CHAPTER 22

QUALITY CONTROL FOR SAMPLING AND LABORATORY ANALYSIS

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INTRODUCTION

The measurement of physical entities such as length, volume, weight, electromagnetic radiation and time involves uncertainties which cannot be eliminated entirely, but when recognized can be reduced to tolerable limits by meticulous attention to detail and close control of the significant variables. In addition, errors often unrecognized, are introduced by undesirable physical or chemical effects and by interferences in chemical reaction systems. In many cases, absolute values are not directly attainable; and, therefore, standards from which the desired result can be derived by comparison must be established. Errors are inherent in the measurement system. Although the uncertainties cannot be reduced to zero, methods are available by which reliable estimates of the probable true value and the range of measurement error can be made.

In this chapter the fundamental procedures for the administration of an effective quality control program are presented with sufficient explanation to enable the investigator to both understand the principles and to apply the techniques. First, the detection and control of determinate and indeterminate error will be considered. Based on this foundation, the types of errors and meanings of the common terms used to define an accurate method are discussed as a basis for application of quality control to sampling and analysis. The theory, construction, applications and limitations of control charts are developed in sufficient depth to provide practical solutions to actual quality control problems. Additional statistical approaches are included to support those systems which may require further refinement of precision and accuracy to evaluate and control sampling and analysis reliability.

Finally, a discussion of collaborative testing projects and intralaboratory quality control programs designed to improve and test the integrity of the laboratory's performance completes the survey of quality control principles and practices.

QUALITY CONTROL PRINCIPLES

Total Quality Control

A quality control program concerned with sampling and laboratory analysis is a systematic attempt to assure the precision and accuracy of future analyses by detecting determinate errors in analysis and preventing their recurrence. Confidence in the accuracy of analytical results and improvements in analysis precision are established by identification of the determinate sources of error. The precision will be governed by the indeterminate error inherent in the procedure, and can be estimated by statistical techniques. For a result to be accurate, the procedure must not only be precise, but must also be without bias. Techniques have been developed for the elimination of bias. The quality control program should cover instrumental control as well as total analysis control. The use of replicates submitted in support of the quality control program provides assurance that the procedure will remain in statistical control.

Quality must be defined in terms of the characteristic being measured. Control must be related to the source of variation which may be either systematic or random. Usually the basic variable is continuous (any value within some limit is possible). A numerical value of an analysis for which the range of uncertainty inherent in the method has not been established cannot be reliably considered a reasonable estimate of the true or actual value. The basic quality control program incorporates the concepts of:

1. Calibration to attain accuracy
2. Replication to establish precision limits
3. Correlation of quantitatively related tests to confirm accuracy, where appropriate.

Evaluation of the overall effectiveness of the quality control program encompasses a number of parameters:

1. Equipment and instruments
2. The current state of the art
3. Expected ranges of analytical results
4. Precision of the analytical method itself
5. Control charts to determine trends as well as gross errors
6. Data sheets and procedures adopted for control of sample integrity in the laboratory
7. Quality control results on a short term basis (daily if appropriate) as well as on an accumulated basis.

The manipulative operations which are directly influenced by quality control include:

1. Sampling techniques
2. Preservation of sample integrity (identification, shipping and storage conditions, contamination, desired component losses, etc.)
3. Aliquoting procedures
4. Dilution procedures

5. Chemical or physical concentration, separation and purification
6. Instrument operation.

Statistical Quality Control

Statistical quality control involves application of the laws of probability to systems where chance causes operate. The technique is employed to detect and separate assignable (determinate) from random (indeterminate) causes of variation. "Statistics" is the science of uncertainty; therefore, any conclusions based on statistical inference contain varying degrees of uncertainty, which is expressed in terms of probability statements. Uncertainty can be quantified in terms of well defined statistical probability distributions, which can be applied directly to quality control. The application of statistical quality control can most efficiently indicate when a given procedure is in statistical control, and a continuing program that covers sampling, instrumentation and overall analysis quality will assure the validity of the analytical program. Further development of statistical techniques and applications will be found in the following sections in this chapter.

Quality Control Charts[1]

The Shewhart Control Chart[2] is one of the most generally applicable and easily adapted statistical quality control techniques which can be applied to almost any phase of production, research or analysis. Control charts originally were developed for control of production lines where large numbers of manufactured articles were inspected on a continuous basis. Since analyses frequently are produced on an intermittent basis, or on a greatly reduced scale, less data are available to work with. Therefore, certain concessions must be made in order to respond quickly to objectionable changes in the analytical procedure.

This control chart may serve several functions:

1. To determine empirically and to define acceptable levels of quality
2. To achieve the acceptable level established
3. To maintain performance at the established quality level.

Certain assumptions reside in this technique. The first and major assumption is that there will be variation. No process or procedure has been so well perfected, or so unaffected by its environment that exactly the same result will always be produced. Either the device used for measurement is not sufficiently sensitive or the operator performing the measurement is not sufficiently skilled. The sources of variation present in analytical work include:

1. Differences among analysts
2. Instrumental differences
3. Variations in reagents and related supplies
4. Effect of time on the differences found in items 1, 2 and 3
5. Variations in the interrelationship of items 1, 2 and 3 with each other and with time.

A "system of chance causes" is inherent in the nature of processes and procedures and will produce a pattern of variation. When this pattern is stable, the process or procedure is considered to be "in statistical control" or just "in control." Any result which falls outside of this pattern will have an assignable cause which can be determined and corrected.

The control chart technique provides a means for separating the assignable cause variant from the stable pattern. The chart is a graphical presentation of the process or procedure test data which compares the variability of all results with the average or expected variability from small arbitrarily defined groups of the data. The control chart also compares "within group" variability to "between group" variability. The technique in effect is a graphical analysis of variance.

The data from such a system can be plotted with vertical scale in test result units and the horizontal scale in units of time or sequence of results. The average value or mean, and the limits of the dispersion (spread, or range of results) can be calculated. Details for the construction and interpretation of quality control charts can be found in later sections of this chapter.

ERRORS

Introduction

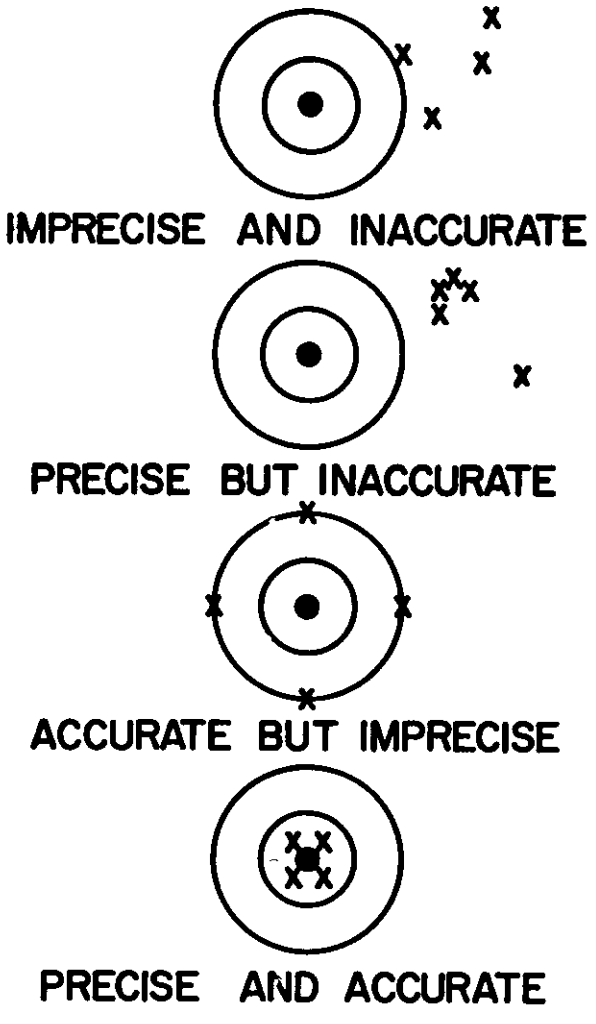
Numbers are employed to either enumerate objects or to delineate quantities. If sixteen air samples are taken simultaneously at different locations in a warehouse where gasoline-powered fork lift trucks are in motion, the number, i.e., the count, would be the same regardless of who counted them, when the count was made or how the count was made. However, if each individual sample is analyzed for carbon monoxide, sixteen different numbers, i.e., the concentration, undoubtedly would be obtained: Furthermore, when replicate determinations are made on each sample, a range of carbon monoxide concentrations would be found.[3]

Experimental errors are classified as determinate or indeterminate. A fifteen count of the warehouse samples would be a determinate error quickly disclosed by recount. An indeterminate error would be encountered due to the inherent variability in repetitive determinations of carbon monoxide by gas chromatography, infrared or a colorimetric technique.

If the estimation of carbon monoxide concentration is made with a length of stain detector tube and a 6.5-mm stain length equivalent to 57 ppm is recorded by the observer, whereas the true stain length is 6.0 mm and equivalent to 50 ppm, the observational error would be $(57\text{-}50) \times 100 \div 50 = 14\%$.

All analytical methods are subject to errors. The determinate ones contribute constant error or bias while the indeterminate ones produce random fluctuations in the data. The concepts of accuracy and precision as applied to the detection and control of error have been clearly defined and should be used exactly.

A concept of the difference between accuracy and precision can be visualized by the pattern formed by shots aimed at a target as shown in Fgure 22-1. From the scatter of four shots, one can see that a high degree of precision can be attained without accuracy and that accuracy without precision is possible. The ultimate goal is,



Powell CH, Hosey AD (eds): The Industrial Environment — Its Evaluation and Control, 2nd Edition. Public Health Services Publication No. 614, 1965.

Figure 22-1. Precision and Accuracy

of course, accuracy with precision target number 4. (See also ASTM Designation D-1129-68 for definitions.)[5]

Accuracy. Accuracy relates the amount of an element or compound recovered by the analytical procedure to the amount actually present. For results to be accurate, the analysis must yield values close to the true value.

Precision. Precision is a measure of the method's variability when repeatedly applied to a homogeneous sample under controlled conditions, without regard to the magnitude of displacement from the true value as the result of systematic or constant determinate errors which are present during the entire series of measurements. Stated conversely, precision is the degree of agreement among results obtained by repeated measurements or "checks" on a single sample under a given set of conditions.[4]

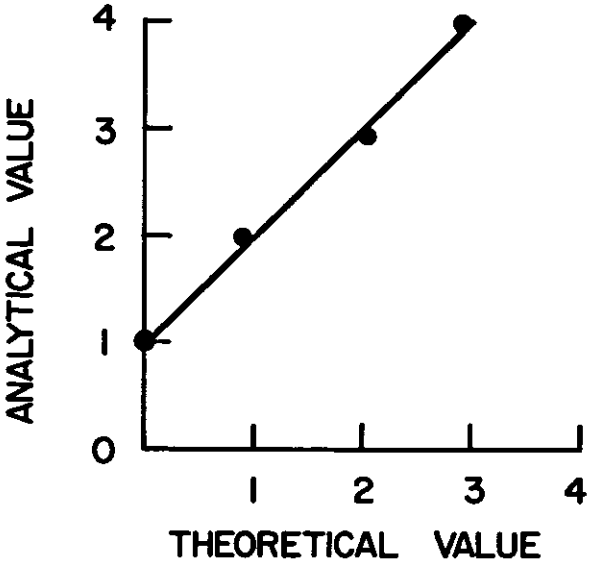
Detection and Elimination of Determinate Error

The terms "determinate" error, "assignable" error, and "systematic" error are synonymous. A determinate error contributes constant error or bias to results which may agree precisely among themselves.

Sources of Determinate Error. A method may be capable of reproducing results to a high degree of precision, but only a fraction of the component sought is recovered. A precise analysis may be in error due to inadequate standardization of solutions, inaccurate volumetric measurements, inaccurate balance weights, improperly calibrated instruments or personal bias (color estimation). Method errors that are inherent in the procedure are the most serious and most difficult to detect and correct. The contribution from interferences is discussed later.

Personal errors other than inherent physical visual acuity deficiencies (color judgment) include consistent carelessness, lack of knowledge and personal bias which are exemplified by calculation errors, use of contaminated, or improper reagents, nonrepresentative sampling or poorly calibrated standards and instruments.

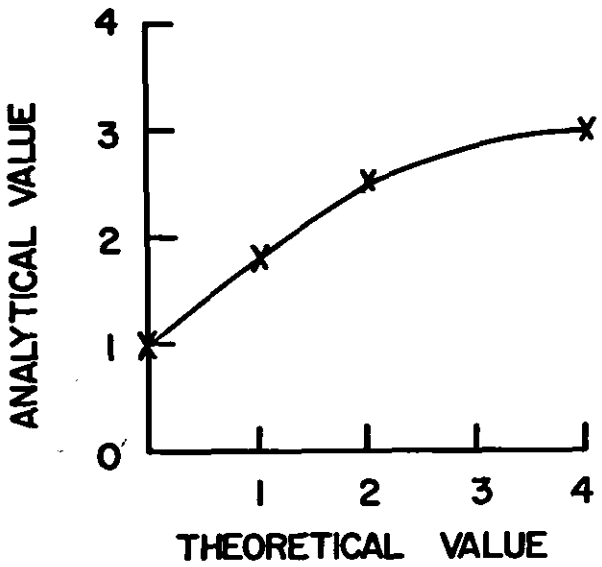
Types of Determinate Error. Additive: An additive error occurs when the mean error has a constant value regardless of the amount of the constituent sought in the sample. A plot of the analytical value versus the theoretical value (Figure 22-2) will disclose an intercept somewhere other than zero.



Powell CH, Hosey AD (eds): The Industrial Environment — Its Evaluation and Control, 2nd Edition. Public Health Service Publication No. 614, 1965.

Figure 22-2. Additive Error

Proportional: A proportional error is a determinate error in which magnitude is changed according to the amount of constituent present in the sample. A plot of the analytical value versus the theoretical value (Figure 22-3) not only fails to pass through zero, but discloses a curvilinear rather than a linear function.



Powell CH, Hosey AD (eds): The Industrial Environment — Its Evaluation and Control, 2nd Edition. Public Health Service Publication No. 614, 1965.

Figure 22-3. Proportional Error

Recovery of "Spiked" Sample Procedures. A recovery procedure in which spiked samples are used provides a technique for the detection of determinate errors. Although it does not provide a correction factor to adjust the results of an analysis, the technique does provide a basis for evaluating the applicability of a particular method to any given sample. It allows derivation of analytical quality control from the results, thus providing the basis for an excellent quality control program.

The recovery technique applies the analytical method to a reagent blank; to the sample itself, in at least duplicate; and to "spiked" samples, prepared by adding known quantities of the substance sought, to separate aliquots of the sample which are equal in size to the unspiked sample taken for analysis. The substance sought should be added in sufficient quantity to exceed in magnitude the limits of analytical error, but the total should not exceed the range of the standards selected.

The results are first corrected for reagent influence by subtracting the reagent blank from each standard, sample, and "spiked" sample result. The average unspiked sample result is then subtracted from each of the "spiked" determinations, the remainder divided by the known amount originally added, and expressed as percentage recovery. Table 22-1 illustrates an application of this technique to the analysis of blood for lead content.

Specifications for acceptance of analytical results usually are determined by the state of the art and the final disposition of the results. Recoveries of substances within the range of the method may be very high or very low and approach 100 percent as the errors diminish and as the upper limit of the calibration range is approached. Trace analysis procedures which inherently have relatively large errors when operated near the limits of sensitivity deliver poor recoveries based on classical analytical criteria and yet, from a practical viewpoint of usefulness may be quite acceptable (Table 22-1 — 2 μg spike). Poor recovery may reflect interferences present in the sample, excessive manipulative losses, or the method's technical inadequacy in the range of application. The limit of sensitivity may be considered the point beyond which indeterminate error is a greater quantity than the desired result.

Control Charts. Trends and shifts in control chart responses also may indicate determinate error. The standard deviation is calculated from spiked samples and control limits (usually ± 3 standard deviations) for the analysis are established. Calculation of the standard deviation is discussed in Chapter 3 and an in-depth discussion of control limits is treated in reference[5]. In some cases, such as BOD and pesticide samples, spiking to resemble actual conditions is not possible. However, techniques for detecting bias under these conditions have been developed.[6]

Control charts may be prepared even for samples which cannot be spiked or for which the recovery technique is impractical. A reference value is obtained from the average of a series of

TABLE 22-1
LEAD IN BLOOD ANALYSIS

Basis: 10.0 g blood from blood bank pool, ashed and lead determined by double extraction, mixed color, dithizone procedure.

