

action in the den and the first part of the maturing period. Later, during maturing in the piles the temperature decreases, and the system is moving into region II, where the semihydrate can convert into dihydrate, if the supersaturation is high enough for dihydrate nucleation. Within those two regions there is a trend of semihydrate and dihydrate conversion into anhydrite II, but without high temperatures, as in the first part of the reaction in the den, this is known as an extremely slow process.

A matured and bagged superphosphate with a normal moisture content has a temperature and acid concentration in the liquid phase that correspond to region I, where anhydrite may go into solution and crystallize as dihydrate. This can proceed until so much water has been removed from the liquid phase that,

because of the corresponding increase in acid concentration, the equilibrium curve is reached.

With extra hard drying all semihydrate probably converts into anhydrite II. Therefore in region II nothing can happen and the acid concentration in the liquid phase of the superphosphate will be so high that region I may not be reached. The above is in good agreement with several observations reported by Scheel (6) and the remedies recommended to prevent caking of the superphosphate.

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FERTILIZER QUALITY CONTROL

Fertilizer Sampling to Protect Consumers and Producers

Methods are given for devising fertilizer sampling plans which manufacturers can use for assessing the quality of their products with confidence, or on which government regulations can be based. The sampling plans use defined consumer's and producer's risks to avoid the false information that single snap samples usually give. The methods can be applied to other chemicals which require costly chemical analyses.

THE SOUTH AFRICAN Department of Agricultural Technical Services is revising its regulations which control the qualities of fertilizers and fertilizer mixtures that may be sold to consumers. The regulations will be based on an acceptance sampling plan which recognizes that fertilizers cannot be produced without some unavoidable variation in quality. Hence, whenever a fertilizer is sampled by a government inspector, a number of samples instead of one snap sample will be taken. By this means the true quality of the material sampled will be realistically estimated. However, there remains the possibility that a bad estimate may be obtained by chance. Thus producers run a risk of being penalized although their fertilizers are of good quality and consumers run a risk of accepting poor quality material. The sampling plan envisaged in South Africa is based on defined small producer's and consumer's risks.

This paper discusses not the particular plan adopted in South Africa, but general sampling plans for fertilizers. With the formulas provided it is possible

to devise plans to suit particular needs and purposes.

The first part of the discussion introduces the concept of defined risks. This may be tediously obvious to many, but it has been included because a sampling plan cannot efficiently be used without fully understanding its principles and operation. The second part shows how to devise a sampling plan for accepting or rejecting a particular batch of fertilizer. The third part shows how to devise a sampling plan to judge the performances of fertilizer producers over a period of time.

The Concept of Defined Risks

Variation in Fertilizer Quality. Consider the chemical analyses of single samples taken from consecutive batches of superphosphate produced by a hypothetical manufacturer. If the phosphate content is plotted against the order in which the batches were made, a diagram such as Figure 1 will be obtained.

Figure 1 shows that variation has occurred, and it must be admitted that a certain amount of variation is unavoidable. In fact, to produce absolutely

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uniform material would require absolute control of all variables, including the quality of the raw materials used. Such perfect control is impossible.

In the absence of perfect control, some variation must be accepted. The degree of variation can be reduced with better quality control of manufacture, but an irreducible amount of variation remains.

Representation of Variation by Distribution Curves. Figure 1 helps to view as a whole the variation in quality of the superphosphate. It shows that although the average phosphate content is 19.0% P_2O_5 , about half the points fall below this value.

The data can be summarized in a more useful way. If the graph in Figure 1 is turned on end, the % P_2O_5 scale can be divided into classes, or intervals, and the number of points falling into each class can be counted. The percentage frequency with which the points fall into each class can be calculated and the histogram shown in Figure 2 can be constructed.

This histogram is only an approximate representation of the true variation in the superphosphate, because only single samples were taken from each batch.

