 \tag{11.81}$$

It must be borne in mind – particularly if the "preset count" method is used – that R_i represents the count rate at the time $t_i + 0.5\,\Delta t_i$ (if $\Delta t_i \ll T_{1/2}$) and not at the starting time. Since increasing periods of counting may be necessary as the counting rate falls, this method is not recommended for the determination of short half-lives, e.g. < 15 m.

In the general case when $c_1, c_2, c_3 \ldots$ are the numbers of counts observed at times $t_1, t_2, t_3 \ldots$ taken over counting periods $\Delta t_1, \Delta t_2, \Delta t_3 \ldots$ the general formulas ((11.68), (11.69), (11.70)) must be used, with $W_i = c_i$ (thus $A = 1$, as appears from equation (11.71)):

$$b = -\lambda = \left(\sum c_i \sum c_i t_i \ln R_i - \sum c_i t_i \sum c_i \ln R_i\right)/D \tag{11.82}$$

$$a = \ln R_0 = \left(\sum c_i t_i^2 \sum c_i \ln R_i - \sum c_i t_i \sum c_i t_i \ln R_i\right)/D \tag{11.83}$$

$$D = \sum c_i \sum c_i t_i^2 - \left(\sum c_i t_i\right)^2 \tag{11.84}$$

With $W_i = c_i$ and $A = 1$, the general formulas for the variances become:

$$\begin{aligned}\sigma^2(b) &= \sigma^2(\lambda) = \sum c_i/D = \sum c_i/\left[\sum c_i \sum c_i t_i^2 - \left(\sum c_i t_i\right)^2\right] \\ &= \left[\sum c_i t_i^2 - \left(\sum c_i t_i\right)^2/\sum c_i\right]^{-1}\end{aligned} \tag{11.85}$$

$$\sigma^2(a) = \sigma^2(\ln R_0) = \sum c_i t_i^2/D \tag{11.86}$$

A representative example for the general case is described by Cook and Duncan (39). The method described above is obviously much more tedious than the graphical determination of λ and R_0 (see Chapter 5), although it is more difficult to assess the statistical errors in the latter case. In Chapters 5 and 9, reference is made to computer programs for half-life determinations.

A theoretical analysis of the evaluation of short half-lives (e.g. on multiscaler) by means of the graphical method (measurement of counting rate in a sufficiently great number of short time intervals and plotting on a semilog scale) has been described by Sterlinski (40). The best

accuracy and the smallest systematic error is obtained if the measurements are programmed as follows:

(a) *Choice of total measurement time:*

If the total measurement time is too short, all possible information is not utilized. On the other hand, if it is too long, the counting rate becomes negligible compared to the background rate. Obviously there exists an optimum measuring time (expressed in terms of $T_{1/2}$) which depends mainly on the ratio background to signal R_B/R_S at the beginning of the measurement as appears from Figure 11.14 (40).

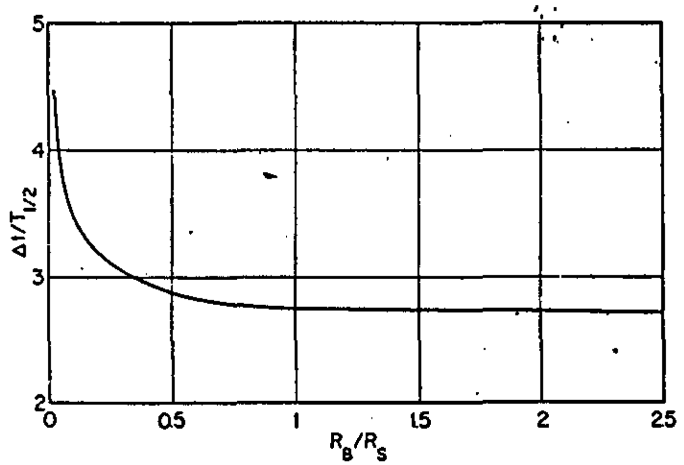

Fig. 11.14. The optimum measurement time (expressed in terms of $T_{1/2}$) as a function of the counting rate ratio of the background to that of the effect R_B/R_S, at the beginning of the measurement (40).