Analyst: DJM

μg Pb added	Optical Density	μg Pb found Total	μg Pb found Recovered	Recovery, %
None-blank	0.0969	—	—	—
5-Calibration Point	0.2596	—	—	—
None	0.1427	1.6	—	—
None	0.1337	1.3	—	—
None	0.1397	1.4	—	—
None	0.1397	1.4	—	—
Average	0.1389	1.4	—	—
2.0	0.1805	2.9	1.5	75
4.0	0.2636	5.4	4.0	100
6.0	0.3372	7.8	6.4	107
8.0	0.3925	9.4	8.0	100
10.0	0.4437	11.4	10.0	100
30.0 Total	—	36.9	29.9	96

Calculation of mean error[5]

Mean error = 36.9 − (30.0 + 5 × 1.4) = 0.1 μg for entire set
= 2.9 − (2.0 + 1.4) = 0.5 μg for 2 μg spike

Calculation of relative error

Relative Error = (0.1 × 100)/37.0 = 0.27% for entire set
= (0.5 × 100)/3.4 = 14.7% for 2 μg spike

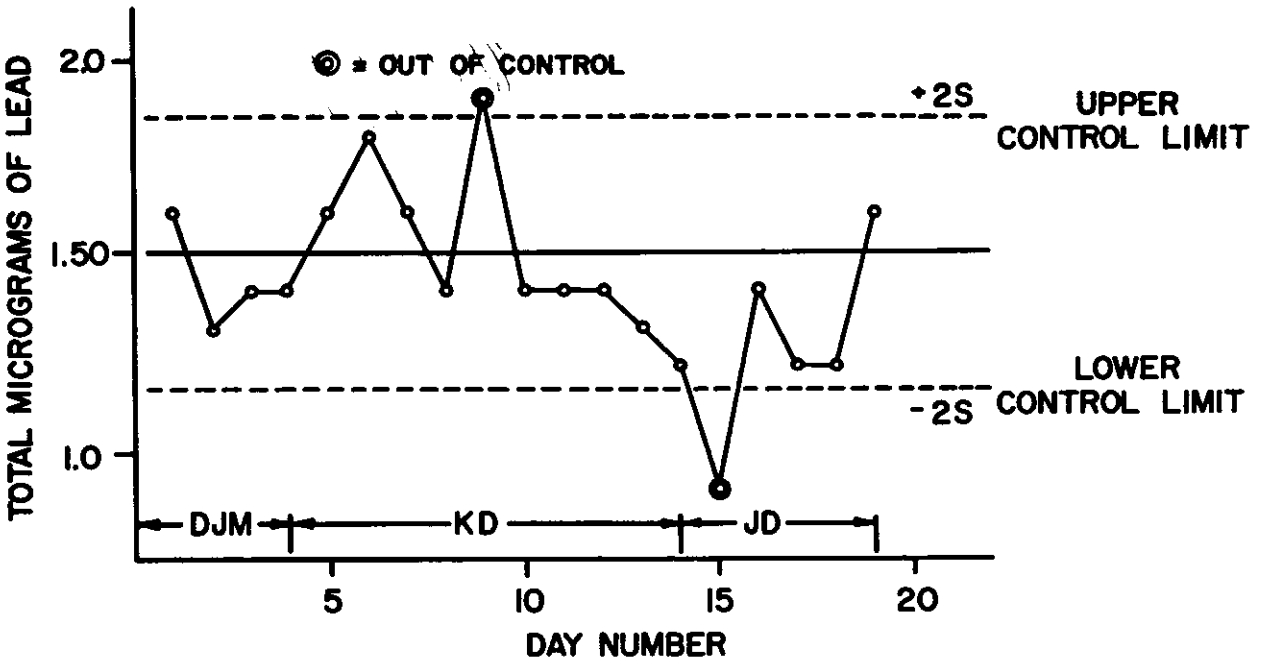


Figure 22-4. Lead in Blood Control Chart

replicate determinations performed on a composite or pooled sample which has been stabilized to maintain a constant concentration during the control period (nitric acid in urine). An example has been prepared from a blood lead study (Figure 22-4). Although these data were drawn from the same blood pool used to illustrate the application of the spiking technique for quality control, the consecutive aliquot analyses plotted as a control chart furnish additional information. The control limits were reduced to ± 2 standard deviations to further sharpen the trends. There may be preliminary evidence of personal bias as shown by KD's versus JD's performance.

Change in Methodology. Analysis of a sample for a particular constituent by two or more methods that are entirely unrelated in principle may aid in the resolution of determinate error.

In Table 22-2, an interlaboratory evaluation of three different methods for the determination of lead concentration in ashed urine specimens (mixed color dithizone, atomic absorption and polarography) is summarized. If the highly specific polarographic method was selected as the primary standard, then the dithizone procedure is subject to a +7.4 μg/l bias as compared with a +3.6 μg/l bias in the atomic absorption method for lead.

Effect of Sample Size. If the determinate error is additive, the magnitude may be estimated by plotting the analytical results versus a range of sample volumes or weights. If the error has a constant value regardless of the amount of the component sought, then a straight line fitted to the plotted points will not pass through the origin. The effect of urine volume on the analysis for lead is shown in Figure 22-5.

Elimination. a) Physical. In many cases error can be reduced to tolerable levels by quantitating the magnitude over the operating range and developing either a corrective manipulation directly in the procedure or a mathematical correction in the final calculation. Temperature coefficients (parameter change per degree) are widely applied to both physical and chemical measurements. For example, the stain length produced by carbon monoxide in the detector tubes previously cited for illustration is dependent on the temperature as well as the air sampling rate and CO concentration. Therefore, when these tubes are used outside the median temperature range, a correction must be applied to the observed stain length (Table 22-3).[7]

As a general rule, most instruments exhibit maximum reliability over the center 70% of their range (midpoint ± 35%). As the extreme to either side is approached the response and reading errors become increasingly greater. Optical density measurements, for example, should be confined to the range 0.045 to 0.80 by concentration adjustment or cell path choice. Extrapolation to limits outside the range of response established for the analytical method or instrumental measurement may introduce large errors as many chemical and physical responses are linear only over a relatively narrow band in their total response capability. In absorption spectrophotometric measurements, Beer's law relating optical density to concentration may not be linear outside of rather narrow limits in some instances (colorimetric determination of formaldehyde at high dilution by the chromatropic acid method).

b) Internal Standard. The internal standard technique is used primarily for emission spectrograph, polarographic, and chromatographic (liquid or vapor phase) procedures. This technique enables the analyst to compensate for electronic and mechanical fluctuations within the instrument.

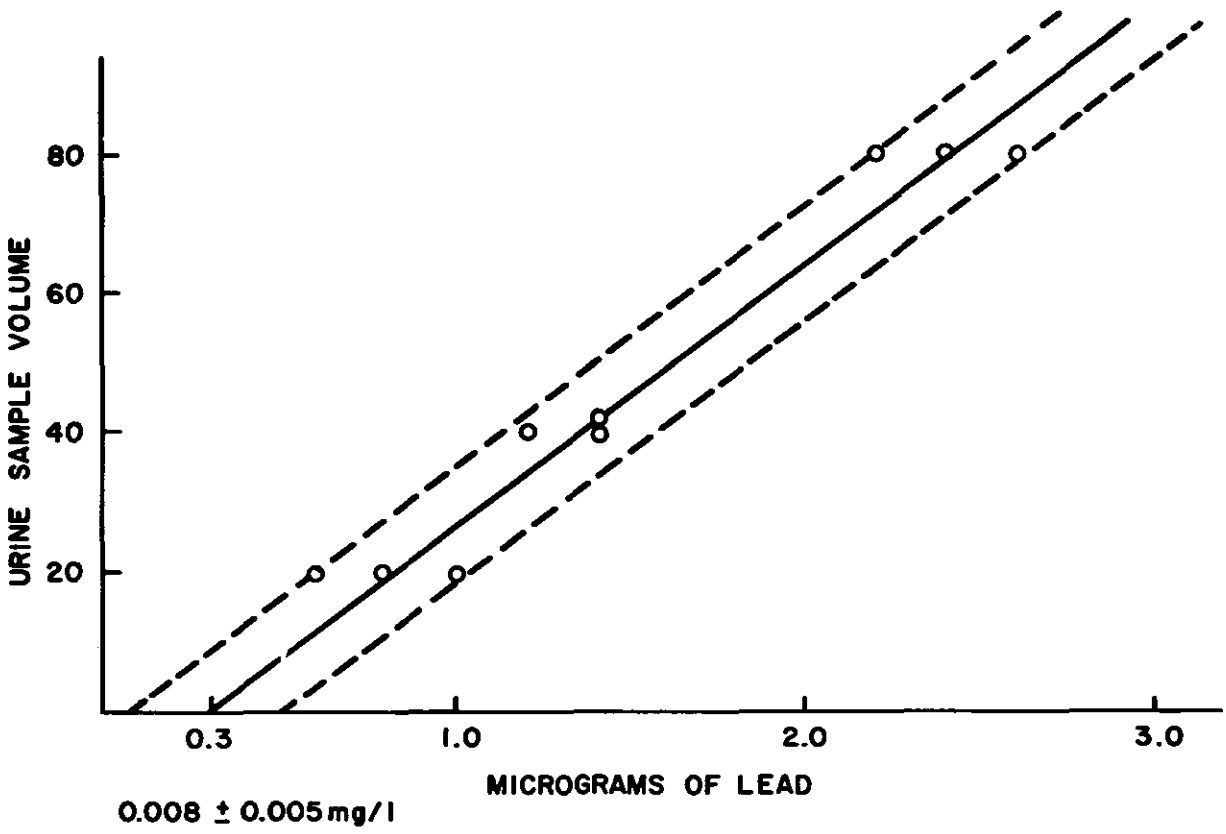


Figure 22-5. Effect of Sample Size on Determination of Lead in Urine

TABLE 22-2
AN INTERLABORATORY STUDY OF THE DETERMINATE ERROR IN THE DITHIZONE PROCEDURE FOR THE DETERMINATION OF LEAD IN NINE URINE SPECIMENS

Polarographic Method	Mixed Color Found	Dithizone Difference	Atomic Absorption Found	Atomic Absorption Difference
10	25	15	10	0
14	28	14	22	8
12	12	0	16	4
15	20	5	16	1
21	20	−1	22	1
22	30	8	24	2
27	40	13	36	9
19	22	3	22	3
12	22	10	16	4
Mean	—	+7.4	—	+3.6

TABLE 22-3
KITAGAWA CARBON MONOXIDE DETECTOR TUBE NO. 100*
Temperature Correction Table

Chart Readings (ppm)	Correction Concentration (ppm) 0°C (32°F)	10°C (50°F)	20°C (68°F)	30°C (86°F)	40°C (104°F)
1,000	800	900	1,000	1,060	1,140
900	720	810	900	950	1,030
800	640	720	800	840	910
700	570	640	700	740	790
600	490	550	600	630	680
500	410	470	500	520	560
400	340	380	400	420	440
300	260	290	300	310	320
200	180	200	200	200	210
100	100	100	100	100	100

*Kitagawa, T., "Carbon Monoxide Detector Tube. No. 100," National Environmental Instruments, Inc., 1971, Fall River, Mass.

In brief, the internal standard method involves the addition to the sample of known amounts of a substance to which the instrument will respond in a manner similar to the contaminant in the system. The ratio of the internal standard response to the contaminant response determines the concentration of contaminant in the sample. Condi-

tions during analyses will affect the internal standard and the contaminant identically, and thereby compensate for any changes. The internal standard should be of similar chemical composition to the contaminant, of approximately the same concentration anticipated for the contaminant, and of the purest attainable quality. A detailed discussion of the sources of physical error, magnitude of their effects, and suggestions for minimizing their contribution to determine bias and error will be found in the literature[8].

c) Chemical Interference. The term "interference" relates to the effects of dissolved or suspended materials on analytical procedures. A reliable analytical procedure must anticipate and minimize interferences.

The investigator must be aware of possible interferences and be prepared to use an alternate or modified procedure to avoid errors. Analyzing a smaller initial aliquot may suppress or eliminate the effect of the interfering element through dilution. The concentration of the substance sought is likewise reduced; therefore, the aliquot must contain more than the minimum detectable amount. When the results display a consistently increasing or decreasing pattern by dilution, then interference is indicated.

An interfering substance may produce one of three effects:

1. React with the reagents in the same manner as the component being sought (positive interference).
2. React with the component being sought to prevent complete isolation (negative interference).
3. Combine with the reagents to prevent further reaction with the component being sought (negative interference).

The sampling and analytical technique employed for the surveillance of airborne toluene diisocyanate (TDI) in the manufacturing environment furnishes a good example in which all three factors can be encountered. The TDI vapor is absorbed and quantitatively hydrolyzed in an aqueous acetic acid-hydrogen chloride mixture to toluene diamine (MTD) which then is diazotized by the addition of sodium nitrite. The excess nitrous acid is destroyed with sulfamic acid and the diazotized MTD coupled with N-1-Naphthylethylenediamine to produce a bluish-red azo dye.[9] In the phosgenation section of the operations, the starting material (MTD) may coexist with TDI in the atmosphere sampled. If so, then a positive interference will occur as the method cannot distinguish between free MTD and MTD from the hydrolyzed TDI.

This problem can be resolved by collecting simultaneously a second sample in ethanol. The TDI reacts with ethanol to produce urethane derivatives which do not produce color in the coupling stage of the analytical procedure. The MTD is determined by the same diazotization and coupling procedure after boiling off the ethanol from the acidified scrubber solution. Then the difference represents the TDI fraction in the air sampled.

On the other hand, if the relative humidity is high or alcohol vapors are present, negative interference will reduce the TDI recovered by formation of the carbanilide (dimer) or the urethane derivative which will not produce color in the final coupling stage. Alternative methods have not been developed for these conditions. If high concentrations of phenol are absorbed, then a negative interference will arise from side reactions with the nitrous acid required to diazotize the MTD. This loss can be avoided by testing for excess nitrous acid in the diazotization stage and adding additional sodium nitrite reagent if a deficiency is indicated.

An estimate of the magnitude of an interference may be obtained by the recovery procedure.

If recoveries of known quantities exceed 100%, a positive interference is present (Condition 1). If the results are below 100%, a negative interference is indicated (Condition 2, or 3: see reference (8) for details).

Indeterminate Error and Its Control

Nature. Even though all determinate errors are removed from a sampling or analytical procedure, replicate analyses will not produce identical results. This erratic variation arises from random error. Examples of this type of variation would be variation in reagent addition, instrument response, line voltage transients and physical measurement of volume and mass. In environmental analysis the sample itself is subject to a great variety of variability. Although indeterminate errors appear to be random in nature, they do conform to the laws of chance; therefore statistical measures of precision can be employed to quantitate their effects.

A measure of the degree of agreement (precision) among results can be ascertained by analyzing a given sample repeatedly under conditions controlled as closely as conditions permit. The range of these replicate results (difference between highest and lowest value) provides a measure of the indeterminate variations.

Quantification. 1) Distribution of Results. Indeterminate error can be estimated by calculation of the standard deviation (σ) after determinate errors have been removed. The calculation of this value is discussed in Chapter 3. When indeterminate or experimental errors occur in a random fashion, the observed results (x) will be distributed at random around the average or arithmetic mean ($\bar{x}$).

Given an infinite number of observations, a graph of the relative frequency of occurrence plotted against magnitude will describe a bell-shaped curve known as the Gaussian or normal curve (Figure 22-6). However, if the results are not occurring in a random fashion, the curve may be flattened (no peak), skewed (unsymmetrical), narrowed, or exhibit more than one peak (multimodal). In these cases the arithmetic mean will be misleading, and unreliable conclusions with respect to deviation ranges (σ) will be drawn from the data. A typical graph illustrating skew, multimodes, and a narrow peak is shown in Figure 22-7.

In any event the investigator should confirm the

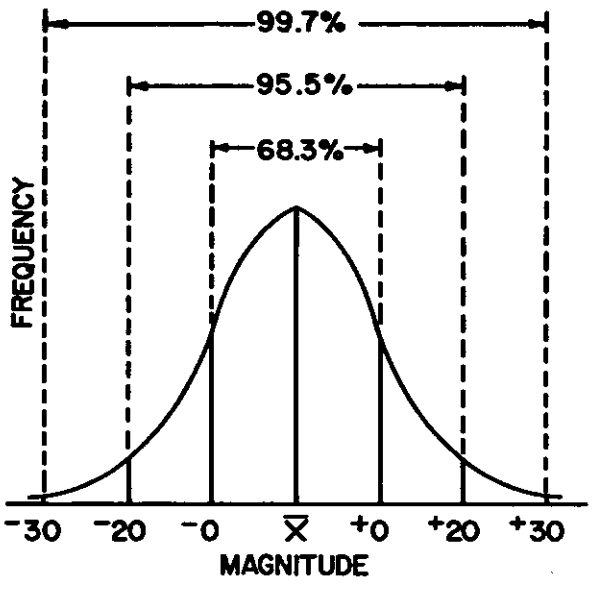


Figure 22-6. Gaussian or Normal Curve of Frequencies

normalcy of the data at hand. Various procedures are available to test this assumption.