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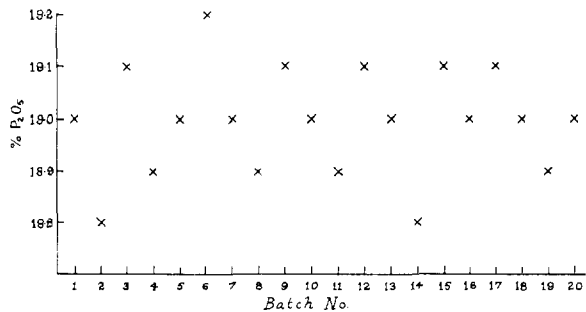


Figure 1. Variation in fertilizer quality

If a number of samples had been taken from each batch and each sample analyzed, the larger number of analyses would allow a histogram as shown in Figure 3 to be constructed. This histogram more closely approximates the true variation in the superphosphate quality.

If the process of taking more and more samples for analysis is continued, the histograms ultimately approach a smooth theoretical distribution curve as shown in Figure 4.

It is convenient to use a theoretical distribution curve to describe the variation in quality of a fertilizer and to assume that the quality of the fertilizer is normally distributed. The normal distribution can be specified by its mean, or average, which is the position of the peak in the distribution curve (mean = 19.0% in Figure 4), and its standard deviation, which is a measure of the spread, or scatter, of the distribution about its mean. A wide flat distribution curve has a larger standard deviation than a narrow peaked curve.

Proportion Failing Specification. Suppose it is required to produce superphosphate that must not contain less than 19% P_2O_5 . In good faith the manufacturer ensures that the mean content of his fertilizer is truly 19.0% P_2O_5 . Then if Figure 4 represents the distribution of the phosphoric oxide content, it is seen from the symmetry of the curve about the mean of 19.0% P_2O_5 that the manufacturer will suffer a 50% chance of failing the specification on a snap sample.

To reduce the chances of failure, the manufacturer could produce material with a mean content greater than the specified value, as shown in Figure 5. Then chances of failing the specification would be given by the ratio of the shaded area to the total area under the curve.

Operating Characteristic Curves. The notion of defined risks of failure can be carried further to construct a graph from which can be read off the mean quality at which to aim for a defined risk of failing the specification.

To conform to the conventions adopted in acceptance sampling plans, the chances of passing the specification must be considered. This offers no difficulties, because if the chances of failure are $p\%$, the chances of passing are $(100-$

$p)\%$. In Figure 5 the chances of passing the specification are given by the ratio to the total area of the unshaded area on the right of the specification limit.

Consider a manufacturer to be producing superphosphate to the specification: not less than 19% P_2O_5 on a snap sample. If the mean phosphate content is 18.8% P_2O_5 , as seen in *i* of Figure 6, *a*, his chance of passing the specification is small. This chance can be calculated and plotted as point *i* in Figure 6, *b*. If now the manufacturer increases the mean content to 18.9% P_2O_5 , then, as shown in *ii* of Figure 6, *a*, the chance of passing on a snap sample is greater but still less than 50%. Again this chance can be calculated and plotted as point *ii* in Figure 6, *b*. When the manufacturer produces with a mean of 19.0% P_2O_5 , he enjoys (or suffers) a 50% chance of the superphosphate passing on a snap sample. This gives point *iii* in Figure 6, *b*. The remaining points, *iv* and *v*, are now evident.

A smooth curve is drawn through the points in Figure 6, *b*, and found to be a cumulative normal distribution curve. This is called an operating characteristic curve. It is characteristic of the specification "not less than 19% P_2O_5 " and the standard deviation of the distributions shown in Figure 6, *a*, all the distributions having the same standard deviation.

Using the operating characteristic curve, the manufacturer can read off at what average to aim in order to ensure a chosen large chance of the materials passing the specification (or small chance of its failing). Thus the manufacturer can produce with a defined risk.

The operating characteristic curve also gives the consumer's risk, because it shows the chances of his accepting material of a particular mean quality.

Acceptance Sampling Plans. The operating characteristic curve in Figure 6, *b*, enables a manufacturer to operate at a defined risk of failing on a snap sample. However, if he uses such a curve he will find that to reduce his risk of failure to a reasonably small level an uneconomically high grade material must be produced to pass the specification. The fault lies with taking a single snap sample.