(b) *Choice of number of intervals:*

At a given total measurement time, $\sigma(T_{1/2})/T_{1/2}$ depends on the number of intervals n. If n is too small, optimum accuracy will not be obtained. If n is too large, the number of counts recorded per interval will be too low and often the count difference ($c_S = c_G - c_B$) will become negative at relatively low values of t, see Figure 11.15 (40).

According to Sterliński (40) the number of intervals should be 10 to 15. To avoid loss of information about the value of $T_{1/2}$ – particularly in the case of low activities – there should be no break between the successive short time intervals. The background is measured during a sufficiently long time.

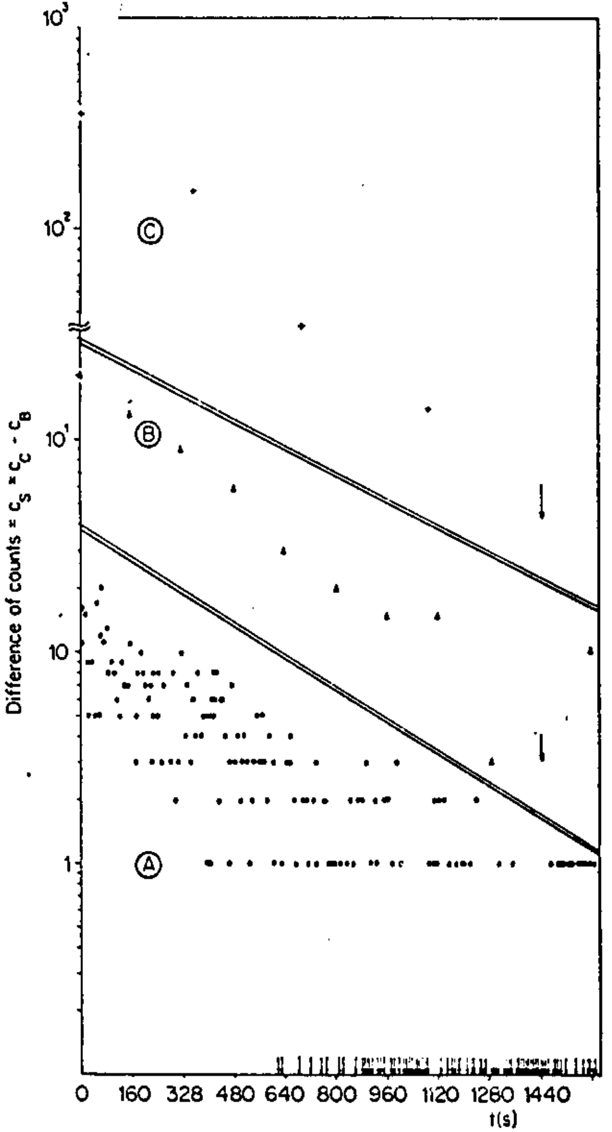

Fig. 11.15. Influence of the number of time intervals for a given total measurement time, on the univocality of the graphical estimate of $T_{1/2}$, using ^{52}V. All the plots were made using the same experimental data. Case A: $n = 220$; case B: $n = 11$; case C: $n = 5$. The arrow indicates that the count difference for that interval is negative.

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2. *Background not Negligible, but Constant*

So far the assumption has been made that the background at each point is negligible. If it is not, the analysis is the same, but weights are changed. If the background rate is constant, the background measurements taken at various times can be pooled to determine its average value. In this way the error in background is negligible, since it can be counted for a sufficiently long total time.

The net counting rate is given by $R_i = c_i/\Delta t_i - R_B$ whereas $\sigma^2(R_i) \simeq c_i/\Delta t_i^2$ (see equation (11.16)), as the error of R_B is negligible. Hence:

$$\sigma^2(y_i) = \frac{\sigma^2(R_i)}{R_i^2} = \frac{c_i/\Delta t_i^2}{(c_i - R_B\Delta t_i)^2/\Delta t_i^2} = \frac{c_i}{(c_i - R_B\Delta t_i)^2}$$

(*cf.* equation (11.74)). Thus, setting $A = 1$, equation (11.71) becomes:

$$W_i = (c_i - R_B\Delta t_i)^2/c_i \tag{11.87}$$

instead of $W_i = c_i$, and equations (11.82) to (11.86) should be modified accordingly.

