In practice there are several different methods of dispersing the various molecules—180 degree magnetic, 60 degree segment, radio-frequency and ion-resonance.

Again the need for more exacting means of measurement during World War II in development of atomic research prompted the phenomenal growth of mass spectrometry. As recently as 1940 there were less than a dozen instruments throughout the country. Now there are hundreds.

The analytical mass spectrometer has been used extensively for both liquid and gas samples, usually analyzing mass from 2 to 150, although it can be operated on masses somewhere over 400. This type of instrumentation is extremely useful in the petroleum field, where compounds have properties that are so nearly similar that they are quite difficult to identify by ordinary chemical means. The outstanding features of this means of measurement is the speed by which samples can be measured without previous fractionation or concentration.

Because of the high resolution and detectability of the instrument it is used for measuring trace materials in process streams as well as the key component or components in the process stream.

In order to reach the ultimate goal of practical automation for the chemical plant, more and better analytical measurements will have to be made continuously on the plant streams. The preceding paper tells of some of the useful laboratory instruments and how they are being successfully used in plant operation today.

Statistics Applied to Research and Control in the Oil and Fat Industry

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FOR MANY YEARS the subject of statistics was considered to be associated chiefly with the collection of large masses of data and the presentation of such data in tables, charts, or graphs. Today that conception is extremely outmoded, and those more or less routine operations are now only an incidental part of the function of statistics in research and industry.

H. P. Andrews

Prof. George W. Snedecor, of Iowa State College, considers statistics to be an integral part of the scientific method. "Some people," he says, "seem to think that it is only an aid to science, a luxury to be indulged in by only the more leisurely scientists. At the other extremes there are those who attribute to statistics a kind of magic to elicit reliable information from shoddy and inadequate experimental data."

As a vital and integral part of the scientific method, statistics provides special tools and techniques for the research workers who pursue scientific investigations. It is concerned with two main features of the scientific method: the performance of experiments and the drawing of objective conclusions from the experimental observations. Accordingly the science of statistics may be thought of as being divided into the two corresponding areas: the design of experiments and the analysis of data leading to statistical inference.

In practically every field of inquiry the attainment of new knowledge and the development of specialized technology has been chiefly by the process of inductive reasoning: the process of arguing from observational facts to the theories which might explain them. In this process it is necessary to draw inferences from the results of testing or experimentation, to argue from consequences to causes, from the particular to the general; in statistical terms, to argue from a sample to the population from which it was drawn.

This process is logically hazardous, and the conclusions must always be considered to have a degree of uncertainty. All of us—laymen, specialists, administrators, or research workers are constantly sampling, estimating, and drawing conclusions, often without even being conscious of it and frequently with little or no actual knowledge of the hazards involved.

In the last few years public opinion surveys have come into great popularity, and although they are admittedly fraught with considerable possible error, they have been invaluable in many economic and business decisions. Often in research a dozen experimental animals may suffice to disclose useful information concerning a population of millions; a carload of oil may be accepted or rejected upon evidence gained from testing a sample of only a few pounds; the physician makes inferences about a patient's blood from the examination of only a single drop. Yet anyone who has ever taken samples, run analyses, or conducted experiments knows that the results from any one sample, analysis, or experiment may be far from the true values for the aggregate of material or population.

The conclusions drawn by these procedures are not altogether infallible and are attended always with a degree of uncertainty. The process of statistical inference provides a quantitative evaluation of this uncertainty. It utilizes the theories of mathematical probability and enables the scientist to assess the reliability of his conclusions in terms of probability statements.

ONE of the simplest yet most fundamental problems to which the statistical approach may effectively be applied concerns the answer to such questions as: how accurate is my observation, what is the precision of my method? Proceeding further, these questions arise: whether the difference between observations is real, is it significant, do the quantities differ from each other to an extent greater than might reasonably be accounted for by the chance variations to which they are known to be subject? Such questions as these must be answered when one tries to ascertain whether real or significant changes have been brought about by research, or processing, or storage treatments. In such decisions one is confronted with the many possible errors or variations inherent in the nature of the material or in the conduct of the experiment: errors of analysis, errors in sampling, errors related to the treatment, processing, or storage effects themselves.

In the statisitcal interpretation attempts are made to evaluate the magnitude of these many variations and to take them into consideration in predicting whether or not the treatments have had a real effect. Consequently mathematical estimates are made of the probabilities or chances associated with the experimental observations. These make it possible to predict with estimated confidence the likelihood of such observations as a result of the treatments.