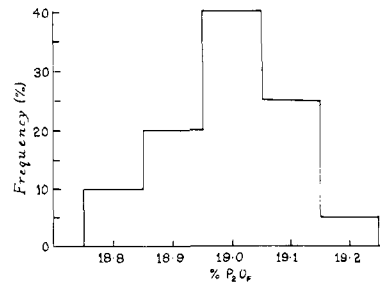


Figure 2. Histogram depicting variation in fertilizer quality

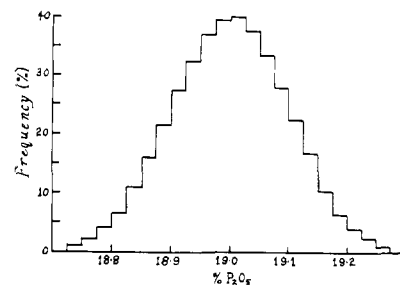


Figure 3. Histogram approximating theoretical distribution

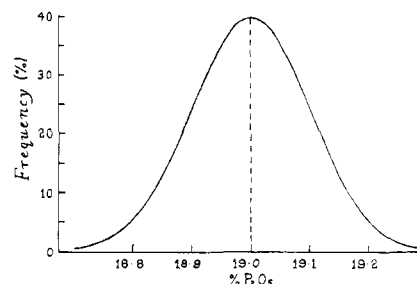


Figure 4. Normal distribution curve

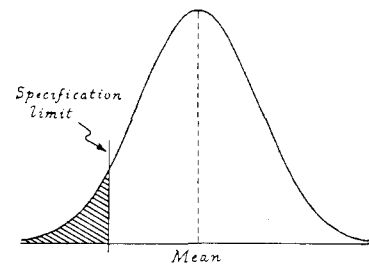


Figure 5. Shaded area gives risk of failing specification

To overcome this, a sampling inspection plan can be devised whereby a lot, or batch or consignment, of fertilizer is judged on the quality of several samples taken from the batch instead of a single snap sample.

There are two ways in which sampling inspection plans for fertilizers can be devised. The first kind of inspection plan requires a number of samples to be taken from a lot and each sample analyzed. From the analyses the mean and standard deviation of the sampled lot are calculated and from the mean and standard deviation the proportion of the lot which fails a specified limit is calculated. If this proportion of de-