3. *Changing Background*

Jaffey (1) discusses the case in which the background changes and needs evaluation at each counting interval. This may occur when a NaI(Tl) detector is activated in the neighborhood of a reactor or accelerator. If sample plus background are counted for a period Δt_i giving c_i counts, and the background alone for a period Δt_{Bi} giving c_{Bi} counts, then the net counting rate is:

$$R_i = c_i/\Delta t_i - c_{Bi}/\Delta t_{Bi}$$

and

$$\sigma^2(R_i) = c_i/(\Delta t_i)^2 + c_{Bi}/(\Delta t_{Bi})^2$$

since in this case the error in background is not negligible. Hence:

$$\sigma^2(y_i) = \frac{\sigma^2(R_i)}{R_i^2} = \frac{c_i/(\Delta t_i)^2 + c_{Bi}/(\Delta t_{Bi})^2}{(c_i/\Delta t_i - c_{Bi}/\Delta t_{Bi})^2} = \frac{c_i + c_{Bi}\left(\dfrac{\Delta t_i}{\Delta t_{Bi}}\right)^2}{\left[c_i - c_{Bi}\left(\dfrac{\Delta t_i}{\Delta t_{Bi}}\right)\right]^2}$$

Setting $\Delta_i = \Delta t_i/\Delta t_{Bi}$ and $A = 1$, the statistical weight for a measurement can be calculated from the above equation and equation (11.71)

$$W_i = \frac{(c_i - c_{Bi}\Delta_i)^2}{c_i + c_{Bi}\Delta_i} \qquad (11.88)$$

Thus equations (11.82) to (11.86) can also be used when the background is not negligible, on condition that c_i is replaced by $(c_i - R_B\Delta t_i)^2/c_i$ (constant background, accurately known) or by $(c_i - c_{Bi}\Delta_i)^2/(c_i + c_{Bi}\Delta_i)$ respectively (changing background).

(C) THE ADDITION METHOD OF ANALYSIS

The procedure of the addition method in activation analysis is described in Chapter 7, section II, E.

If increasing quantities w_i of the element to be determined, are added to the sample, increasing activities will be induced during activation resulting in increasing measured count rates R_i. The function is linear and has the form $Y = a + bx$.

Assuming that the experimental error in w is much smaller than that in R, equations (11.68) to (11.70) can be used to calculate the most probable values of a and b. The statistical weights are defined by $W_i = A/\sigma_i^2$ (equation (11.71)). According to equation (11.7)

$$\begin{aligned}\sigma_i^2 &= \sigma_i^2\,(\text{sample}) + \sigma_i^2\,(\text{anal})\\ &= \sigma_i^2\,(\text{sample}) + \sigma_i^2\,(\text{irrad}) + \sigma_i^2\,(\text{chem}) + \sigma_i^2\,(\text{count})\end{aligned}$$

In many cases, the analytical work is much better than the sampling, thus $\sigma_i^2 \approx \sigma_i^2$ (sample), i.e. the overall reproducibility σ_i is determined by variations in the sample composition. But even when the reproducibility of the samples is a good deal better than that of the analytical work, i.e.