One method is to construct a histogram, if the sample is large enough, and then to plot a normal curve having the same mean and standard deviation with the histogram to see how well the normal curve fits. This is an imprecise method at best and, unless there is an extremely good fit of a normal curve laid over the resulting histogram or polygon, the cumulated distribution should be plotted on normal probability paper before proceeding.

As an example the following table gives the frequency distribution of the results of a series of 145 similar tests:

Grams	Frequency	Grams	Frequency
0.8485	2	0.8275	21
0.8455	1	0.8245	14
0.8425	2	0.8215	5
0.8395	6	0.8185	4
0.8365	7	0.8155	3
0.8335	23	0.8125	2
0.8305	55		

These data are plotted in Figure 22-8. Now having looked at the fit, we decide how good it is. The graph does not really tell whether the depar-

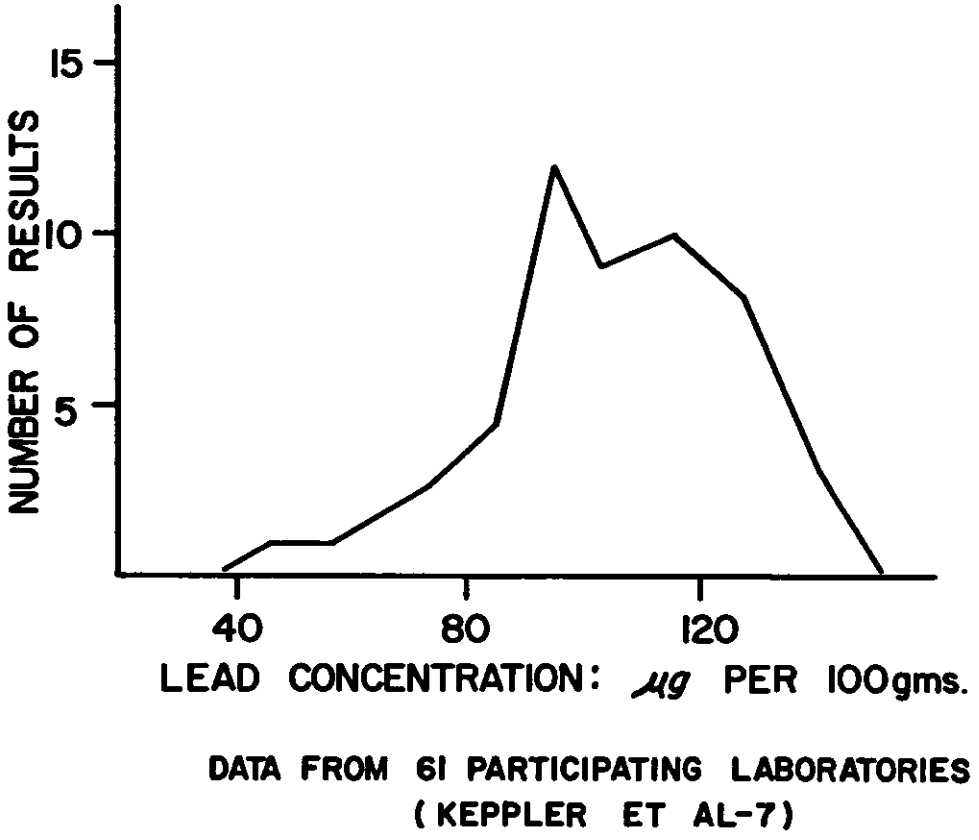


Figure 22-7. Frequency Distribution of Lead in Blood: Analytical Results

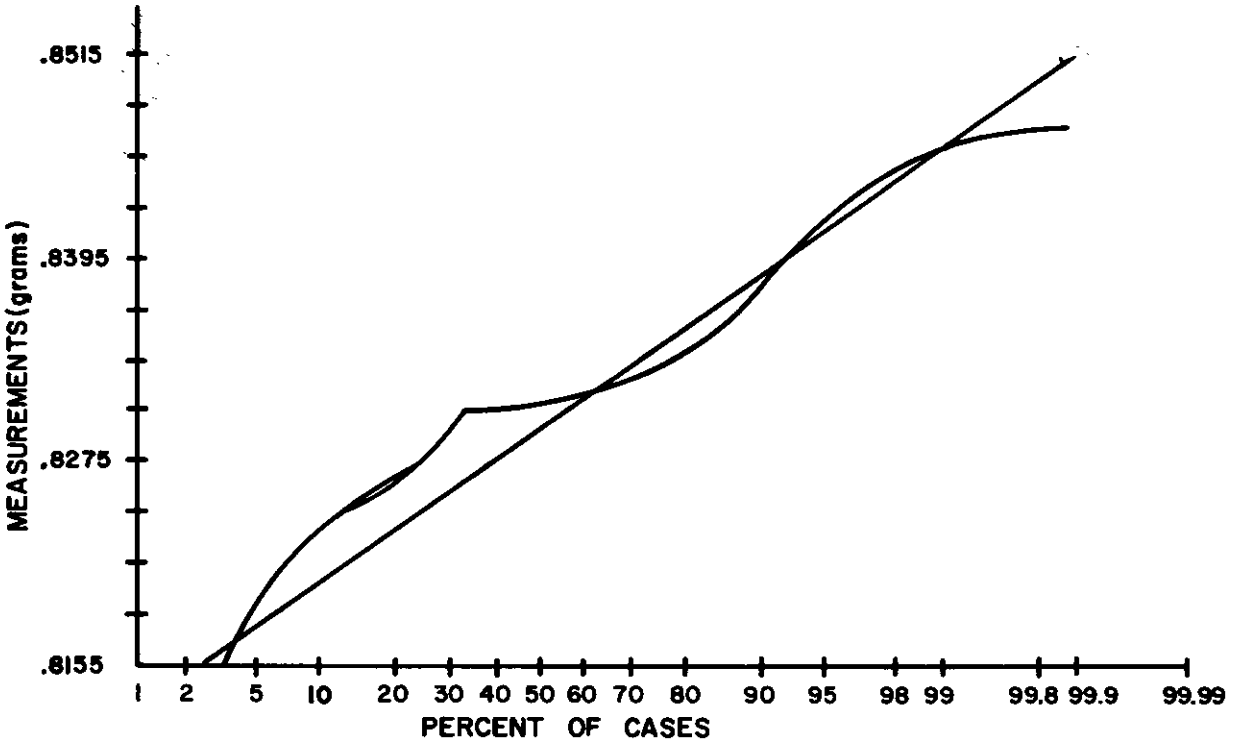


Figure 22-8. Plot of a Frequency Distribution

ture from fit is significant. The most accurate way of testing for normality is to use the X^2 test for normality of data. However, the calculations are tedious and time consuming for desk calculator computation. Standard X^2 computer programs are commonly available, but judgment must be used to weigh the cost of getting an accurate determination against the value of the information.

The distribution of results within any given range about the mean is a function of σ. The proportion of the total observations which reside within $\bar{x} \pm 1\ \sigma$, $\bar{x} \pm 2\ \sigma$ and $\bar{x} \pm 3\ \sigma$ have been thoroughly established and are delineated in Figure 22-6. Although these limits do not define exactly any finite sample collected from a normal group, the agreement with the normal limits improves as n increases. As an example, suppose an analyst were to analyze a composite urine specimen 1000 times for lead content. He could reasonably expect 50 results would exceed $\bar{x} \pm 2\ \sigma$ and only 3 results would exceed $\bar{x} \pm 3\ \sigma$. However, the corollary condition presents a more useful application. In the preceding example, the analyst has found $\bar{x}$ to be 0.045 mg. per liter with $\sigma = \pm$ 0.005 mg/1. Any result which fell outside the range 0.035-0.055 mg/1 ($0.045 \pm 2\ \sigma$) would be questionable as the normal distribution curve indicates this should occur only 5 times in 100 determinations. This concept provides the basis for tests of significance, a concept which is discussed in detail in any good statistical reference such as those cited in this chapter or Chapter 3.

2) Range of Results. The difference between the maximum and minimum of n results (range) also is related closely to σ. The range (R) for n results will exceed σ multiplied by a factor d_n only 5% of the time when a normal distribution of errors prevails.

Values for d_n:

n	d_n
2	2.77
3	3.32
4	3.63
5	3.86
6	4.03

Since the practice of analyzing replicate (usually duplicate) samples is a general practice, application of these estimated limits can provide detection of faulty technique, large sampling errors, inaccurate standardization and calibration, personal judgment and other determinate errors. However, resolution of the question whether the error occurred in sampling or in analysis can be answered more confidently when single determinations on each of three samples rather than duplicate determinations on each of two samples are made. This approach also reduces the amount of analytical work required.[6] Additional information relative to the evaluation of the precision of analytical methods will be found in ASTM Standards.[10]

3) Collaborative Studies or "Round Robins." After an analytical method has been evaluated fully for precision and accuracy, collaborative testing should be initiated. The values for precision and accuracy as determined by the results from a number of laboratories can be expected to be in-

ferior when compared with the performance of the originating laboratory. Because technicians in different laboratories apply to their procedure their own characteristic determinate and indeterminate errors which may differ significantly from the original technique, the values for precision and accuracy will disclose the true reliability (*ruggedness, or immunity to minor changes*) of the method. Participation in collaborative programs will aid the investigator in evaluating his laboratory's performance in relation to other similar facilities and in locating sources of error.

Duplicate analyses are employed for the determination and control of precision within the laboratory and between laboratories. Initially, approximately 20% of the routine samples, with a minimum of 20 samples, should be analyzed in duplicate to establish internal reproducibility. A standard or a repeatedly analyzed control, if available, should be included periodically for long-term accuracy control. The control chart technique is directly applicable, and appropriate control limits can be established by arbitrarily subgrouping the accumulated results or by using appropriate estimates of precision from an evaluation of the procedure.

CONTROL CHARTS

Description and Theory

The control chart provides a tool for distinguishing the pattern of indeterminate (stable) variation from the determinate (assignable cause) variation. This technique displays the test data from a process or method in a form which graphically compares the variability of all test results with the average or expected variability of small groups of data — in effect, a graphical analysis of variance, and a comparison of the "within groups" variability versus the "between group" variability (see Figure 22-6 for the pattern of variation of data).

The data from a series of analytical trials can be plotted with the vertical scale in units of the test result and the horizontal scale in units of time or sequence of analyses. The average or mean value can be calculated and the spread (dispersion or range) can be established (Figure 22-4).

The determination of appropriate control limits can be based on the capability of the procedure itself or can be arbitrarily established at any desirable level. Common practice sets the limits at $\pm$ 3 σ on each side of the mean. If the distribution of the basic data exhibits a normal form, the probability of results falling outside of the control limits can be readily calculated.

The control chart is actually a graphical presentation of quality control efficiency. If the procedure is "in control," the results will fall within the established control limits. Further, the chart will disclose trends and cycles from assignable causes which can be corrected promptly. Chances of detecting small changes in the process average are improved when several values for a single control point (an x chart) are used. As the sample statistical size increases, the chance that small changes in the average will not be detected is decreased. A sample size of $n = 4$ usually is selected.

The basic procedure of the control chart is to compare "within group" variability to "between group" variability. For a single analyst running a procedure, the "within group" may well represent one day's output and the "between group" represents between days or day-to-day variability. When several analysts or several instruments or laboratories are involved, the selection of the subgroup unit is critical. Assignable causes of variation should show up as "between group" and not "within group" variability. Thus, if the differences between analysts should provide assignable causes of variation, their results may not be lumped together in a "within group" subgrouping.

Application and Limitations

In order for quality control to provide a means for separating the determinate from indeterminate sources of variation, the analytical method must clearly emphasize those details which should be controlled to minimize variability. A check list would include:

1. Sampling procedures
2. Preservation of the sample
3. Aliquoting methods
4. Dilution techniques
5. Chemical or physical separations and purifications
6. Instrumental procedures
7. Calculation and reporting results.

The next step to be considered is the application of control charts for evaluations and control of these unit operations. Decisions relative to the basis for construction of a chart are required:

1. Choose method of measurement
2. Select the objective
   a. Precision (Figure 22-4) or accuracy evaluation (Figure 22-9)
   b. Observe test results, or the range of results
   c. Measurable quality characteristics (Figure 22-4), (Figure 22-9) and (Figure 22-10)
3. Select the variable to be measured (from the check list above)
4. Basis of subgroup, if used:
   a. Size
      A minimum subgroup size of $n = 4$ is frequently recommended. The chance that small changes in the process average remain undetected decreases as the statistical sample size increases.
   b. Frequency of subgroup sampling
      Changes are detected more quickly as the sampling frequency is increased.
5. Control Limits
   Control limits (CL) can be calculated, but judgment must be exercised in determining whether or not the values obtained satisfy criteria established for the method, i.e., does the deviation range fall within limits consistent with the solution or control of the problem. After the mean ($\bar{X}$) of the individual results (X), and the mean of the range ($\bar{R}$) of the replicate re-

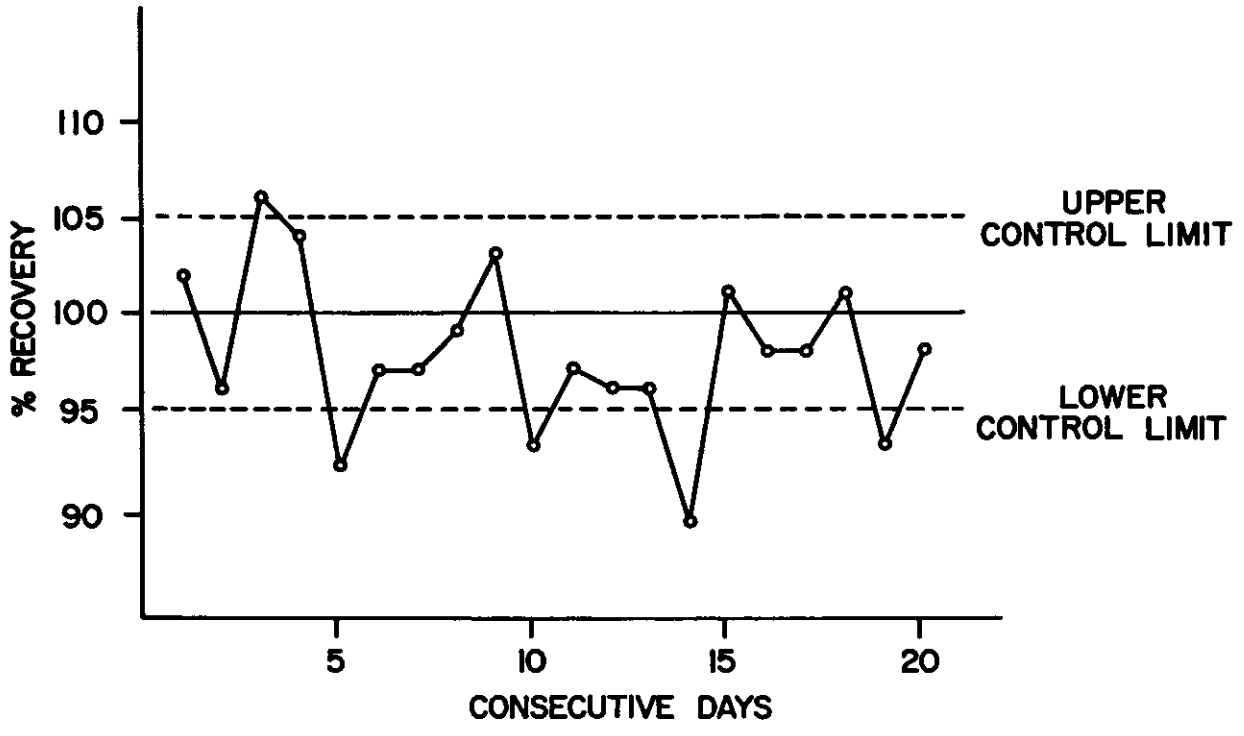


Figure 22-9. Recovery of Lead from Blood

sult differences (R) have been calculated, then CL can be calculated from data established for this purpose (Table 22-4).[5]

Grand Mean $(\overline{\overline{X}}) = \Sigma\overline{X}/k$

CL's on Mean $= \overline{\overline{X}} \pm A_2$

Range $(\overline{R}) = \Sigma R/k$, or $d_2\,\sigma$

Upper Control Limit (UCL) on Range $= D_4\overline{R}$

Lower Control Limit (LCL) on Range $= D_3\overline{R}$

Where: k = number of subgroups A_2, D_4 and D_3 are obtained from Table 22-4, R

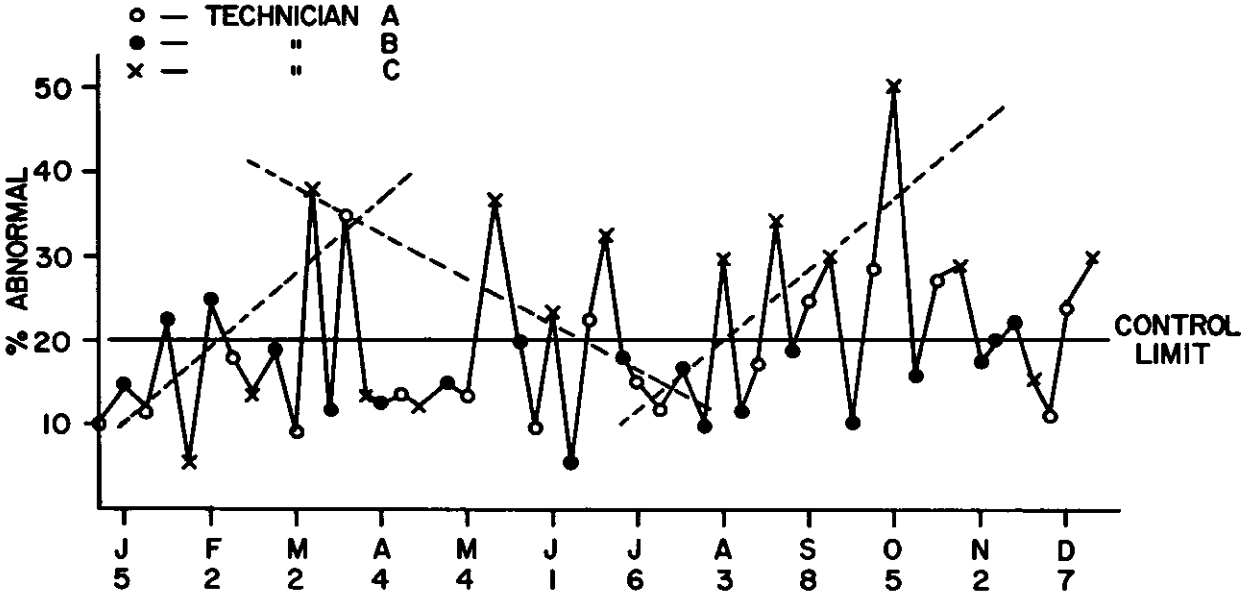


Figure 22-10. Lead in Urine Analysis — % Exceeding Threshold Limit (0.1 mg/Liter) on Weekly Basis

may be calculated directly from the data, or from the standard deviation (σ) using factor d_2. The lower control limit for R is zero when n ≦6.