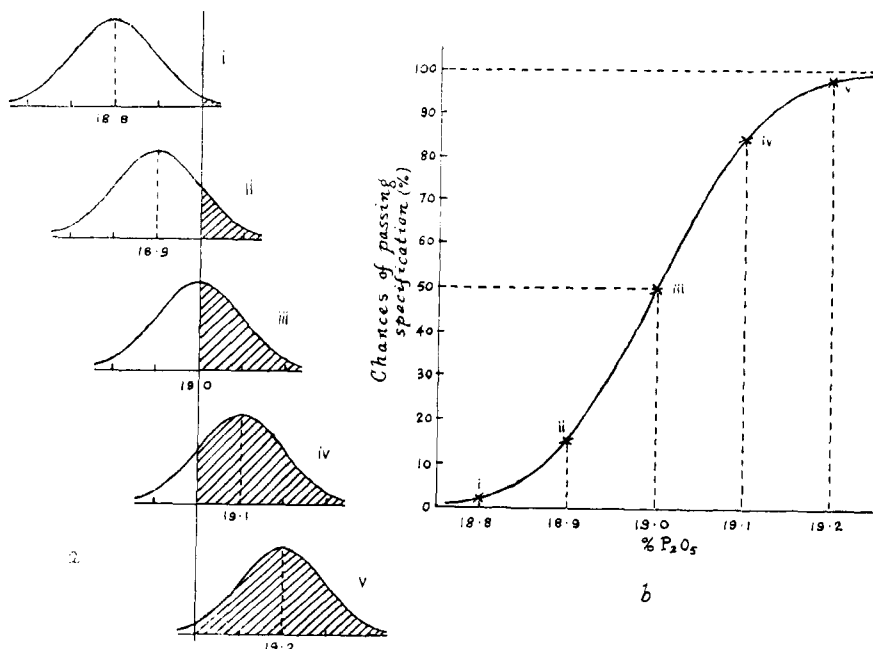


Figure 6. Construction of operating characteristic curve

fective material is too high, the lot is considered unacceptable and failed. This first kind of plan has many advantages, but it requires a larger number of samples than the second kind, which is outlined in the next paragraph. It also requires individual analyses of each sample. Because the quality of a fertilizer is judged on the results of chemical analyses, the plan is too costly to operate. If cheaper tests of fertilizer quality could be devised, the plan would be eminently suitable. This first type of plan is not discussed further in this paper.

In the second kind of sampling plan the number of samples to be taken is reduced by using a fixed standard deviation. A number of samples are taken and analyzed, either individually or composited, to find the mean content of the sampled lot. This mean is compared with a specified limit; if it is less than the limit; the sampled lot is failed. This second type of plan is not so powerful a tool as the first type, but it has the virtue of economy. If the samples can be well composited, it allows a large number of samples to be taken but requires only a few chemical analyses.

Only the second type of sampling plan is considered in this paper and it is used in two ways: to judge the quality of a lot and to judge the over-all performance of a manufacturer.

Although this paper discusses fertilizer sampling, the plans can just as usefully be applied to other chemicals which require costly analyses.

Use of Sampling Plans for Judging Lots

Throughout this second part of the discussion acceptance sampling plans

will be devised to judge the quality of a lot, batch, or consignment of fertilizer. The results of sampling therefore apply only to the lot sampled.

Parameters of Sampling Plan. The principles developed above are applied to devise a sampling plan which will be based on the following parameters, or defined constants:

α = producer's risk of having a good quality fertilizer fail because bad samples are taken by chance

β = consumer's risk of accepting a poor quality fertilizer because good samples are taken by chance

σ = standard deviation of the lot sampled (assumed to be the same for all lots)

U_0 = measure of what is considered a good quality fertilizer

U_2 = measure of what is considered a poor quality fertilizer

From these parameters the following are calculated:

n = the number of samples which must be taken

C = the specification limit below which the mean of the n samples must not fall

Derivation of Mathematical Formulas. It is a consequence of the normal distribution that if n samples are taken from a batch of fertilizer having a standard deviation σ , then the mean, \bar{x} , of the n samples will have a standard deviation $\sigma_{\bar{x}}$, where

$$\sigma_{\bar{x}} = \sigma/n^{1/2} \quad (1)$$

Suppose that a manufacturer has produced a batch of superphosphate which is normally distributed with a standard deviation, σ , about a true mean phosphate content equal to $U_0\%$ P_2O_5

as shown in Figure 7. If C is the specification limit below which the mean, \bar{x} , of n samples taken at random from the batch must not fall, then the probability, α , that the sampled batch will fail the specification because n bad samples are taken by chance is given by

$$\alpha = \{1/(2\pi)^{1/2}\sigma_{\bar{x}}\} \int_{-\infty}^C \exp\left[-\frac{1}{2}\left(\bar{x} - U_0\right)^2/\sigma_{\bar{x}}^2\right] d\bar{x}$$

Putting

$$t = (U_0 - \bar{x})/\sigma_{\bar{x}}$$

the integral transforms to

$$\alpha = -\{1/(2\pi)^{1/2}\} \int_{\infty}^{t_{\alpha}} \exp\left[-\frac{1}{2}t^2\right] dt$$

where

$$t_{\alpha} = (U_0 - C)/\sigma_{\bar{x}} \quad (2)$$

or, by virtue of the symmetry of the normal distribution,

$$\alpha = \{1/(2\pi)^{1/2}\} \int_{-\infty}^{t_{\alpha}} \exp\left[-\frac{1}{2}t^2\right] dt \quad (3)$$

As this integral has been tabulated as the cumulative normal distribution, α can be read off from those tables if t_{α} is known—that is, if U_0 , C , and $\sigma_{\bar{x}}$ are known.