$$\sigma_i^2 \approx \sigma_i^2\,(\text{irrad}) + \sigma_i^2\,(\text{chem}) + \sigma_i^2\,(\text{count})$$

one observes that the overall precision σ_i is not determined by σ_i (count) alone (as was the case for the decay curve, section V, B), but depends on other parameters too, such as variations in irradiation conditions, variations in chemical work, variations in counting geometry etc. These parameters being subject to approximately the same variations for all of the samples, it is allowed to give the same statistical weight to all measurements (all $W_i = 1$). This is certainly true, if all the samples are counted so as to obtain approximately the same total number of counts. This principle can thus be maintained even if the measured counting rates are low as compared to the background rate. Moreover, the added weights w_i are so chosen that they do not exceed ca. 2–3 times the weight w_0 originally present. Hence equations (11.68) to (11.70) will be simplified:

$$b = \left(n \sum w_iR_i - \sum w_i \sum R_i\right)/D' = \text{specific rate (per unit of weight)} \qquad (11.89)$$

$$a = \left(\sum w_i^2 \sum R_i - \sum w_i \sum w_iR_i\right)/D' = \text{intercept with ordinate (rate of the element in the sample without addition)} \qquad (11.90)$$

$$D' = n \sum w_i^2 - \left(\sum w_i\right)^2 \qquad (11.91)$$

where n is the number of experimental points.

The best estimate of the weight of the element in the original sample is given by

$$w_0 = a/b \text{ (in units of weight)} \qquad (11.92)$$

The standard deviations of a and b can be calculated by means of equations (11.72) and (11.73) setting $W_i = 1$.

According to equation (11.71) one can write:

$$\sigma^2(b) = \sigma^2 n/D' \qquad (11.93)$$

$$\sigma^2(a) = \sigma^2 w_i^2/D' \qquad (11.94)$$

The quantity σ^2 is not known *a priori*, as was the case for the decay curve, but a good estimate is possible from the residuals Z_i between the experimental R_i-values, $(R_i)_{\text{exp}}$ and the R_i-values, which are calculated from the best estimates of a and b, $(R_i)_{\text{calc}}$:

$$Z_i = \left|(R_i)_{\text{exp}} - (R_i)_{\text{calc}}\right| \qquad (11.95)$$

It can be shown that

$$\sigma^2 = \sum Z_i^2/(n - 2) \qquad (11.96)$$

where σ^2 is a reliable estimate of the variance of an observation with a statistical weight $W = 1$ and where n is the number of experiments. The term $(n - 2)$ instead of the more familiar $(n - 1)$ (see equation (11.3)) arises from the fact that at least two points are required to characterize a straight line.

Equation (11.96) is tedious to handle and is therefore replaced by an equivalent one:

$$\sum Z_i^2 = (n-2)\sigma^2 = \sum R_i^2 - (\sum R_i)^2/n - b^2D'/n \qquad (11.97)$$

This equation allows the calculation of σ^2, hence that of $\sigma^2(a)$ and $\sigma^2(b)$ without calculating the individual differences Z_i. When using equation (11.97), a sufficient number of decimals must be calculated, since in many cases (see Table 11.7) $\sum R_i^2 \approx (\sum R_i)^2/n + b^2D'/n$. Even if very small errors of computation are made, they can strongly influence the resulting value of σ.

Starting from equations (11.92), (11.93) and (11.94) it is possible to estimate the standard deviation $\sigma(w_0)$ on the original content w_0 of the element in the sample, using item 2 in Table 11.3.

$$\frac{\sigma^2(w_0)}{w_1^2} \approx \frac{\sigma^2(a)}{a^2} + \frac{\sigma^2(b)}{b^2} \qquad (11.98)$$

It can be shown that the variance $\sigma^2(b)$ decreases if a large concentration interval is investigated, i.e. $|w_i - \overline{w}| > 0$, where $\overline{w}$ represents the arithmetic mean of the w-values. On the other hand, the more $w_i \neq \overline{w}$, the larger the error of R_i. For that reason extrapolation to $w = 0$ ($R = a$) should be carried out only if a small concentration range is used.

It can be shown that the error of a and w_0 is a minimum if the weights w_i added do not exceed ca. 2–3 times the weight w_0 originally present (41). It should be remembered that equation (11.98) only applies if each of the terms $\sigma(a)/a$, $\sigma(b)/b$ and $\sigma(w_0)/w_0$ is small ($\lesssim 0.20$) and if a and b are statistically independent of one another. The former condition is normally fulfilled, the latter however is not, as cov $(a, b) \neq 0$ (44). For that reason equation (11.98) is only an approximation, and a term $2\rho[\sigma(a)/a][\sigma(b)/b]$ should be added, where ρ is the correlation coefficient.