The calculated CL's include approximately the entire data under "in control" conditions, and therefore, are equivalent to ± 3 σ limits which are commonly used in place of the more laborious calculation. Warning limits (WL) set at ± 2 σ limits (95%) of the normal distribution serve a very useful function in quality control (see Figure 22-4 and 22-9). The upper warning limit (UWL) can be calculated by:

$$UWL = \bar{R} + 2\,\sigma_R$$

$$UWL = \bar{R} \pm 2/3\,(D_4 R)$$

Where the subgrouping is n=2, UWL reduces to

$$UWL = 2.51\,\bar{R}.$$

CONSTRUCTION OF CONTROL CHARTS

Precision Control Charts

The use of range (R) in place of standard deviation (σ) is justified for limited sets of data n ≦10 since R is approximately as efficient and is easier to calculate. The average range ($\bar{R}$) can be calculated from accumulated results, or from a known or selected σ ($d_2\,\sigma$). $LCL_R = 0$ when n ≦6. (LCL = lower control limit).

The steps employed in the construction of a precision control chart for an automatic analyzer illustrate the technique (Table 22-5):

1. Calculate R for each set of side-by-side duplicate analyses of identical aliquots.
2. Calculate $\bar{R}$ from the sum of R values divided by the number (n) of sets of duplicates.
3. Calculate the upper control limit (UCL_R) for the range:
   $$UCL_R = D_4\bar{R}$$
   Since the analyses are in duplicates, D_4 = 3.27 (from Table 22-4).
4. Calculate the upper warning limit (UWL):
   $UWL_R = \bar{R} + 2\sigma_R = \bar{R} \pm 2/3(D_4\bar{R}) = 2.51\bar{R}$

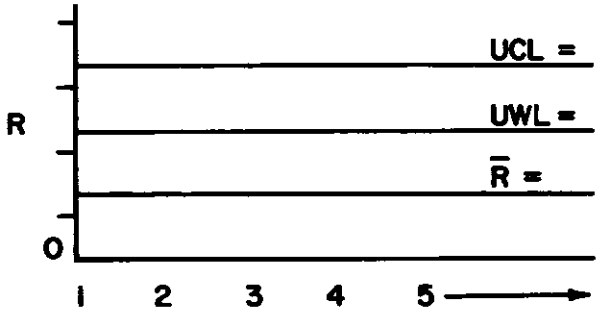


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Figure 22-11. Precision Control Chart

TABLE 22-4

FACTORS FOR COMPUTING CONTROL CHART LINES*

Observations in Subgroup (n)	Factor A_2	Factor d_2	Factor D_4	Factor D_3
2	1.88	1.13	3.27	0
3	1.02	1.69	2.58	0
4	0.73	2.06	2.28	0
5	0.58	2.33	2.12	0
6	0.48	2.53	2.00	0
7	0.42	2.70	1.92	0.08
8	0.37	2.85	1.86	0.14

*ASTM Manual on Quality of Materials, American Society of Testing and Materials, Philadelphia, 1951.

TABLE 22-5

PRECISION (DUPLICATES) DATA

Date	Data	Range (R)
9/69	# 8 25.1 24.9	0.2
	#16 25.0 24.5	0.5
	#24 10.9 10.6	0.3
10/69	# 7 12.6 12.4	0.2
	#16 26.9 26.2	0.7
	#24 4.7 5.1	0.4
2/70	# 6 9.2 8.9	0.3
	#12 13.2 13.1	0.1
	#16 16.2 16.3	0.1
	#22 8.8 8.8	0.0
4/70	# 6 14.9 14.9	0.0
	#12 17.2 18.1	0.9
	#18 21.9 22.2	0.3
5/70	# 6 34.8 32.6	2.2
	#12 37.8 37.4	0.4
6/70	# 6 40.8 39.8	1.0
	#10 46.0 43.5	2.5
	#17 40.8 41.2	0.4
	#24 38.1 36.1	2.0
7/70	# 6 12.2 12.5	0.3
	#12 25.4 26.9	1.5
	#18 20.4 19.8	0.6
		$\bar{R} = 14.9/22 = 0.68$
		$UCL = 3.27 \times 0.68 = 2.2$
		$UWL = 2.51 \times 0.68 = 1.7$

(D_4 from Table 22-4) which corresponds to the 95% confidence limits.

5. Chart $\bar{R}$, UWL_R and UCL_R on an appropriate scale which will permit addition of new results as obtained as shown in Figure 22-11 and Table 22-5.

6. Plot results (R) and take action on out-of-control points.

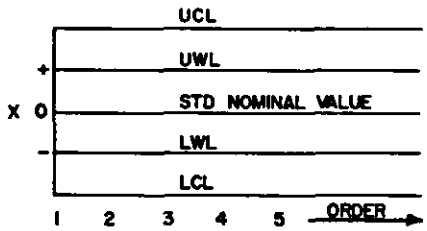

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Figure 22-12. Accuracy Control Chart

ACCURACY CONTROL CHARTS — MEAN OR NOMINAL VALUE BASIS

$\bar{X}$ charts simplify and render more exact the calculation of CL since the distribution of data which conforms to the normal curve can be completely specified by $\bar{X}$ and σ. Stepwise construction of an accuracy control chart for the automatic analyzer based on duplicate sets of results obtained from consecutive analysis of knowns serves as an example (Table 22-6):

1. Calculate $\bar{X}$ for each duplicate set
2. Group the $\bar{X}$ values into a consistent reference scale (in groups by orders of magnitude for the full range of known concentrations).
3. Calculate the UCL and lower control limit (LCL) by the equation:
   $CL = \pm A_2\bar{R}$ (A_2 from Table 22-4).
4. Calculate the Warning Limit (WL) by the equation:
   $WL = \pm 2/3\ A_2\bar{R}$
5. Chart CL's and WL's on each side of the standard which is set at zero as shown in Figure 22-12 ("order" related to consecutive, or chronological order of the analyses) and Table 22-6.
6. Plot the difference between the nominal value and $\bar{X}$ and take action on points which fall outside of the control limits.

CONTROL CHARTS FOR INDIVIDUAL RESULTS

In many instances a rational basis for subgrouping may not be available, or the analysis may be so infrequent as to require action on the basis of individual results. In such cases X charts are employed. However, the CLs must come from some subgrouping to obtain a measure of "within group" variability. This alternative has the advantage of displaying each result with respect to tolerance, or specification limits (Figures 22-4, 5, 9 and 13). The disadvantages must be recognized when considering this approach.

1. The chart does not respond to changes in the average.
2. Changes in dispersion are not detected unless an R chart is included.

TABLE 22-6

ACCURACY DATA

Date	Calibration Range	Nominal (N)	Values	$\bar{X}$	N-$\bar{X}$
9/69	10-400 ppm	100 ppm	22.9, 21.5/	22.2	−0.7
			22.7, 22.3	22.5	−0.4
	1.7-69.7 scale	22.9			
10/69	10-400	100	21.6, 21.3/	21.5	0.0
	1.5-67.6	21.5			
2/70	10-400	100	23.6, 24.1/	23.9	−0.6
	1.4-62.5	24.5			
4/70	10-400	100	25.8, 26.5/	26.2	+0.2
	1.6-59.4	26.0	26.0, 26.7	26.4	+0.4
5/70	10-150	100	72.2, 70.2/	71.2	+1.2
	6.3-83.0	70.0			
6/70	10-150	100	71.0, 70.8/	71.1	+0.1
			71.0, 71.3	71.2	+0.2
	6.6-85.0	71.0			
7/70	10-150	60	14.9, 14.7/	14.8	−0.2
			15.1, 14.4	14.8	−0.2
	1.8-33.5	15.0			

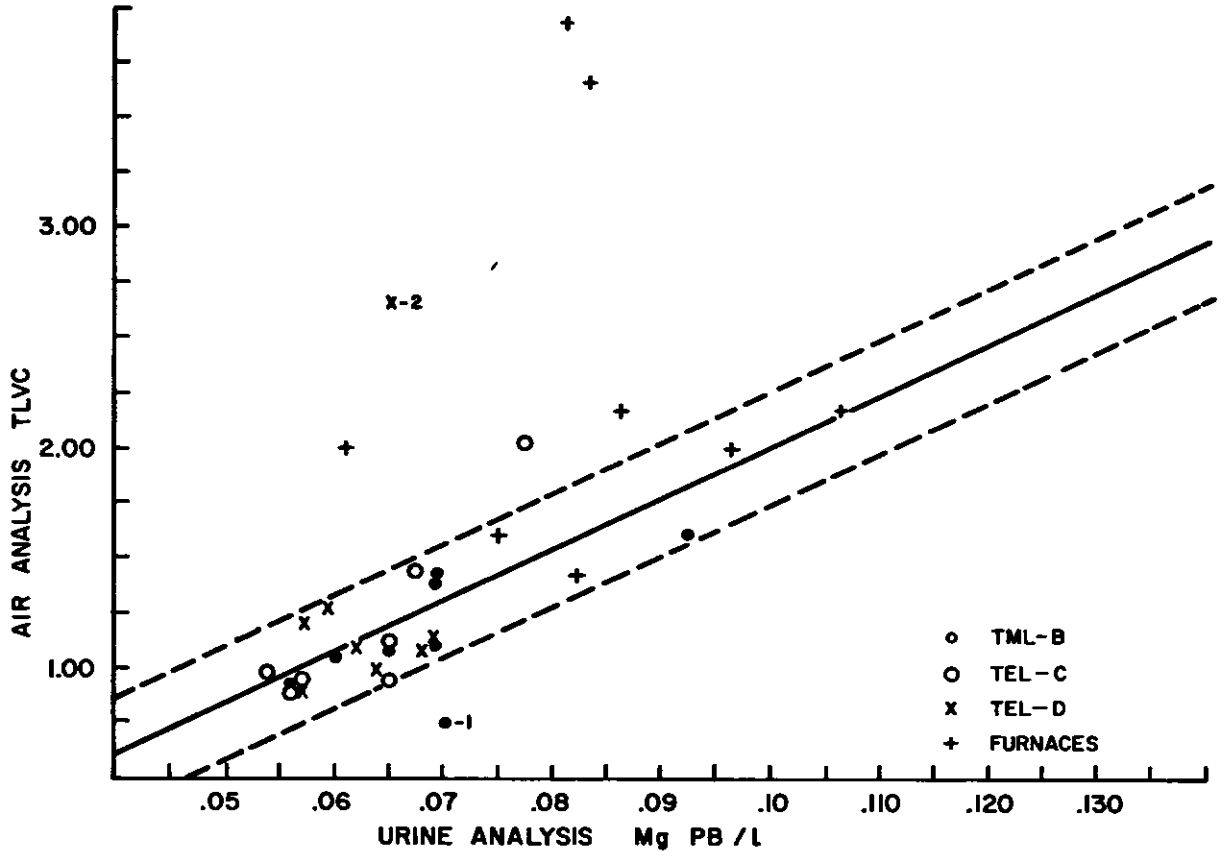


Figure 22-13. Relationship of Previous Monthly TLV Coefficient to Urinary Lead Excretion

3. The distribution of results must approximate normal if the control limits remain valid.

Additional refinements, variations and control charts for other variables will be found in standard texts.[1, 11, 12]

MOVING AVERAGES AND RANGES

The $\bar{X}$ control chart is more efficient for disclosing moderate changes in the average as the subgrouping size increases. A logical compromise between the X and $\bar{X}$ approach would be application of the moving average. For a given series of analyses, the moving average is plotted. Such a set of data is shown in Table 22-7. The moving range serves well as a measure of acceptable variation when no rational basis for subgrouping is available or when results are infrequent or expensive to gather.

OTHER CONTROL CHARTS FOR VARIABLES

Although the standard $\bar{X}$ and R control chart for variables is the most common, it does not always do the best job. Several examples follow where other charts are more applicable.

Variable Subgroup Size

The standard $\bar{X}$ and R chart is applicable for a constant size subgroup of n=2,3,4,5. In some cases such a situation does not exist. Control limit values must be calculated for each sample size. Plotting is done in the usual manner with the control size limits drawn in for each subgroup depending on its size.

R or σ Charts

In some situations the dispersion is equal over a range of assay values. In this case, a control chart for either range or standard deviation is appropriate.

When the dispersion is a function of concentration, control limits can be expressed in terms of a percentage of the mean. In practice such control limits would be given as in the example below:

± 5 units/liter for 0-100 units/liter concentration

± 5% for >100 units/liter concentration

An alternative procedure involves transformation of the data.[13] For example, logarithms would be the appropriate transformation.

$\bar{X}$ and σ Charts

If the subgroup size exceeds 10, the Range Chart becomes inefficient. The use of a σ chart would then be appropriate. Where the cost of obtaining the test data is high, the increase in efficiency using σ rather than R may be worthwhile.

OTHER STATISTICAL TOOLS

Rejection of Questionable Results

The question whether or not to reject results which deviate greatly from $\bar{x}$ in a series of other-

TABLE 22-7
MOVING AVERAGE AND RANGE TABLE
(N=2)

Sample No.	Assay Value	Sample Nos. Included	Moving Average	Moving Range
1	17.09	—	—	—
2	17.35	1-2	17.22	+0.26
3	17.40	2-3	17.38	+0.05
4	17.23	3-4	17.32	−0.17
5	17.00	4-5	17.12	−0.23
6	16.94	5-6	16.97	−0.16
7	16.68	6-7	16.81	−0.26
8	17.11	7-8	16.90	+0.43
9	18.47	8-9	17.79	+1.36
10	17.08	9-10	17.78	−1.39
11	17.08	10-11	17.08	0.00
12	16.92	11-12	17.00	−0.16
13	18.03	12-13	17.48	+1.11
14	16.81	13-14	17.42	−1.22
15	17.15	14-15	16.98	+0.34
16	17.34	15-16	17.25	+0.19
17	16.71	16-17	17.03	−0.63
18	17.28	17-18	17.00	+0.57
19	16.54	18-19	16.91	−0.74
20	17.30	19-20	16.92	+0.76

wise normal (closely agreeing) results frequently arises. On a theoretical basis, no result should be rejected, as the one or more errors which render the entire series doubtful may be determinate errors that can be resolved. Tests which are known to involve mistakes, however, should not be reported exactly as analyzed. Mathematical basis for rejection of "outliers" from experimental data may be found in statistics text books.[14]

Correlated Variables — Regression Analysis

A major objective in scientific investigations is the determination of the effect that one variable exerts on another. For example a quantity of sample (x) is reacted with a reagent to produce a result (y) The quantity x represents the independent variable over which the investigator can exert control.