The probability, α , is referred to as the producer's risk because it gives the risk of failure through bad samples being taken by chance, even though the producer manufactured a batch of good fertilizer with a true mean U_0 which is above specification limit C .

CONSUMER'S RISK OF ACCEPTING A BATCH OF POOR QUALITY FERTILIZER. Suppose the batch of superphosphate is normally distributed with a standard deviation σ about a true mean phosphate content equal to $U_2\%$ P_2O_5 , which is below the specification limit $C\%$ P_2O_5 , as shown in Figure 8.

The probability, β , that the sampled batch will pass the specification because n good samples are taken by chance is given by

$$\beta = \{1/(2\pi)^{1/2}\sigma_{\bar{x}}\} \int_C^{\infty} \exp\left[-\frac{1}{2}\left(\bar{x} - U_2\right)^2/\sigma_{\bar{x}}^2\right] d\bar{x}$$

Putting

$$t = (\bar{x} - U_2)/\sigma_{\bar{x}}$$

the integral transforms to

$$\beta = \{1/(2\pi)^{1/2}\} \int_{t_{\beta}}^{\infty} \exp\left[-\frac{1}{2}t^2\right] dt \quad (4)$$

where

$$t_{\beta} = (C - U_2)/\sigma_{\bar{x}} \quad (5)$$

As the integral in Equation 4 has been tabulated as the cumulative normal distribution, β can be read off from those

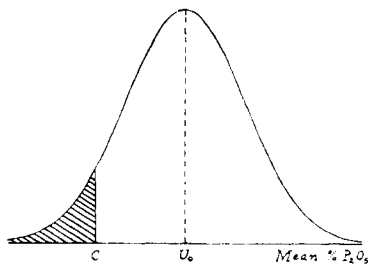


Figure 7. Shaded area gives producer's risk

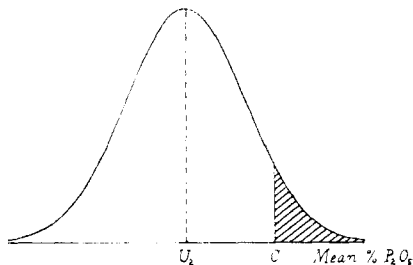


Figure 8. Shaded area gives consumer's risk

tables if t_β is known—that is, if C , U_2 , and $\sigma_{\bar{x}}$ are known.

The probability, β , is referred to as the consumer's risk because it gives the risk that the consumer runs of accepting a batch of poor quality fertilizer, of which the true mean U_2 is below the specification limit, C , by the chance happening that n good samples may be selected at random.

Now the process must be reversed to determine the n and C which will give defined risks α and β . Equations 2 and 5 can be rewritten as

$$U_0 - C = t_\alpha \sigma_{\bar{x}} = t_\alpha \sigma/n^{1/2} \text{ by Equation 1}$$

$$C - U_2 = t_\beta \sigma_{\bar{x}} = t_\beta \sigma/n^{1/2} \text{ by Equation 1}$$