If, together with the addition series, s "foreign" samples (i.e. different from the sample, containing w_0 of the element) are irradiated, giving an average induced activity R', the content w' of the element in these samples can be read from the calibration curve or calculated from

$$w' = (R' - a)/b + w_0 \qquad (11.99)$$

A good estimate of the expected standard deviation $\sigma(w')$ is found by classical statistical methods (42):

$$\sigma(w') = \sigma(w)t \qquad (11.100)$$

where the quantity t (from t-test) has $(n - 2)$ degrees of freedom (D.F.). The value of t can be found in statistical tables. At the probability level $P = 0.68$, or $P' = 0.32$, $t \simeq 1$ assuming D.F. $\gtrsim 10$.

$\sigma(w)$ can be calculated from:

$$\sigma^2(w) = \sigma^2[(n + r)/nr + (R' - \bar{R})^2 n/b^2D]/b^2 \qquad (11.101)$$

where r = number of determinations of w'

$$\bar{R} = (\sum R_i)/n$$

The error on R' is a minimum if $R' = \bar{R}$ and increases for $R' \gtrless \bar{R}$.

As an illustration, a practical example will be described.

Example: Determination of traces of osmium in ruthenium. (Spectrographically pure and commercial quality)

Procedure, irradiation conditions, chemical separations, counting equipment: see ref. (43).

Twelve 10 mg samples of spectrographically pure ruthenium (added amounts of osmium: 0; 0.10; 0.25; 0.50; 0.80 and 1.00 μg, see Table 11.7) were irradiated together with three 10 mg samples of commercial

TABLE 11.7

Calculations for the determination of osmium in spectrographically pure ruthenium, using an addition method of analysis

Sample number	R = net ^{191}Os activity (c/5m)	$w = \mu$g Os added	Rw	w^2	R^2
1	4,530	0	0	0	20,520,900
2	4,872	0	0	0	23,736,384
3	—	0.1	—	—	—(a)
4	6,411	0.1	641	0.01	41,100,921
5	8,667	0.25	2,167	0.0625	75,116,889
6	9,710	0.25	2,428	0.0625	94,284,100
7	12,384	0.50	6,192	0.25	153,363,456
8	13,391	0.50	6,695	0.25	179,318,881
9	13,507	0.50	6,754	0.25	182,439,049
10	17,630	0.80	14,104	0.64	310,816,900
11	17,350	0.80	13,844	0.64	299,463,025
12	18,757	1.00	18,757	1.00	351,825,049
comm. Ru	2,435	—	—	—	—
"	2,520	—	—	—	—
"	2,707	—	—	—	

(a) Sample 3 discarded, separated osmium partly lost.

ruthenium. The ^{191}Os activity was counted after chemical separation, using a NaI(Tl) detector. The calculations are summarized in Table 11.7.

SUMMATIONS

$n = 11$ $\quad \sum Rw = 71{,}581 \quad \sum R^2 = 1{,}731{,}985{,}554$

$\sum R = 127{,}164 \quad \sum w = 4.70 \quad \sum w^2 = 3.165$

COEFFICIENTS a and b

$$D' = n\sum w^2 - (\sum w)^2 = 12.725$$

$$b = (n\sum Rw - \sum w\sum R)/D' = 14{,}909 \quad \text{c/5 m/}\mu\text{g Os}$$

$$a = (\sum w^2 \sum R - \sum w \sum Rw)/D' = 5{,}190 \quad \text{c/5 m}$$

CALCULATED OSMIUM CONTENT

$w_0 = a/b = 0.348\ \mu$g Os (in 10 mg Ru), i.e. 34.8 ppm.