The science of statistics can be of greatest service to industrial research and control pursuits through the fundamental designing of investigations so that valid interpretations may be made, thereby obtaining the maximum amount of information with a maximum of confidence and a minimum expenditure of time, labor, and materials. Contrary to the belief of many research workers, statistical methods in scientific experimentation do not always require vast quantities of data. The amount of data needed for a particular objective is a direct function of the amount of variation encountered. Carefully designed investigations or experiments, aimed at the previously mentioned efficiency objectives, very often require less experimental work than the more common hit-or-miss approach to a problem.

Statistical planning by someone trained in the field of experimental design is certainly very much to be desired. However there are numerous opportunities for chemists, analysts, and research workers in all fields to apply some of the fundamentals of statistics in their daily work. For this reason a familiarity with and even a basic working knowledge of some of the simpler statistical techniques will prove useful to any scientist. There has appeared a very large and excellent literature on the applications of statistics in practically every field of scientific investigation, and many books are available to introduce the non-statistician to some of its applications. In this paper, in a very general manner, an introduction to some of the fundamental but highly practicable statistical manipulations will be made; and a list of the selected references has been included.

IN the interpretation of the results of an experiment, or a series of observations, one of the first steps is the resolution of the data into a few meaningful values. Perhaps the most widely used technique is the computing of "means" or arithmetic averages to obtain the most valid and concise representation of multiple observations. The mean is a well known statistic; also well known among those who interpret data is the fact that a mean standing alone may "hide a multitude of sins." The reliability of any mean value depends largely upon the number of observations that go to make it up and the degree of variation among the individual observations. We shall come to see how implicitly the confidence in a mean is dependent upon these two factors.

TABLE I

Samples from a Carload of Tallow

Titer Values (X)	Deviations from mean	
	$(X-\bar{X})$	$(X-\bar{X})^2$
Group 1		
41.8	−0.5	0.25
42.6	0.3	0.09
42.8	0.5	0.25
42.6	0.3	0.09
42.1	−0.2	0.04
Group 2		
42.3	0.0	0.00
42.3	0.0	0.00
41.9	−0.4	0.16
42.5	0.2	0.04
41.9	−0.4	0.16
Group 3		
42.3	0.0	0.00
42.6	0.3	0.09
42.4	0.1	0.01
42.4	0.1	0.01
42.0	−0.3	0.09
Group 4		
42.9	0.6	0.36
41.8	−0.5	0.25
42.7	0.4	0.16
41.6	−0.7	0.49
42.4	0.1	0.01
Group 5		
42.0	−0.3	0.09
42.2	−0.1	0.01
42.1	−0.2	0.04
42.2	−0.1	0.01
43.1	0.8	0.64
(Sum) 1057.5	(Sum) 0.0	(Sum) 3.34

Mean $(\bar{X}) = 1057.5/25 = 42.30$

Standard Deviation $(\sigma) = \sqrt{3.34/24} = 0.37$

When there is no variation among the observations, the mean represents them perfectly. But as the variation increases, the mean becomes less and less reliable, and it becomes necessary to have some description of the adequacy with which the mean value represents the sample of observations, furthermore of the adequacy with which the sample represents the whole or true situation or population. This description can be achieved in a number of ways, the most effective of which will occupy the detailed section of this paper.

It is simple and convenient in support of the mean to cite the range from the highest to the lowest values, but this has a rather limited workability. A somewhat more sophisticated term which was widely used in early analytical work is the average or mean deviation. That value, computed as the average of the absolute deviations from the group mean, provided an objective and somewhat meaningful picture of the variability inherent in the mean. More recently, however, some of the practical mathematicians in studying the nature of variability have defined a much more workable characteristic of dispersion which they have found to be related to probability and called the "standard deviation." This standard deviation and its implications are rudimentary in the statistical approach and deserve some detailed attention in an introductory discussion of applied statistics.

LET us suppose that it is desired to know the titer of a carload of a certain grade of tallow which is being obtained from a new supplier. Unless there is some advance knowledge of the nature of the product, it will also be important to know something about the variation or lack of homogeneity of the product. If, for example, five sets of five samples each were taken from the carload and analyzed, giving a total of 25 observations on the titer, the results might be those shown in Table I.

In order to show more clearly the nature of the variability among the samples, the results have been plotted in Figure 1.

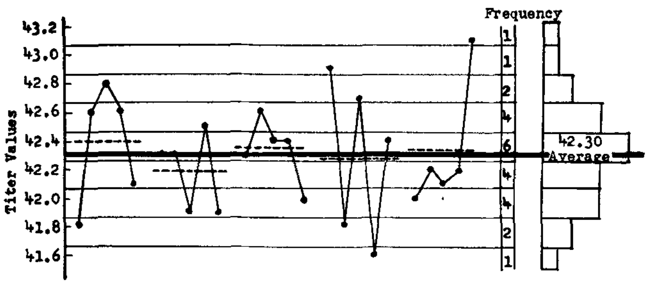

FIG. 1. Distribution of samples from a carload of tallow.