The dependent variable (y) is the direct response to changes made in x, and varies in a random fashion about the true value. If the relationship is linear, the equation for a straight line will describe the effect of changes in x on the response y: $y=a+b\,x$, in which a is the intercept with the y axis and b is the slope of the line (the change in y per unit change in x). In chemical analysis a is a measure of constant error arising from a colorimetric determination, trace impurity, blank, or other determinate source. The slope b may be controlled by reaction rate, equilibrium shift or the resolution of the method. The term "regression analysis" is applied to this statistical tool.

A typical application is exhibited in Figure 22-14 which relates the concentration of lead in blood to the standard deviation of the method.[11] For this relationship, $y=0.0022+0.054x$. Addi-

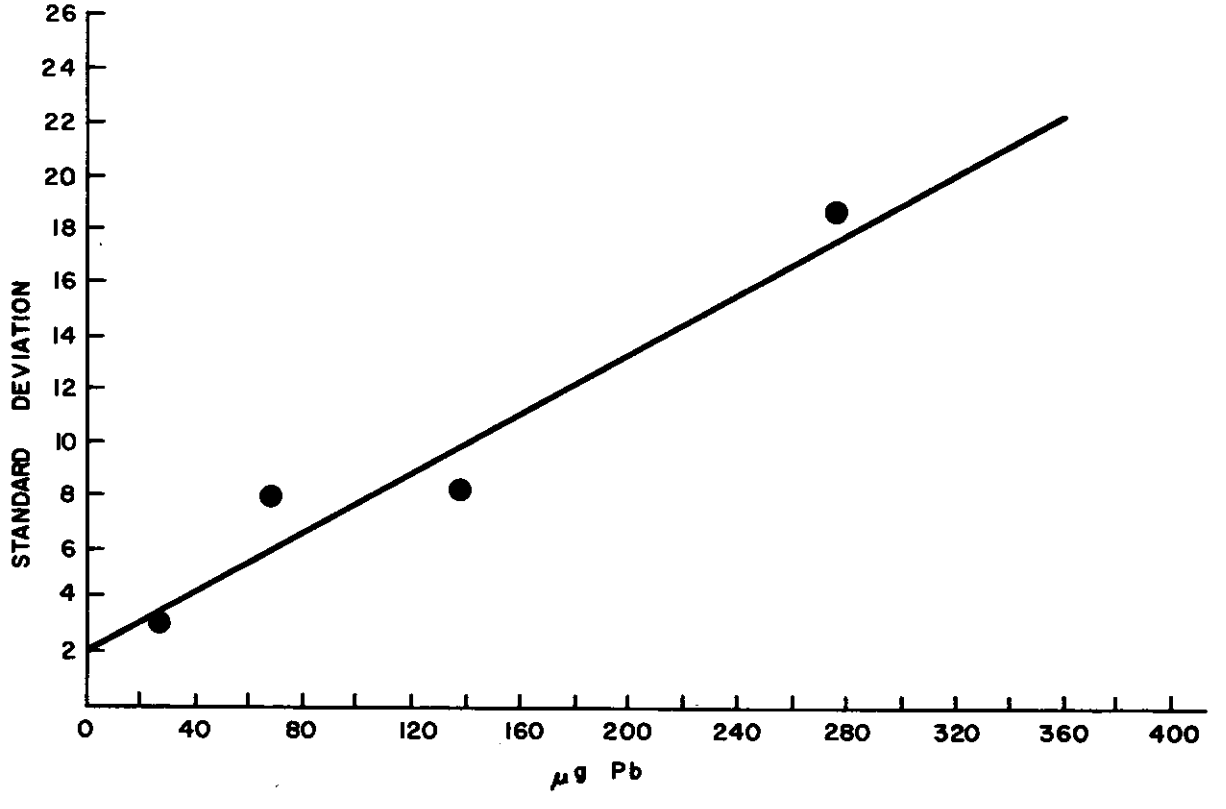


Figure 22-14. Standard Deviation of Data from 10 Laboratories (Keenan et al)

tional useful information can be obtained by certain transformations and shortcuts. [6, 14, 15, 16]

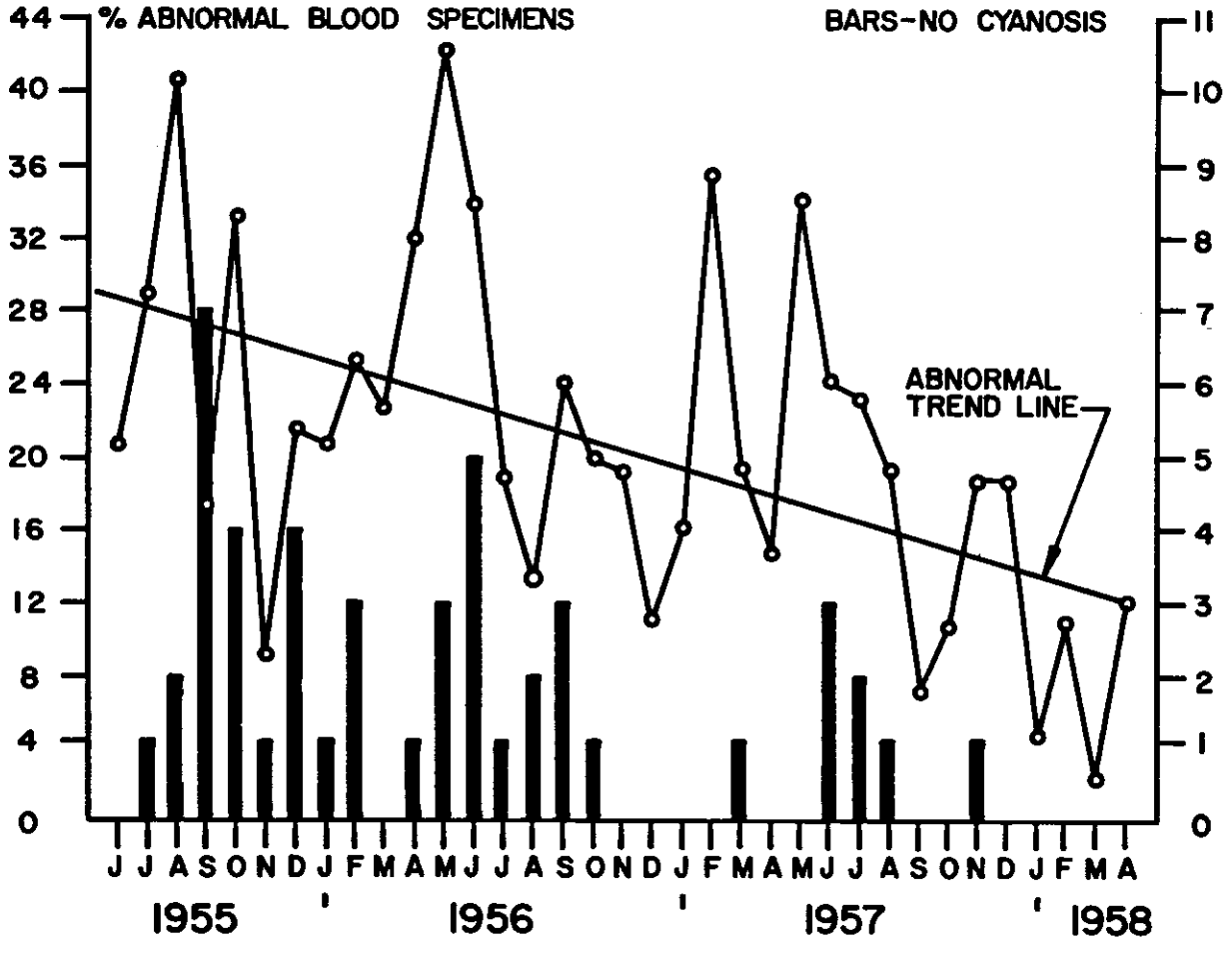
GRAPHIC ANALYSIS FOR CORRELATIONS

Useful shortcuts may be elected to determine whether a significant relationship exists between x and y factors in the equation for a straight line ($y=a+bX$). The data are plotted on linear cross section paper and a straight line drawn by inspection through the points with an equal number on each side or fitted by the least squares method. If the intercept a must be zero (a blank correction may produce such a situation), the fitting is greatly simplified. Then on each side equidistant from this line draw parallel lines corresponding to the established deviation (σ) of the analytical procedure, tally up the points falling inside of the band formed by the $\pm\ \sigma$ lines and calculate percent correlation (conformance = No. within band x 100/total points plotted). This technique is illustrated in Figure 22-13 which was used to relate urinary lead excretion to the airborne lead concentration obtained by personnel monitor surveys.[17] In this case more than one TLV was involved, so the TLV coefficient (TLVC) transformation was used for estimation of total lead exposure (TLVC =

$$\frac{\text{alkyl Pb found}}{\text{TLV}} + \frac{\text{Inorganic Pb found}}{\text{TLV}}).$$

A plot of the monthly coefficients versus corresponding average urinary excretion disclosed only a 69% conformance, whereas a plot of the previous month's TLVC's versus current month's average urinary excretion gave a 78% conformance. Furthermore, inspection of the chart indicated most of the "outliers" were contributed by the furnace crew. Deletion of this group raised conformance to 86% for the balance of the operation.[17] Correlations above 80% are considered quite good [see also reference (16)].

Curvilinear functions can be accommodated, especially if a log normal[14] function is involved and a plot of the data on semi-log paper yields a straight line.[18] Log-Log paper also is available for plotting complex functions.



(J. M. Wetherhold, A. L. Linch and R. C. Charsha. Amer. Ind. Hyg. Assoc. J. *20:* 396, 1959)

Figure 22-15. Relation of Abnormal Blood Specimens to Cyanosis Incidents

A combination of curvilinear and bar charts in some cases will reveal correlations not readily detected by mathematical processes. The data derived from an industrial cyanosis control program[19] illustrate an application which revealed a rather significant relationship between abnormal blood specimens and the frequency of cyanosis cases on a long-term basis (Figure 22-15). In fact one trend line could be fitted to both variables, and the predicted ultimate improvement was attained in 1966 when abnormal blood specimens dropped below 2% and the cyanosis cases below 4%.[20]

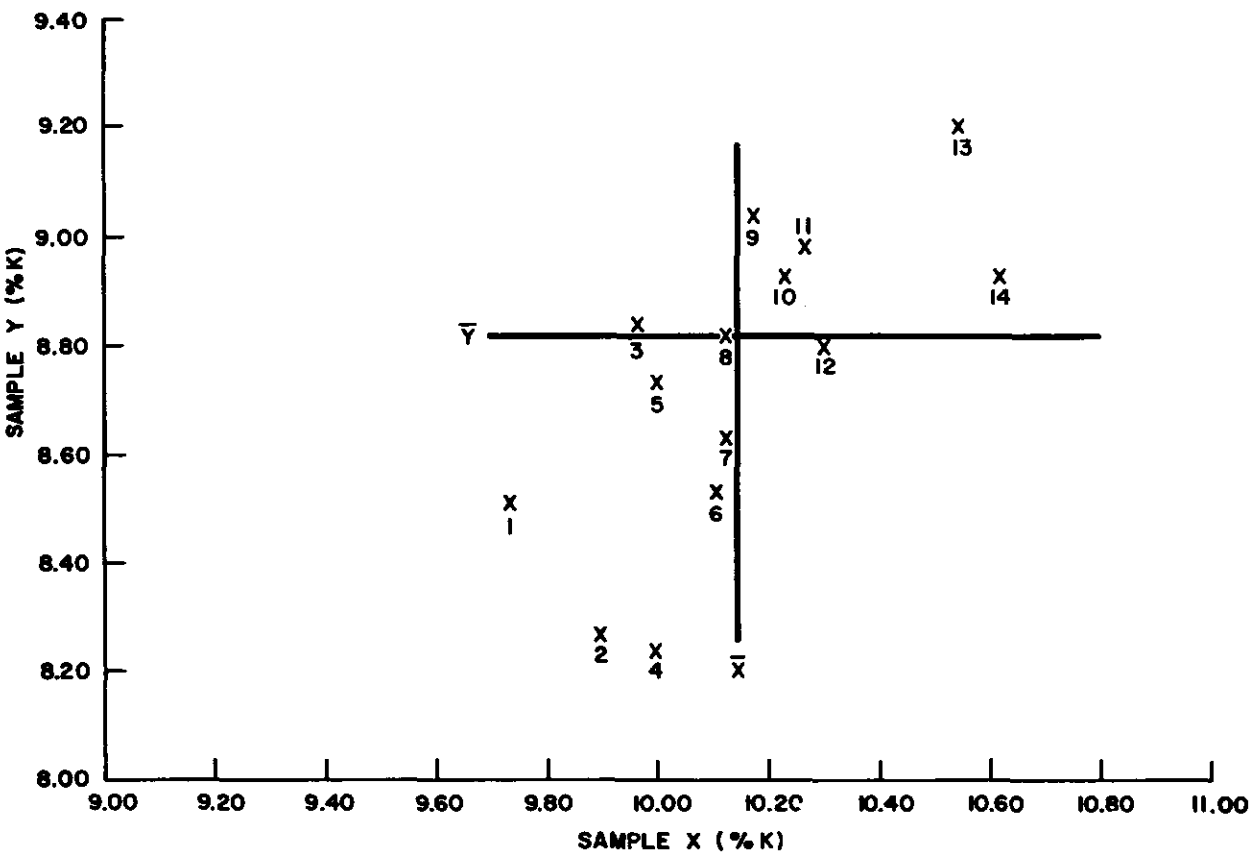
Grouping data on a graph and approximating relationships by the quadrant sum test (rapid corner test for association) can provide useful results with a minimum expenditure of time.[16, 21]

In those cases where application of mathematical tools are tedious or completely impractical, a system of ranking is sometimes applicable to the restoration of order out of chaos. Again with reference to the cyanosis control program, a relationship between causative agent structure and biochemical potential for producing cyanosis and anemia was needed. Ten factors (categories) common to some degree for each of the 13 compounds under study had been recognized. The 13 compounds were ranked in each category in reverse order of activity (No. 1 most, No. 13 least active) and the sum of the rankings obtained for each compound. These sums then were divided by the number of categories used in the total ranking to obtain the "score." The scores were then arranged in increasing numerical order in columnar form. The most potent cyanogenic and anemiagenic compounds then appeared at the top of the table and the least at the bottom.[20]

CHI SQUARE TEST

Control charts are a convenient tool for daily checking with reference standards, but the answers are not always as nearly quantitative as needed. Periodic checking of the accumulated daily reference results to determine more rigorously whether all of the data belong to the same normal distribution may become necessary. One approach to this question and to assign a probability to the answer is provided by the Chi Square (X^2) test.

The Chi Square distribution describes the probability distribution of the sums of the squares of independent variables that are normally or approximately normally distributed. The general form of the expression provides a comparison of observed versus expected frequencies.[22] The Chi



Powell CH, Hosey AD (eds): The Industrial Environment — Its Evaluation and Control, 2nd Edition. Public Health Service Publication No. 614, 1965.

Figure 22-16. Youden's Graphical Technique

Square test is applied to variables which fall within the Poisson distribution.[28]

THE ANALYSIS OF VARIANCE (ANOVA)

The analysis of variance is one of the most useful statistical tools. Variation in a set of results may be analyzed in such a way as to disclose and evaluate the important sources of the variation. For a detailed description of this technique consult standard statistics textbooks.

YOUDEN'S GRAPHICAL TECHNIQUE[1,6,24]

Dr. W. J. Youden has devised an approach to test for determinate errors with a minimum of effort on the part of the analyst.

Two different test samples (X and Y) are prepared and distributed for analysis to as many individuals or laboratories as possible. Each participant is asked to perform only one determination on each sample (NOTE: It is important that the samples are relatively similar in concentration of the constituent being measured.)

Each pair of laboratory results can then be plotted as a point on a graph (Figure 22-16).

A vertical line is drawn through the average of all the results obtained on sample X; a horizontal line is drawn through the average of all the results obtained on sample Y. If the ratio of the bias to standard deviation is close to zero for the determinations submitted by the participants, then one would expect the distribution of the paired values (or points) to be close to equal among the four quadrants. The fact that the majority of the points fall in the (+,+) and (−,−) quadrants indicates that the results have been influenced by some source of bias.

Furthermore, one can even learn something about a participant's precision. If all participants had perfect precision (no indeterminate error), then all the paired points would fall on a 45° line passing through the origin. Consequently the distance from such a 45° line to each participant's point provides an indication of that participant's precision.

INTRA-LABORATORY QUALITY CONTROL PROGRAM

Responsibilities

The attainment and maintenance of a quality control program in the laboratory is the direct responsibility of the laboratory manager or supervisor. The fundamental quality control techniques are based on:

1. Calibration to ensure accuracy
2. Duplication to ensure precision
3. Correlation of quantitatively related tests to confirm accuracy and continual scrutiny to maintain the integrity of the results reported.