STANDARD DEVIATIONS

(Equation 11.97) $= 1{,}731{,}985{,}554 - 1{,}470{,}062{,}081 - 257{,}135{,}557 = 4{,}787{,}916$. Hence $\sigma^2 = \sum Z^2/(n-2) = 531{,}991$

$$\sigma^2(b) = \sigma^2 n/D' = 459{,}874 \text{ thus } \sigma(b) = 678 \text{ or } 4.54\%$$

$$\sigma^2(a) = \sigma^2 \sum w^2/D' = 132{,}318 \text{ thus } \sigma(a) = 364 \text{ or } 7.01\%$$

$$\sigma^2(w_0) = \sigma^2(a/b) = 0.000841 \text{ thus } \sigma(w_0) = 0.029\ \mu\text{g or } 8.4\%$$

Taking the covariance term into account, one finds $\sigma(w_0) \simeq 11\%$.

COMMERCIAL RUTHENIUM

(Equation 11.101) $R' = 2{,}435;\ 2{,}520;\ 2{,}707$, average value 2554 c/5 m.

Hence $w' = 16.8$ ppm.

Estimated standard deviation $r = 3$, $n = 11$, 9 degrees of freedom, $t \approx 1$: $\sigma(w') \simeq 0.018\ \mu$g or 1.8 ppm.

(*Note:* the commercial sample contained less osmium than the spectrographically pure sample.)

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TABLE 12.2 (*continued*)

Element determined	Matrix	References
Rare earths	Rare earths	B 102–G 100–K 142–R 42–W 80
	Metals + alloys	A 153
	Minerals + meteorites	A 156–C 68–C 105–D 79–F 90–H 42–H 43–H 44–L 124–L 143–S 49–S 52–S 53
	Organic	B 186–K 12–S 20–S 94–S 96–S 98
	Air	G 62
	Molten salts	B 178
	Solutions	T 24
	Matrix not defined	B 133–B 188–C 104–L 106–N 27–R 106–Y 21

APPENDIX 1

THERMAL NEUTRON CROSS SECTIONS

The experimental data for the tables of this appendix are based on the compilation "Neutron Cross Sections" by D. J. Hughes and R. B. Schwartz (BNL–325, 2nd ed. 1958) and by D. J. Hughes, B. A. Magurno and M. K. Brussel (BNL–325, Supplement 1, 1960; U.S. Government Printing Office, Washington D.C.); and on the "Chart of the Nuclides" by N. E. Holden and F. W. Walker (General Electric, Schenectady, N. Y., (1968).

In Table 1, the total cross section (σ_T), the capture or absorption cross section (σ_c, σ_{abs}) and the average scattering cross section ($\bar{\sigma}_s$) for thermal neutrons are given for the elements. It should be noted that the absorption cross section listed is the 2.2×10^5 cm s^{-1} (0.025 eV) value, $\sigma_{abs}(v_0)$, although the value consistently used in more accurate calculations is $(\sqrt{\pi})/2$ or 1/1.128 times this value, if the neutron temperature is 293.6°C. For a neutron temperature T, the value

$$\sigma_{abs}(\bar{v}) = \sigma_{abs}(v_0)\,\frac{\sqrt{\pi}}{2}\left(\frac{293.6}{T}\right)^{1/2}$$

must be used. More details are given in Chapter 10, section II, B, 4b.

In Table 2, the isotopic neutron activation cross sections for thermal neutrons are given (in barn). As already mentioned in Chapter 3, section V, C, 1, the reaction rate can be calculated from the knowledge of the cross section σ_0 at a particular velocity v_0, on condition that $\sigma \propto 1/v$. The velocity v_0 is taken as 2.2×10^5 cm s^{-1}, the most probable velocity of a Maxwellian distribution at 20°C (corresponding energy 0.025 eV). The cross sections in the table are given for this velocity, except in some cases where they refer to a reactor neutron spectrum (values with asterisk). The activation cross sections are for (n, γ) reactions, except when explicitly stated for (n, p) or (n, α). For heavy nuclei ($Z > 88$) the cross section for fission is also included.

For practical use in activation analysis (induced activity calculations, see equation (10.1)), the per cent abundance of the target isotope in the natural element and the half-life of the activity produced are also given. (Symbols: a = year, d = day, h = hour, min = minute, s = second.)