Dividing the range of results into intervals of equal size and counting the number of observations within each interval gives rise to the histogram at the right of the graph. Immediately obvious is the fact that the observations are not uniformly distributed over the entire range. Instead more values are found clustered near the center, in the area of the calculated mean (42.30), than are scattered near the extremes. The histogram roughly approximates a bell-shaped curve which is commonly known as the normal distribution curve, shown in Figure 2.

Actually, the relatively small number of samples has afforded only a rough approximation of the curve. But continued sampling and analysis would bring about a smoothing of the curve, and extension to an infinitely large number of samples would result in a frequency distribution quite closely approximated by this theoretical curve.

The normal distribution occurs widely in nature, and the representative curve has been accurately defined by the mathematicians in terms of the mean, the standard deviation, and the frequency function which relates these two statistics to probability. Its great utility lies in the fact that an approximately normal distribution can be fully characterized by the mean and the standard deviation, both of which may be calculated directly from data obtained in a sampling study. The mean estimates the central tendency or "true" value, and the standard deviation characterizes the scatter or deviations of the individuals from the mean.

The mean for this set of data has been calculated, and in Table I the steps are outlined for computing the standard deviation, commonly designated by the Greek letter "sigma" (σ). In algebraic form $\sigma = \sqrt{\Sigma(X-\overline{X})^2/(N-1)}$ where $(X-\overline{X})$ represents the deviation of the individual from the mean and "N" is the number of individual obseravtions. For these samples, then $\sigma = \sqrt{3.34/24} = 0.37$ and is expressed in the same titer units as the mean.

Having characterized the titer of the carload with these two statistics and from them constructed the theoretical normal curve in Figure 2, some probability relationships are forthcoming. In the normally distributed population approximately 68% of the results can be expected to fall within one standard deviation on either side of the mean $(\overline{X} \pm \sigma)$. Furthermore the range of two standard deviations on either side of the mean $(\overline{X} \pm 2\sigma)$ will include approximately 95% of all the results. Consequently about 5% of the results can be expected to fall outside the two sigma limits $(\overline{X} \pm 2\sigma)$, and less than 1% will be expected to fall outside the three sigma limits $(\overline{X} \pm 3\sigma)$.

Accordingly, from the carload of tallow having the mean titer value of 42.30 and standard deviations of 0.37, subsequent samplings might be expected with 95% probability to give results falling within 42.30 ± 2 (0.37) or within the limits 41.56 to 43.04. There is about 5% probability of results falling outside those limits, and less than 1% probability of results falling outside the limits 42.30 ± 3 (0.37) or 41.19 to 43.41.

By this initial sampling the mean and variability in the titer of the tallow have been estimated. It is now quite clear that any single value may have been considerably in error, or in disagreement with other values which might have been obtained. In view of these demonstrated errors or variations it is naturally desirable to know how good these estimates are—how near to the true mean of the carload was the mean value estimated from the sampling. Based upon the observed variation, it is possible to compute an actual measure of the reliability of the observed mean. That measure of reliability is called the "standard error" of the mean.

IN Figure 1 the averages for each of the groups of five samples have been drawn in as dotted lines in order to demonstrate that the averages of groups of individuals are less variable than the individuals themselves. In fact, the variation of group means is inversely proportional to the square root of the number of individuals in the groups, and it can be shown quite rigorously that the standard error of the mean of "N" observations is equal to $\sigma/\sqrt{N}$ where "σ" is the standard deviation of the individual observations.

From sampling the carload, an estimate of 42.30 titer was obtained for the mean of 25 tallow samples