The individual technician can contribute significant assistance in this effort by his desire to deliver the best possible answers within the inherent limits of the equipment and procedure. Part of supervision's responsibility is adequate instruction to provide the "man on the bench" with sufficient "know how" to apply the principles on a routine basis.

The guidelines established by the American Industrial Hygiene Association for Accreditation of Industrial Hygiene Analytical Laboratories[12] delineate the minimum requirements which must be satisfied in order to qualify for proficiency recognition.

Precision Quality Control

In addition to the use of internal standards, recovery procedures and statistical evaluation of routine results, the laboratory should subscribe to a reference sample service to confirm precision and accuracy within acceptable limits. Apparatus should be calibrated directly or by comparison with National Bureau of Standards (NBS) certified equipment or its equivalent, reagents should meet or exceed ACS standards, calibration standards should be prepared from AR (analytical reagent) grade chemicals,[25] and standardized with NBS standards if available. To illustrate, in a laboratory engaged in an exposure control program based on biological monitoring by trace analysis of blood and urine for lead content, at least two calibration points, blanks and a recovery should be included in each batch analyzed by the dithizone procedure. In addition, the wavelength integrity and optical density response of the spectrophotometer should be checked and adjusted — if necessary by calibration with NBS cobalt acetate standard solution. Until the standard deviation for the analytical procedure has been established within acceptable limits, replicate determinations should be made on at least two samples in each batch (either aliquot each sample or take duplicate samples), and thereafter with a frequency sufficient to ensure continued operation within these limits.

Control charts are probably the most widely recognized application of statistics. They provide "instant" quality control status when plotted daily, or at other intervals sufficiently short to disclose trends without undue oscillations from over-refinement of the data. Examples selected from a lead surveillance program illustrate the value of control charts. Figure 22-9 for analytical control is based on recoveries of known quantities of lead added to blood. From this chart and an analysis of the data itself, several conclusions may be drawn:

1. Background ("natural" lead) concentrations lay very close to the ultimate sensitivity of the method (35 ± 5 μg).
2. The variability of the back-ground lead concentration exerts a relatively strong controlling effect on the recovery.
3. Although only a short period is covered, a downward trend is noticeable.
4. A control limit set at 98% ± 5% probably is more realistic.

The same technique was applied to the evaluation of the quality of an exposure control program. A one year section from the control chart is presented in Figure 22-10. The graph provided several significant conclusions upon which action was initiated:

1. An alleged bias in the technician's performance was ruled out as each had about the same number of peaks and valleys dur-

ing the period (each technician in turn analyzed all of the urine specimens for the entire week plotted).
2. Trend lines which were drawn in by inspection disclosed a much closer correlation with production rate than with an alleged seasonal (temperature) cycle.
3. The peaks in the short term oscillations were connected with particular rotating shift crews who engaged in "dirty" work habits that were corrected from time to time.
4. No correlation could be established with fixed station air analysis data.

These examples are but two applications of a very extensive specialty within the field of statistics; therefore, the reader is referred to standard texts for additional information on refinements and procedures for extracting significant information from control charts.[14, 26] On the basis of its raw simplicity, amount of information available for a minimum expenditure of time and effort, graphic presentation and the ease of comprehension, the control chart cannot be over-recommended.

Accuracy Quality Control

A standard or well defined control sample should be analyzed periodically to confirm accuracy of a procedure. The control chart technique is directly applicable to long-term evaluation of the reliability of the analyst as well as the accuracy of the procedure. To attain and maintain the high level of analytical integrity presented earlier in this chapter the three major sources of "assignable cause" errors must be reduced to a minimum level which is consistent with cost penalties and the objective of the study for which the analytical service is rendered:

1. Equipment errors can be reduced to tolerable limits by calibration with primary physical standards such as those supplied by the National Bureau of Standards.
2. Method errors can be controlled by precise standardization of reagents, use of calibrated volumetric glassware and weights, refined manipulative techniques (personal errors), recognition and correction of personal bias (color estimation), elimination of chemical interferences, and corrections for physical influences such as the effect of temperature and actinic light.
3. Personal errors other than inherent physical visual acuity (color judgment) include consistent carelessness, lack of knowledge, calculation errors, use of contaminated or improper reagents, poor sampling technique and use of poorly calibrated standards and instruments.

Interlaboratory Reference Systems

Participation in interlaboratory studies whether by subscription from a certified laboratory supplying such a service or from a voluntary program initiated by a group of laboratories in an attempt to improve analytical integrity[11] is highly recommended. Evaluation of the analytical method as well as evaluation of the individual laboratory's performance can be derived by specialized statistical methods applied to the data collected from such a study. However, inasmuch as most investigators will not be called upon to conduct or evaluate interlaboratory surveys, the reader is referred to the literature in the event such specialized information is needed.[11, 26, 27, 28] In the absence of such programs, the investigator, or laboratory supervisor, should make every effort to locate colleagues engaged in similar sampling and analytical activity and arrange exchange of standards, techniques, and samples to establish integrity and advance the art.

SUMMARY

Identification of the determinate sources of error of a procedure provides the information required to reduce assignable error to a minimum level. The remaining (residual) indeterminate errors then determine the precision of analyses produced by the procedure. Statistical techniques have been developed to estimate efficiently the precision. For a procedure to be accurate, the results must be not only precise, but bias must be absent. Several approaches are available to eliminate bias both within the laboratory and between laboratories by collaborative testing. Quality control programs based on appropriate control charts must be employed on a routine basis to assure adherence to established performance standards. The total analysis control program must include instrumental control, procedural control and elimination of personal errors. The use of replicate determinations, "spiked" sample techniques, reference samples, standard samples and quality control charts will provide assurance that the procedure remains in control.

The guidelines established by the American Industrial Hygiene Association for Accreditation of Industrial Hygiene Analytical Laboratories[12] further summarizes in a succinct fashion the requirements for proficiency.

Quality Control and Equipment

Routine quality control procedures shall be an integral part of the laboratory procedures and functions. These shall include:

1. Routinely introduced samples of known content along with other samples for analyses.
2. Routine checking, calibrating, and maintaining in good working order of equipment and instruments.
3. Routine checking of procedures and reagents.
4. Good housekeeping, cleanliness of work areas, and general orderliness.
5. Proficiency Testing — The following criteria shall be used in the proficiency testing of industrial hygiene analytical laboratories accredited by the American Industrial Association.
   a) Reference Laboratories
      Five or more laboratories shall be designated as reference laboratories by the American Industrial Hygiene Association based on the appraisal of

competence of the laboratories by the Association. The reference laboratories may be judged competent:

(1) in all industrial hygiene analyses or

(2) specific industrial hygiene analyses.

Proficiency samples shall be sent to designated reference laboratories for analyses. These data will be used for grading analytical data received from laboratories seeking or maintaining accreditation by the Association.

b) Method of Grading

Laboratories shall be graded on the basis of their ability to perform analyses within specified limits determined by the reference laboratories. Satisfactory performance shall be the reporting of results within two standard deviations of the mean value obtained by the reference laboratories. Exception shall be made in cases where too few laboratories are in existence, a new procedure has not been adequately tested, or the range in variation from reference laboratories is too great to apply this method of grading.

c) Number and Suitability of Samples

Samples shall be either environmental materials, biological fluids, or tissues or synthetic mixtures approximating these. They shall be packaged, as nearly possible, in an identical manner and the containers will be chosen so as to avoid exchange of the test material between the samples and container. Samples shall be analyzed by each participating laboratory in sufficient number and at proper intervals for the results to form an adequate basis for accreditation in the opinion of AIHA.

d) Frequency of Samples

Samples shall be submitted to each laboratory quarterly.

e) Satisfactory Performance

Satisfactory performance is a considered scientific judgment and is not to be judged exclusively by any inflexible set of criteria. The judgment shall be made, however, on the basis of the results submitted by the laboratories and a statistical estimation of whether the results obtained are probably representative of analytical competence considering inherent variables in the method.

6. Records

The industrial hygiene analytical laboratory shall maintain records and files proper and adequate for the services given. These shall include:

a) The proper identification and numbering of incoming samples.

b) An adequate and systematic numbering system relating laboratory samples to incoming samples.

c) An adequate record system on internal logistics of each sample including date of incoming sample, analysis and procedures, and reporting of data.

d) A records checking system of the calibration and standardization of equipment and of internal control samples.

The program includes:

1. Nature, extent of use and results of routine interlaboratory quality control procedures.
2. Procedures for routine calibration and maintenance of reagents, equipment and instruments.
3. Nature, extent and results of routine checking and evaluation of analytical procedures. Intra- and inter-laboratory evaluations of precision and accuracy.

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Preferred Reading

In addition to references 6, 8, 9, 10, 14, 15, the following periodicals are recommended:

American Industrial Hygiene Association Journal

Journal of the Air Pollution Control Association

Analytical Chemistry (American Chemical Society)

Environmental Science & Technology (American Chemical Society)

Pollution Engineering (Technical Publishing Co.)

Air Pollution Manual — 2nd edition — American Industrial Hygiene Association, 1971.

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CHAPTER 23

PHYSICS OF SOUND

Paul L. Michael, Ph.D.

INTRODUCTION

The sensation of sound is produced when pressure variations having a certain range of characteristics reach a responsive ear. These pressure variations may be produced by any object that vibrates in a conducting medium with the proper cycle rate, or frequency, and amplitude. Sound may consist of a single frequency and amplitude; however, common noise spectra have many different frequency components with many different amplitudes.

This chapter is concerned primarily with those practical aspects of sound that are related to its characteristics in a given space and to its propagation through specified media. Basic terminology, noise measurement, and practical calculation procedures such as combining sound levels are emphasized.

BASIC TERMINOLOGY

Amplitude:

The amplitude of sound may be described in terms of either the quantity of sound produced at a given location away from the source or the overall ability of the source to emit sound. The amount of sound at a location away from the source is generally described by the sound pressure or sound intensity, while the ability of the source to emit sound is described by the sound power of the source.

Free Field:

A free field exists in a homogeneous, isotropic medium free from boundaries. In a free field, sound radiated from a source can be measured accurately without influence from the test space. True free-field conditions are rarely found except in expensive anechoic (echo-free) test chambers; however, approximate free-field conditions may be found in any homogeneous space where reflecting surfaces are at great distances from the measuring location as compared to the wavelengths of the sound being measured.

Frequency (f):

The frequency of sound describes the rate at which complete cycles of high and low pressure regions are produced by the sound source. The unit of frequency is the cycle per second (cps) which is also called the hertz (Hz). The frequency range of the human ear is highly dependent upon the individual and the sound level, but a normal-hearing young ear will have a range of approximately 20 to 20,000 cps at moderate sound levels. The frequency of a propagated sound wave heard by a listener will be the same as the frequency of the vibrating source if the distance between the source and the listener remains constant; however, the frequency detected by a listener will increase or decrease as the distance from the source is decreasing or increasing (Doppler effect).[1]

Loudness:

The loudness of a sound is an observer's impression of its amplitude, an impression also dependent on the characteristics of the ear.

Noise and Sound:

The terms noise and sound are often used interchangeably, but generally, sound is descriptive of useful communication or pleasant sounds, such as music, while noise is used to describe discord or unwanted sound.

Period (T):

The period is the time required for one cycle of pressure change to take place; hence, it is the reciprocal of the frequency. The period is measured in seconds.

Pitch:

Pitch is used as a measure of auditory sensation that depends primarily upon frequency but also upon the pressure and waveform of the sound stimulus.

Pure Tone:

A pure tone refers to a sound wave with a single simple sinusoidal change of level with time.

Random Noise:

Random noise is made up of many frequency components whose instantaneous amplitudes occur randomly as a function of time.

Resonance:

Resonance of a system exists when any change in the frequency of forced oscillation causes a decrease in the response of the system.

Reverberation:

Reverberation occurs when sound persists after direct reception of the sound has stopped. The reverberation characteristic of a space is specified by the "reverberation time" which is the time required after the source has stopped radiating sound for the rms sound pressure to decrease 60 dB from its steady-state level.

Root-Mean-Square (rms) Sound Pressure:

The root-mean-square (rms) value of a changing quantity, such as sound pressure, is the square root of the mean of the squares of the instantaneous values of the quantity.

Sound Intensity (I):

The sound intensity at a specific location is the average rate at which sound energy is transmitted through a unit area normal to the direction of sound propagation. The units used for sound intensity are joules per square meter per second.

Sound intensity is also expressed in terms of a level (sound intensity level L_I) in decibels referenced to 10^{-12} watts per square meter.

Sound Power (P):

The sound power of a source is the total sound energy radiated by the source per unit time. Sound power is normally expressed in terms of watts. Sound power is also expressed in terms of a level (sound power level L_P) in decibels referenced to 10^{-12} watts.

Sound Pressure (p):

Sound pressure normally refers to the rms value of the pressure changes above and below atmospheric pressure when used to measure steady-state noise. Short term or impulse-type noises are described by peak pressure values. The units used to describe sound pressures are newtons per square meter (N/m^2), dynes per square centimeter (d/cm^2), or microbars. Sound pressure is also described in terms of a level (sound pressure level L_p) in decibels referenced to 2×10^{-5} newtons per square meter.

Velocity (c):

The speed at which the regions of sound-producing pressure changes move away from the sound source is called the velocity of propagation. Sound velocity varies directly with the square root of the density and inversely with the compressibility of the transmitting medium as well as with other factors; however, for practical purposes, the velocity of sound is constant in a given medium over the normal range of conditions. For example, the velocity of sound is approximately 1130 ft/sec in air, 4700 ft/sec in water, 13,000 ft/sec in wood, and 16,500 ft/sec in steel.

Wavelength (λ):

The distance required for one complete pressure cycle to be completed is called one wavelength. The wavelength (λ), a very useful tool in noise control work, may be calculated from known values of frequency (f) and velocity (c):

$$\lambda = c/f \qquad (1)$$

White Noise:

White noise has an essentially random spectrum with an equal-energy-per-unit frequency bandwidth over a specified frequency band.

NOISE MEASUREMENT

Steady-state sounds, ones that have relatively constant levels over time, are usually measured with instruments having root-mean-square (rms) characteristics. The time interval over which simple periodic sound pressure patterns must be measured is equal to an integral number of periods of that sound pattern, or the interval must be long compared to a period. If the sound pressures do not follow a simple periodic pattern, the interval must be long enough to make the measured value essentially independent of small changes in the interval length. In all cases, there must be more than 10 peaks per second for the noise to be considered to be steady-state for measurement purposes.

Single prominent peak pressures which may occur over a very short period of time, and peak pressures that are repeated no more than 2 per second, cannot be measured by conventional rms-type instruments because the peaks are not repeated often enough for long-time integrations to be meaningful. These single pressure peaks are normally measured in terms of the maximum instantaneous level that occurs during a specified time interval.

Just as rms measuring instruments cannot be used to measure single or widely spaced peak pressures, peak measuring instruments cannot be used to measure sustained noises unless the waveform is known to be sinusoidal or is otherwise predictable. In most cases, the relationship of the peak reading to the rms reading of common noises with complex waveforms cannot be established in a practical way. Peak pressure value of a sinusoidal waveform is about 3 dB greater than the rms value of that signal; however, as the waveform becomes more complex the differences may exceed 25 dB for common noises.

Noises with peak pressures occurring at rates between 2 and 10 peaks per second are difficult to measure in that they cannot be clearly defined as peak- or sustained-type noises. If the waveforms of the pressure peaks are complex and repeat between 2 and 10 times per second, an oscilloscope should be used to determine the pressure or energy contribution of the noise.

The Decibel (dB)

The range of sound pressures commonly encountered is very wide. For example, sound pressures well above the pain threshold (about 20 newtons per square meter, N/m^2) are found in many work areas, while pressures down to the threshold of hearing (about 0.00002 N/m^2) are also of wide interest. This range of more than 10^6 N/m^2 cannot be scaled linearly with a practical instrument because such a scale might be many miles in length in order to obtain the desired accuracy at various pressure levels. In order to cover this very wide range of sound pressures with a reasonable number of scale divisions and to provide a means to obtain the required measurement accuracy at extreme pressure levels, the logarithmic decibel (dB) scale was selected. By definition, the dB is a dimensionless unit related to the logarithm of the ratio of a measured quantity to a reference quantity. The dB is commonly used to describe levels of acoustic intensity, acoustic power, hearing thresholds, electric voltage, electric current, electric power, etc., as well as sound-pressure levels; thus, it has no meaning unless a specific reference quantity is specified.

Sound Pressure and Sound-Pressure Level

Most sound-measuring instruments are calibrated to provide a reading of root-mean-square (rms) sound pressures on a logarithmic scale in decibels. The reading taken from an instrument is called a sound-pressure level (L_p). The term "level" is used because the pressure measured is at a level above a given pressure reference. For sound measurements in air, 0.00002 N/m^2* commonly serves as the reference sound pressure. This reference is an arbitrary pressure chosen many years ago because it was thought to approximate the normal threshold of young human hearing at

1000 Hz. The mathematical form of the L_p is written as:

$$L_p = 20 \log \frac{p}{p_o} \text{ dB} \quad , \qquad (2)$$

where p is the measured rms sound pressure, p_o is the reference sound pressure, and the logarithm (log) is to the base 10. Thus, L_p should be written in terms of decibels referenced to a specified pressure level. For example, in air, the notation for L_p is commonly abbreviated as "dB re 0.00002 N/m^2."

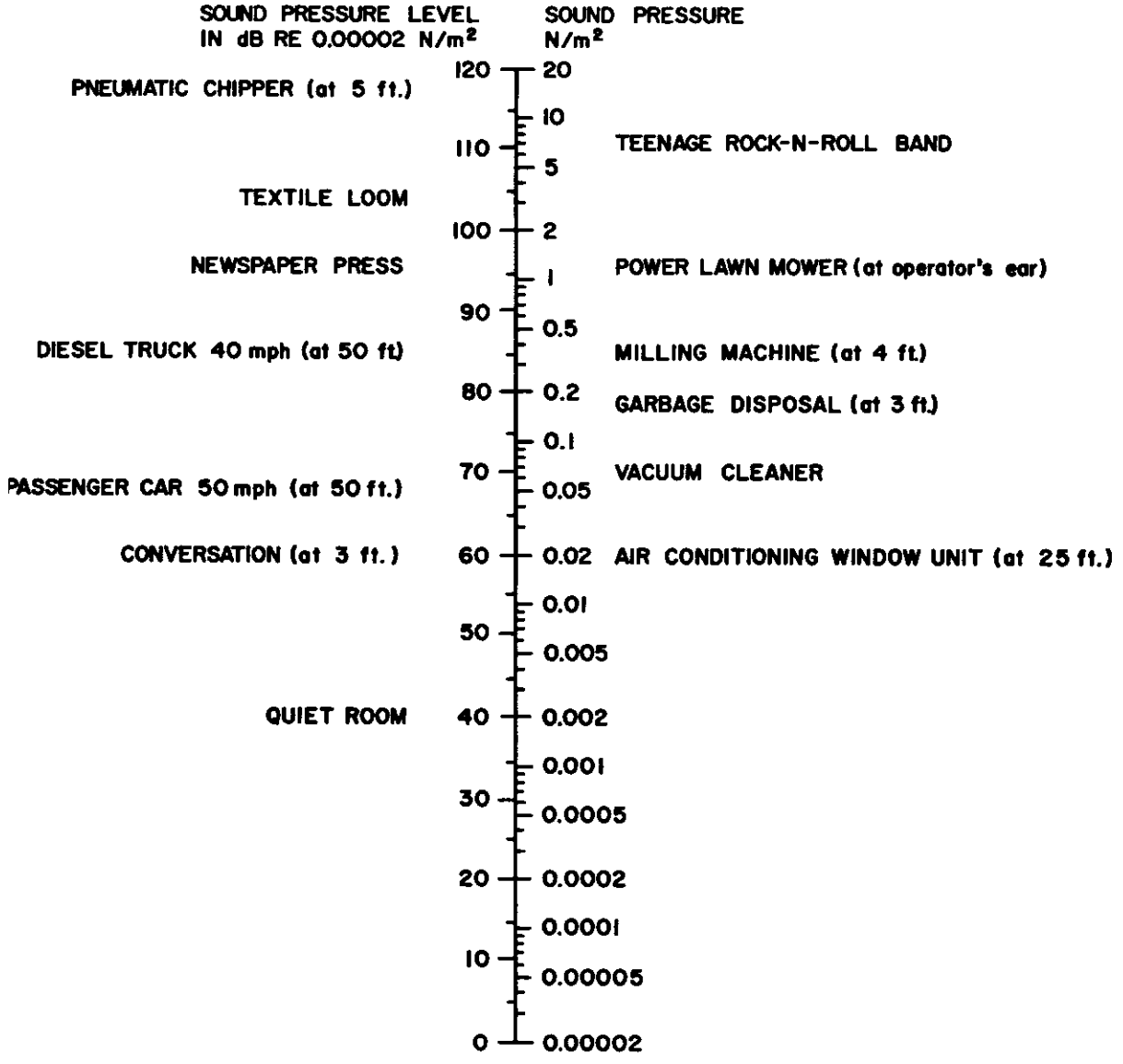

Figure 23-1. Relationship between A-Weighted Sound-Pressure Level in Decibels (dB) and Sound Pressure in N/m^2

Figure 23-1 shows the relationship between sound pressure in N/m^2 and L_p in dB, and illustrates the advantage of using the dB scale rather than the wide range of direct pressure measurements. It is of interest to note that any pressure range over which the pressure is doubled is equivalent to six decibels whether at high or low levels. For example, a range of 0.00002 to 0.00004 N/m^2, which might be found in hearing measurements, and a range of 10 to 20 N/m^2, which might be found in hearing conservation programs, are both ranges of six decibels.

*An equivalent reference 0.0002 dynes per square centimeter is often used in older literature. The microbar is also used in older literature interchangeably with the dyne per square centimeter.

The L_p referenced to 0.00002 N/m^2 may be written in the form:

$$L_p = 20 \log (p/0.00002)$$
$$= 20 \text{ lop } p - \log 0.00002$$
$$= 20 \log p - (\log 2 - \log 10^5)$$
$$= 20 \log p - (0.3 - 5)$$
$$= 20 (\log p + 4.7)$$
$$= 20 \log p + 94 \text{ re } 0.00002 \text{ N/m}^2 \quad . \quad (3)$$

Sound Intensity and Sound-Intensity Level

Sound intensity (I) at any specified location may be defined as the average acoustic energy per unit time passing through a unit area that is normal to the direction of propagation. For a spherical or free-progressive sound wave, the intensity may be expressed by

$$I = \frac{p^2}{\rho c}, \quad (4)$$

where p is the rms sound pressure, ρ is the density of the medium, and c is the speed of sound in the medium. It is obvious from this definition that sound intensity describes, in part, characteristics of the sound in the medium, but does not directly describe the sound source itself.

Sound-intensity units, like sound-pressure units, cover a wide range, and it is often desirable to use dB levels to compress the measuring scale. To be consistent with Equations (2) and (4), intensity level (L_I) is defined as

$$L_I = 10 \log \frac{I}{I_o} \text{ dB} \quad , \quad (5)$$

where I is the measured intensity at some given distance from the source and I_o is a reference intensity. The reference intensity commonly used is 10^{-12} watts/m^2. In air, this reference closely corresponds to the reference pressure 0.00002 N/m^2 used for sound-pressure levels.

Sound Power and Sound-Power Level

Sound power (P) is used to describe the sound source in terms of the amount of acoustic energy that is produced per unit time. Sound power may be related to the average sound intensity produced in free-field conditions at a distance r from a point source by

$$P = I_{avg} \, 4\pi r^2 \quad , \quad (6)$$

where I_{avg} is the average intensity at a distance r from a sound source whose acoustic power is P. The quantity $4\pi r^2$ is the area of a sphere surrounding the source over which the intensity is averaged. It is obvious from Equation (6) that the intensity will decrease with the square of the distance from the source; hence, the well-known inverse-square law.

Power units are often described in terms of decibel levels because of the wide range of powers covered in practical applications. Power level L_P is defined by

$$L_P = 10 \log \frac{P}{P_o}, \quad (7)$$

where P is the power of the source, and P_o is the reference power. The arbitrarily chosen reference power commonly used is 10^{-12} watt. Figure 23-2 shows the relationship between sound power in watts and sound-power level in dB re 10^{-12} watt.

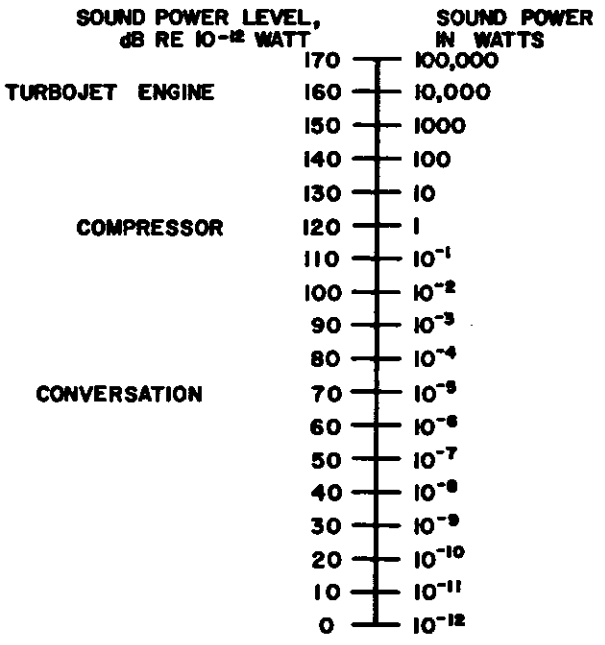

Figure 23-2. Relationship between Sound Power Level in Decibels (dB) and Sound Power in Watts

Relationship of Sound Power, Sound Intensity, and Sound Pressure

Many noise-control problems require a practical knowledge of the relationship between pressure, intensity, and power. An example would be the prediction of sound-pressure levels that would be produced around a proposed machine location from the sound-power level provided for the machine.

Example: Predict the sound-pressure level that would be produced at a distance of 100 feet from a pneumatic chipping hammer. The manufacturer of the chipping hammer states that the hammer has an acoustic power output of 1.0 watt.

From Equations (4) and (6) in free field for an omnidirectional source:

$$P = I_{avg} \, 4\pi r^2 = \frac{p^2 \text{ avg } 4\pi r^2}{\rho c}, \quad (8)$$

where

$$p_{avg} = \sqrt{\frac{P \rho c}{4\pi r^2}}. \quad (9)$$

If P is given in watts, r in feet, and p in N/m^2, then, with standard conditions, Equation (9) may be rewritten as

$$p_{avg} = \sqrt{\frac{3.5p \times 10^2}{r^2}}$$

and, for this example,

$$p_{avg} = \sqrt{\frac{3.5 \times 1.0 \times 10^2}{(100)^2}} = 0.187 \text{ N/m}^2 \quad .$$

The sound-pressure level may be determined from Equation (2) to be:

$$L_p = 20 \log \frac{0.187}{0.00002} = 79.4 \text{ dB re } 0.00002 \text{ N/m}^2.$$

Noise levels in locations that are reverberant can be expected to be somewhat higher than predicted because of the sound reflected back to the point of measurement.

COMBINING SOUND LEVELS

It may be necessary to combine sound-pressure levels (decibels) during hearing conservation or noise-control procedures. For example, it may be necessary to predict the overall levels in an area that will result from existing levels being combined with those of a new machine that is to be installed. The combination of levels in various frequency bands to obtain overall or weighted overall sound-pressure levels is another example.

Sound-pressure levels cannot be added arithmetically because addition of these logarithmic quantities constitutes multiplication of pressure ratios. To add sound-pressure levels, the corresponding sound pressures must be determined and added with respect to existing phase relationships.

For the most part, industrial noise is broadband with nearly random phase relationships. Sound-pressure levels of random noises can be added by converting the levels to pressure, then to intensity units which may be added arithmetically, and reconverting the resultant intensity to pressure and finally to sound-pressure levels in dB. Equations (2) and (4) can be used in free-field conditions for this purpose.

A more convenient way to add the sound-pressure levels of two separate random noise sources is to use Table 23-1. To add one random noise level $L_p(1)$, measured at a point to another, $L_p(2)$, measured by itself at the same point, the numerical difference between the levels, $L_p(2) - L_p(1)$, is used in Table I to find the corresponding value of $L_p(3)$ which, in turn, is added arithmetically to the larger of $L_p(1)$ or $L_p(2)$ to obtain the resultant of $L_p(1) + L_p(2)$. If more than two are to be added, the resultant of the first two must be added to the third, the resultant of the three sources to the fourth, etc., until all levels have been added, or until the addition of smaller values do not add significantly to the total.

Example: The overall sound-pressure level produced by a random-noise source can be calculated by adding the sound-pressure levels measured in octave bands shown in the following table:

Octave Band Center Frequency (Hz)	31.5	63	125	250	500	1000	2000	4000	8000
Sound-Pressure Level (dB)	85	88	94	94	95	100	97	90	88

A good procedure for adding a series of dB values is to begin with the highest levels so that calculations may be stopped when lower values are reached which do not add significantly to the total. In this example, the levels of 100 and 97 have a difference of 3 that corresponds with $L_n(3) = 1.8$ in Table 23-1. Thus, 100 dB + 97 dB = 100 + 1.8 = 101.8 dB. Combining 101.8 and 95, the next higher level, gives 101.8 + 0.8 = 102.6 dB which is the total of the first three bands. This procedure is continued with one band at a time until the overall sound-pressure level is found to be about 104 dB.

The overall sound-pressure level calculated in the above example corresponds to the value that would be found by reading a sound level meter at this location with the frequency weighting set so that each frequency in the spectrum is weighted equally. Common names given to this frequency weighting are flat, linear, 20 kc, and overall.

The corresponding A-weighted sound-pressure level (dBA)* found in many noise regulations may also be calculated from octave band values such as those in the above example if the adjustments given in Table 23-2 are first applied. For example the octave band levels with A-weighting corresponding to the above example would be:

Octave Band Center Frequency (Hz)	31.5	63	125	250	500	1000	2000	4000	8000
Sound Pressure Level (A-Weighted) (dB)	45.8	61.9	77.8	85.4	91.7	100	98.2	91.0	86.9

These octave band levels with A-frequency weighting can be added by the procedure described above to obtain the resultant A-weighted level which is about 103 dBA.

A large majority of industrial noises have random frequency characteristics and may be combined as described in the above paragraphs. However, there are a few cases of noises with pitched or major pure-tone components where these calculations will not hold, and phase relationships must be considered. In areas where pitched noises are present, standing waves will often be recognized by rapidly varying sound-pressure levels over short distances. It is not practical to try to predict levels in areas where standing waves are present.

*The A-weighted frequency weighting approximates the ear's response characteristics for low level sound, below about 55 dB re 0.00002 N/m².

TABLE 23-1

Table for Combining Decibel Levels of Noises with Random Frequency Characteristics

Sum (L_R) of dB Levels L_1 and L_2

Numerical Difference Between Levels L_1 and L_2	L_3: Amount to be Added to the Higher of L_1 or L_2
0.0 to 0.1	3.0
0.2 to 0.3	2.9
0.4 to 0.5	2.8
0.6 to 0.7	2.7
0.8 to 0.9	2.6
1.0 to 1.2	2.5
1.3 to 1.4	2.4
1.5 to 1.6	2.3
1.7 to 1.9	2.2
2.0 to 2.1	2.1
2.2 to 2.4	2.0
2.5 to 2.7	1.9
2.8 to 3.0	1.8
3.1 to 3.3	1.7
3.4 to 3.6	1.6
3.7 to 4.0	1.5
4.1 to 4.3	1.4
4.4 to 4.7	1.3
4.8 to 5.1	1.2
5.2 to 5.6	1.1
5.7 to 6.1	1.0
6.2 to 6.6	0.9
6.7 to 7.2	0.8
7.3 to 7.9	0.7
8.0 to 8.6	0.6
8.7 to 9.6	0.5
9.7 to 10.7	0.4
10.8 to 12.2	0.3
12.3 to 14.5	0.2
14.6 to 19.3	0.1
19.4 to ∞	0.0

Step 1: Determine the difference between the two levels to be added (L_1 and L_2).

Step 2: Find the number (L_3) corresponding to this difference in the Table.

Step 3: Add the number (L_3) to the highest of L_1 and L_2 to obtain the resultant level $L_R = (L_1 \text{ or } L_2) + L_3$

When the sound-pressure levels of two pitched sources are added, it might be assumed that the resultant sound-pressure level $L_p(R)$ will be less, as often as it is greater, than the level of a single source; however, in almost all cases the resultant $L_p(R)$ is greater than either single source. The reason for this may be seen if two pure-tone sources are added at several specified phase differences (see Figure 23-3). At zero phase difference, the resultant of two like pure-tone sources is 6 dB greater than either single level. At a phase difference of 90°, the resultant is 3 dB greater than either level. Between 90° and O°, the resultant is somewhere between 3 and 6 dB greater than either level. At a phase difference of 120°, the resultant is equal to the individual levels; and between 120° and 90°, the resultant is between 0 and 3 dB greater than either level. At 180°, there is complete cancellation of sound. Obviously, the resultant $L_p(R)$ is greater than the individual levels for all phase differences from O° to 120°, but less than individual levels for phase differences from 120° and 180° — a factor of 2:1. Also, most pitched tones are not single tones but combinations thereof: thus, almost all points in the noise fields will have pressure levels exceeding the individual levels.