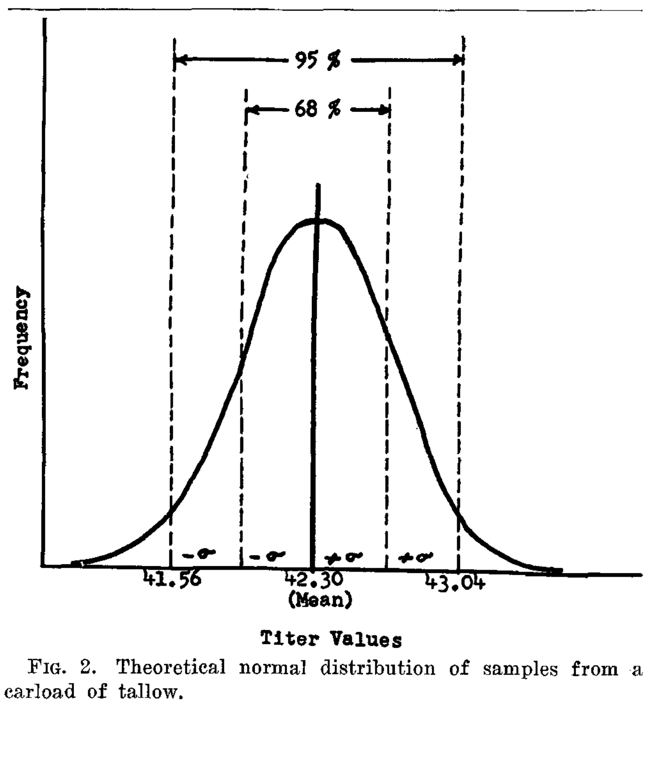

FIG. 2. Theoretical normal distribution of samples from a carload of tallow.

having a standard deviation of 0.37. Therefore that estimate of the mean would have a standard error of $0.37/\sqrt{25}=0.074$, and from this we would predict with 95% probability that the true titer of the carload of tallow would be $42.30\pm2(0.074)$ or between 42.15 and 42.45. These limits then are often referred to as the 95% confidence limits, and they provide an estimate of the precision of the observed mean for a sample or group of samples.

Extending the application of these fundamentals, it can be concluded that the analysis of a single sample from the carload of tallow would provide a value having a precision of ±2 (0.37) or ±0.74. If it were decided to analyze two samples, the mean of the two would have a precision of $\pm0.74/\sqrt{2}$ or ±0.52. And using this relationship of precision to sample size, it would be possible to arrive at the number of samples which would be needed to give a precision of any desired magnitude.

The uncomplicated sampling illustration selected for this discussion appears to reflect errors of sampling, or of analysis, or both. The sampling plan was not designed to isolate the variation associated with these two sources of variation. However, with an appreciation for the application of probability statistics and an understanding of the few fundamental relationships detailed herein, it is a relatively simple matter to design investigations in such a manner that the known sources of variation may be isolated from any system of variables.

Development of new analytical methods frequently necessitates quantitative estimation of the errors associated with the various manipulations involved (*i.e.*, weighing, pipetting, titration, instrument reading, etc.). In collaborative studies of analytical methods it may be desired to obtain estimates of the magnitude of the variations between duplicate analyses on a single day, the day-to-day variation, the variation among analysts within a laboratory, and the variation among laboratories. From such comprehensive studies it is possible to make critical and objective evaluations of methods for use in research or control work.

In studies of manufacturing processes related statistical designs may often be useful. Isolating the sources of variation in an operation and estimating their magnitude is an essential step in the inauguration of a control program; and the formulation of sampling, analysis, and acceptance plans requires a characterization of the variables which cannot be obtained effectively without the aid of the statistical approach.

There are in rather widespread practice more or less classical designs for such investigations, many of which have been described in the technical journals in a variety of fields. The computational techniques are somewhat more extensive than the ones described here but are within easy mastery by nonmathematicians and may be found clearly described in many introductory statistical tests.

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Measurement of Chain Length

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PLASTIC FATS AND edible oils are made up almost exclusively of three units of fatty acid and one unit of glycerol; the combination is called a triglyceride. Whether the combination is a fat or an oil at room temperature depends on the chain length and the degree of unsaturation of the fatty acids which are present in the triglyceride. If the fatty acid chain contains only four carbon atoms, as in butyric acid, the melting point of the fatty acid is much lower than one which contains eighteen carbon atoms as in stearic acid. A change in the degree of unsaturation seems to influence the melting point of a fatty acid even more than a change in the length of the carbon chain. For example, an increase in one double bond decreases the melting point 18°C. as compared with a decrease of only 9°C. between the C_{14} myristic and the C_{16} palmitic acid. Therefore if glycerol is esterified with more than two unsaturated fatty acids, the resulting triglyceride is a liquid or an "oil" at room temperature. If, on the other hand, glycerol is esterified with only long chain saturated fatty acids or only one mole of oleic and two moles of palmitic or stearic acid, the resulting triglyceride is a solid or "fat" at room temperature.


F. A. Kummerow

Natural fats and oils have been found to contain mixtures of triglycerides which are uniquely characteristic of a specific fat. Lard and beef fats contain from 2 to 15% trisaturated glycerides (GS_3) while cottonseed or soybean oil do not contain any trisaturated glycerides (1). Butterfat, which contains a larger proportion of lower saturated fatty acid than any other fat, usually contains less than 1% triunsaturated glycerides although variations up to 7% GU_3 have been reported.

The plastic fats or shortenings actually contain from 15 to 35% of the solid phase; the remainder is in a liquid phase incorporated into the solid phase to improve shortening performance and to keep the melting point of the mixture of triglycerides below body temperature. A shortening can be formulated from vegetable oils by two different methods—one, which