TABLE 23-2

A-Frequency Weighting Adjustments

f(Hz)	Correction
25	−44.7
32	−39.4
40	−34.6
50	−30.2
63	−26.2
80	−22.5
100	−19.1
125	−16.1
160	−13.4
200	−10.9
250	− 8.6
315	− 6.6
400	− 4.8
500	− 3.2
630	− 1.9
800	− 0.8
1000	0.0
1250	+ 0.6
1600	+ 1.0
2000	+ 1.2
2500	+ 1.3
3150	+ 1.2
4000	+ 1.0
5000	+ 0.5
6300	− 0.1
8000	− 1.1
10000	− 2.5
12500	− 4.3
16000	− 6.6
20000	− 9.3

FREQUENCY ANALYSES

General purpose sound-measuring instruments are normally equipped with three frequency-weighting networks, A, B, and C,[2] that can be used to adjust the frequency response of the instrument. These three frequency weightings shown in Figure 23-4 were chosen because: 1) they approximate the ear's response characteristics at different sound levels, and 2) they can be easily produced with a few common electronic components. Also

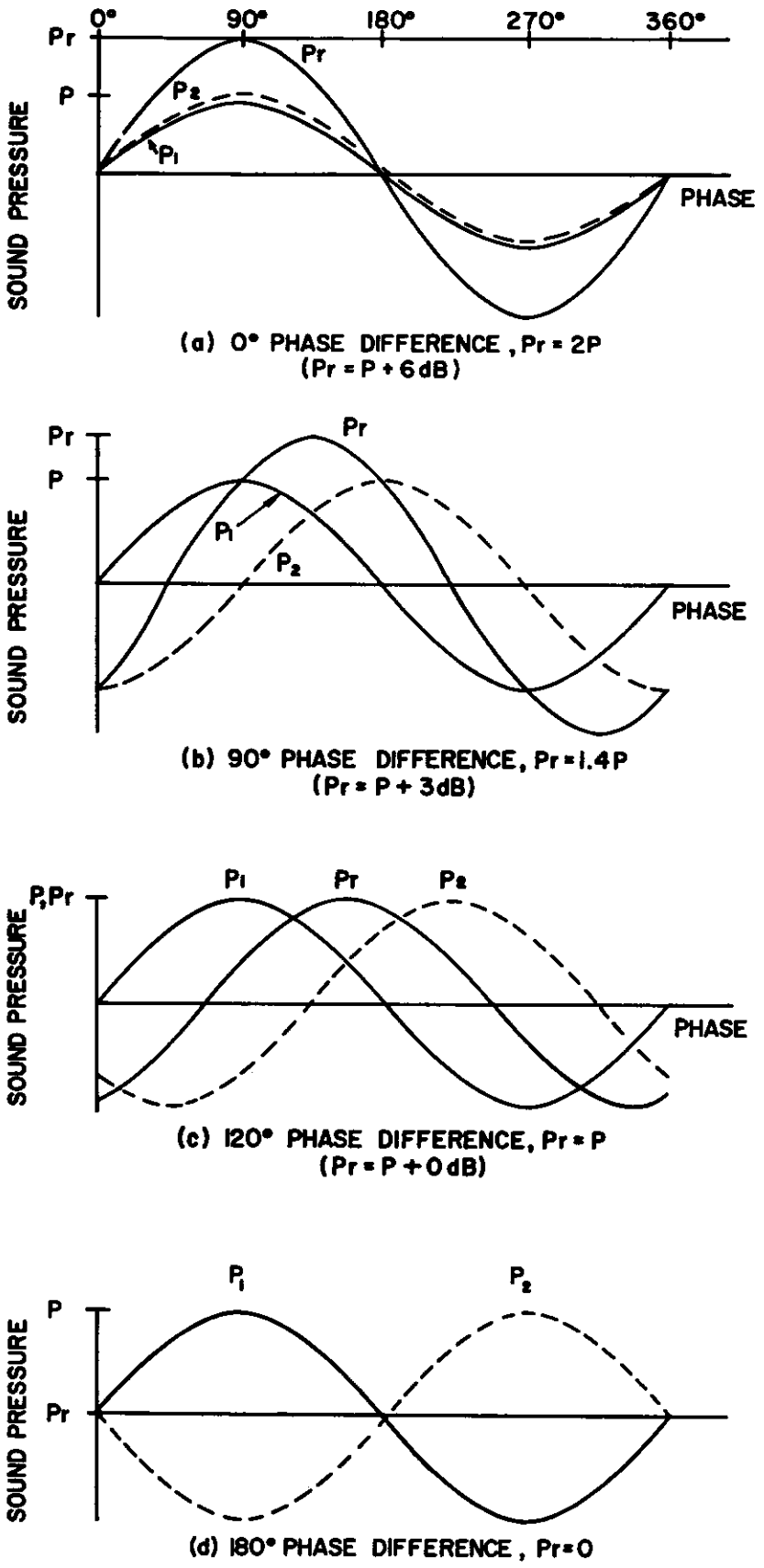

Figure 23-3. Combinations of Two Pure Tone Noises (p_1 and p_2) Phase Differences

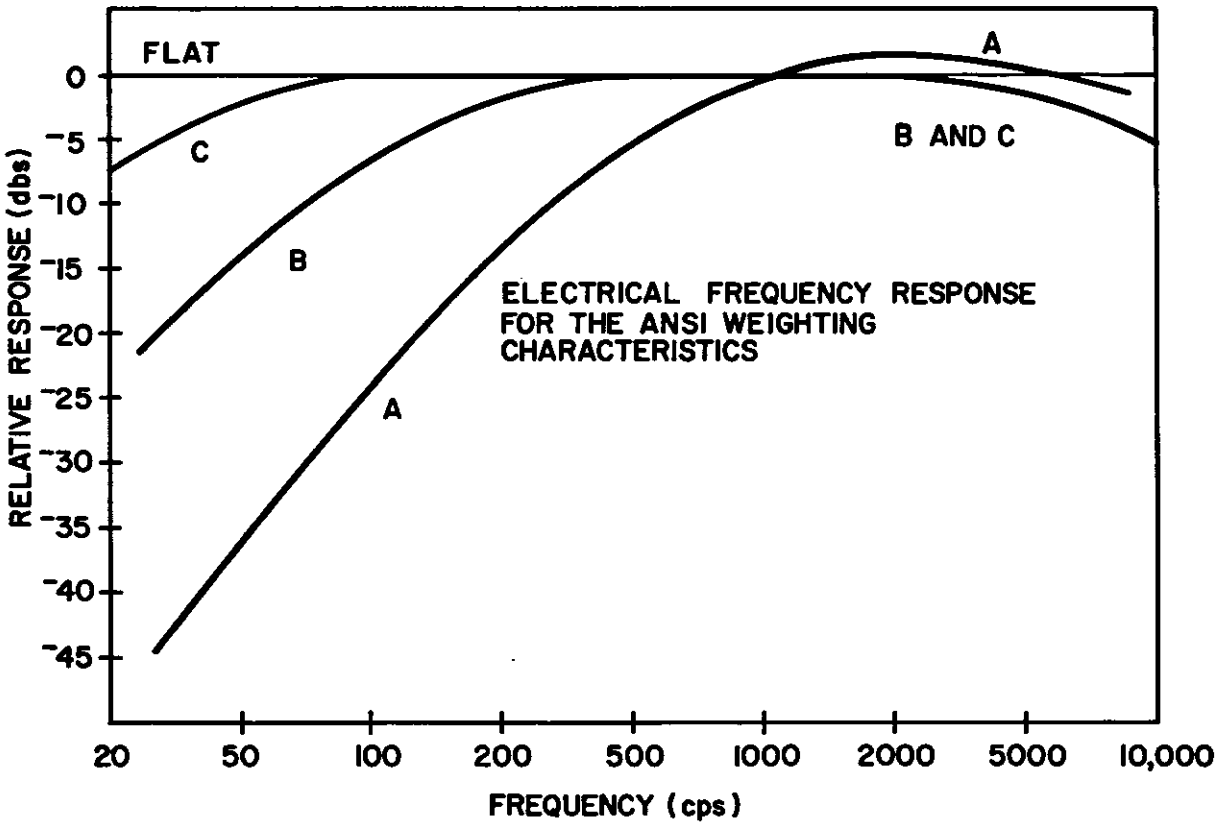

Figure 23-4. Frequency-Response Characteristics for Sound Level Meters (4)

shown in Figure 23-4 is a linear, overall, or flat response that weights all frequencies equally.

The A-frequency weighting approximates the ear's response for low-level sound, below about 55 dB re 0.00002 N/m². The B-frequency weighting is intended to approximate the ear's response for levels between 55 and 85 dB, and the C-frequency weighting corresponds to the ear's response for levels above 85 dB.

In use, the frequency distribution of noise energy can be approximated by comparing the levels measured with each of the frequency weightings. For example, if the A- and C- weighted noise levels are approximately equal, it can be reasoned that most of the noise energy is above 1000 Hz because this is the only position of the spectrum where the weightings are similar. On the other hand, if there is a large difference between these readings, most of the energy will be found below 1000 Hz.

In many cases, such as in noise control procedures, the information supplied by the A, B, and C frequency weightings do not provide enough resolution of frequency distribution of noise energy. Hence, more detailed analyses are needed from analyzers having bandwidths ranging from octaves to only a few cycles in width.

Frequency Bandwidths

The most common frequency bandwidth used for industrial noise measurements is the octave band. A frequency band is said to be an octave in width when its upper band-edge frequency f_2 is twice the lower band-edge frequency f_1:

$$f_2 = 2f_1 \quad . \tag{10}$$

Octave bands are commonly used for measurements directly related to the effects of noise on the ear and for some noise-control work because they provide the maximum amount of information in a reasonable number of measurements.

When more specific characteristics of a noise source are required, such as might be the case for pinpointing a particular noise source in a background of other sources, it is necessary to use narrower frequency bandwidths than octave bands. Half-octave, third-octave, and narrower bands are used for these purposes. A half-octave bandwidth is defined as a band whose upper band-edge frequency f_2 is the square root of 2 times the lower band-edge frequency f_1:

$$f_2 = \sqrt{2}\, f_1 \quad . \tag{11}$$

A third-octave bandwidth is defined as a band whose upper band-edge frequency f_2 is the cube root of 2 times the lower band-edge frequency f_1:

$$f_2 = \sqrt[3]{2}\, f_1 \quad . \tag{12}$$

The center frequency f_m of any of these bands is the square root of the product of the high and low band-edge frequencies (geometric mean):

$$f_m = \sqrt{f_2 f_1} \qquad (13)$$

It should be noted that the upper and lower band-edge frequencies describing a frequency band do not imply abrupt cut-offs at these frequencies. These band-edge frequencies are conventionally used as the 3-dB-down points of gradually sloping curves that meet the American Standard Specification for Octave, Half-Octave, and Third-Octave Band Filter Sets, S1.11-1966.[3]

Comparing Levels Having Different Bandwidths

Noise-measurement data (rms) taken with analyzers of a given bandwidth may be converted to another given bandwidth *if* the frequency range covered has a continuous spectrum with no prominent changes in level. The conversion may be made in terms of sound-pressure levels by

$$L_p(A) = L_p(B) - 10 \log \frac{\Delta f(B)}{\Delta f(A)}, \qquad (14)$$

where $L_p(A)$ = the sound-pressure level, in dB, of the band having a width $\Delta f(A)$ Hz.

where $L_p(B)$ = the sound-pressure level, in dB, of the band having a width $\Delta f(B)$ Hz.

Sound-pressure levels for different bandwidths of flat continuous spectrum noises may also be converted to spectrum levels. The spectrum level describes a continuous-spectrum wide-band noise in terms of its energy equivalent in a band one-hertz wide, assuming that no prominent peaks are present. The spectrum level $L_p(S)$ may be determined by

$$L_p(S) = L_p(\Delta f) - 10 \log \Delta f \ , \qquad (15)$$

where $L_p(\Delta f)$ = the sound-pressure level of the band having a width of Δf Hz,

Δf = the bandwidth in Hz.

It should be emphasized that accurate conversion of sound-pressure levels from one bandwidth to another by the method described above can be accomplished only when the frequency bands have flat continuous spectra.

NOISE PROPAGATION CHARACTERISTICS

The sound-power level supplied by the manufacturer of noise-making equipment can be used to predict sound-pressure levels that will be produced by the equipment in surrounding work areas if the acoustical characteristics of the work area are known. These calculations are complex if all factors are considered, but simple approximate solutions to general cases are often helpful to estimate levels.

Noise Source in Free Field

A free field has been defined as one in which the sound pressure decreases inversely with the distance from the source. These ideal acoustical conditions are rarely found in work environments because of the reflecting surfaces of equipment, walls, ceilings, floors, etc.; however, free-field conditions may sometimes be approached outdoors or in very large rooms. For standard free-field conditions, the sound-pressure level L_p at a given distance r from a small omni-directional noise source can be written in terms of the sound-power level L_P of the source as

$$L_p = L_P - 20 \log r - 0.5 \ , \qquad (16)$$

where r is in feet, L_p is in dB referenced to 0.00002N/m^2, and L_P is in dB referenced to 10^{-12} watts.

Many noise sources have pronounced directional characteristics; that is, they will radiate more noise in one direction than another. Therefore, it will be necessary for the equipment manufacturer to provide the directional characteristics of the source, as well as the power levels, to predict the sound-pressure levels. The directional characteristics of the source are generally given in terms of the directivity factor Q. Q is defined as the ratio of the sound power of a small, omnidirectional, imaginary source to the sound power of the actual source where both sound powers produce the same sound-pressure level at the measurement position. The directivity factor may be added to Equation (16) in the form

$$L_p = L_P - 20 \log r - 0.5 + 10 \log Q \ , \qquad (17)$$

where 10 log Q is called the directivity index.

Example: Predict the sound-pressure level that will be produced in a free field at a distance of 100 feet directly in front of a particular machine. A directivity factor of 5 is provided by the machine manufacturer for this location. The noise source has a continuous spectrum and a sound power of 0.1 watt.

From Equation (17):

$$L_p = 10 \log \left[\frac{0.1}{10^{-12}}\right] - 20 \log 100 - 0.5 + 10 \log 5$$

$$= 10 (\log 0.1 - \log 10^{-12}) - 20(2) - 0.5 + 10(0.7)$$

$$= 10(-1 + 12) - 40 - 0.5 + 7$$

$$= 76.5 \text{ dB re } 0.00002 \text{ N/m}^2.$$

Noise Source in Reverberant Field

In reverberant fields where a high percentage of reflected sound energy is present, the sound-pressure levels may be essentially independent of direction and distance to the noise source. Levels in these reverberant areas depend upon room dimensions, object size, and placement in the room, and upon the acoustical absorption characteristics of surfaces in the room. Additional complications may be present in the form of regions of enforcement and cancellation of sound pressure, standing waves, caused by strong pure-tone components being reflected. Thus, it is extremely difficult to predict sound-pressure levels at a particular point in a reverberant area.

Sound Absorption

The acoustical characteristics of a room are strongly dependent upon the absorption coefficients of its surface areas. A surface that absorbs all energy incident on its surface is said to have an absorption coefficient of one, while a surface that reflects all incident energy has an absorption coefficient of zero. The absorption coefficient depends upon the nature of the material, the frequency characteristics of the incident sound, and the angle of incidence of the sound. The absorption coefficient is expressed in terms of the frac-

tion of the energy absorbed by the material under the conditions described.

A rule of thumb that may be used to determine the amount of noise reduction possible from the application of acoustically absorbent material on room surfaces is as follows:

$$\text{dB reduction} = 10 \log \frac{\text{absorption units after}}{\text{absorption units before}},$$

where the absorption units are the sum of the products of surface areas and their respective noise absorption coefficients.[4, 5, 6] Absorption units are commonly expressed in terms of the sabin, which is the equivalent of 1 square foot of a perfectly absorptive surface.

Transmission Loss (TL) of Barriers

Sound transmission loss (TL) through a barrier may be defined as ten times the logarithm (to the base 10) of the ratio of the acoustic energy transmitted through the barrier to the incident acoustic energy. TL of a barrier may also be defined in terms of the sound pressure level reduction afforded by the barrier. Unless otherwise specified, the sound fields are diffuse on either side of the barrier. The TL of a barrier is a physical property of the material used for a given wall construction. The TL for continuous, random noise commonly found in industry increases about 5 dB for each doubling of wall weight per unit of surface area, and for each doubling of frequency.

Multiple wall construction with enclosed air spaces provides considerably more attenuation than the single-wall mass law would predict.[7, 8, 9] However, considerable care must be taken to avoid rigid connections between multiple walls when they are constructed or any advantages in attenuation will be nullified.[10, 11]

Noise leaks which result from cracks or holes, or from windows or doors, in a noise barrier can severely limit noise reduction characteristics of the barrier. In particular, care must be exercised throughout construction to prevent leaks that may be caused by electrical outlets, plumbing connections, telephone lines, etc., in otherwise effective barriers.

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