Adding these two equations,

$$U_0 - U_2 = (t_\alpha + t_\beta)\sigma/n^{1/2}$$

or

$$n = (t_\alpha + t_\beta)^2 \sigma^2 / (U_0 - U_2)^2 \quad (6)$$

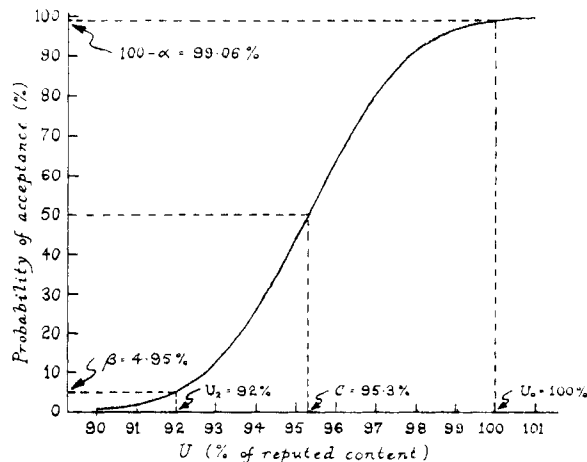
Thus if values are stipulated for α and β , values for t_α and t_β can be obtained from Equations 3 and 4, or from tables of the cumulative normal distribution, and then if σ , U_0 , and U_2 are also stipulated, the number of samples, n , which must be taken can be calculated from Equation 6. The specification limit, C , can then be calculated from Equation 2, which can be rewritten as

$$C = U_0 - t_\alpha \sigma/n^{1/2} \quad (7)$$

Specimen Sampling Plan for Straight Fertilizers. How many samples should be taken, and what should the specification limit be for a superphosphate sampling plan based on the following parameters?

$$\begin{aligned} \alpha &= 1\% \\ \beta &= 5\% \end{aligned}$$

Figure 9. Operating characteristic curve of specimen sampling plan



U_0 = reputed phosphate content, or guaranteed analysis
 U_2 = 92% of reputed phosphate content
 σ = 4% of reputed phosphate content

Here $\alpha = 1\% = 0.01$, so that, from tables of the cumulative normal distribution, $t_\alpha = 2.326$. Similarly, $\beta = 0.05$, so that $t_\beta = 1.645$. Thus, from Equation 6,

$$\begin{aligned} n &= (3.971)^2 (0.04 U_0)^2 / (U_0 - 0.92 U_0)^2 \\ &= (3.971)^2 (0.04)^2 / (1 - 0.92)^2 \\ &= 3.94 \end{aligned}$$

To the nearest whole number, $n = 4$. From Equation 7,

$$\begin{aligned} C &= U_0 - 2.326(0.04 U_0) / (3.94)^{1/2} \\ &= U_0(1 - 0.04687) \end{aligned}$$

i.e.,

$$C = 0.95313 U_0$$

or

$$C \approx 95.3\% \text{ of } U_0$$

The specimen sampling plan then is: "Take four samples at random from the batch and analyze these four samples; if the mean of the four analyses is less than 95.3% of the reputed phosphate content of the batch, then fail the batch."

Where a plan requires a large number of samples, these can be reduced to a smaller number for analysis by suitable methods of compositing.

Operating Characteristic of Specimen Sampling Plan. The specimen plan gives the risk, α , that the producer will run if the sampled lot has mean content U_0 and standard deviation σ . It also gives the risk, β , that the consumer runs if the true mean content is U_2 . The producer's and consumer's risks for intermediate mean values are given by the operating characteristic curve, which can be calculated from the formula

$$t = (U - C)n^{1/2}\sigma \quad (8)$$

which is obtained from Equation 2 by regarding U as a variable and expressing it as a percentage of the reputed content. Thus for the specimen plan

$$\begin{aligned} t &= (U\% \text{ of } U_0 - 95.3\% \text{ of } U_0)(4)^{1/2} / \\ &\quad (4\% \text{ of } U_0) \\ &= (U - 95.3)/2 \end{aligned}$$

i.e.,

$$t = (U - 95.3)/2$$

From this last equation Table I is calculated. The operating characteristic curve is drawn in Figure 9. The ordinates of the curve give the probability of accepting a batch having a given real mean value U . The ordinate for $U = 92\%$ (when $U = U_2$) should be 5%, which is the value of β fixed in the specimen plan. However, it is 4.95% because n was rounded off from 3.94 to 4.

The ordinates subtracted from 100% give the producer's risk. Again, the risk for $U = 100\%$ (when $U = U_0$) should be 1%, which is the value of α fixed in the specimen plan. However, it is $(100 - 99.06) = 0.94\%$ because of the rounding off of n .

Risks for Mixed Fertilizers. So far only producer's and consumer's risks for a single-component, or straight, fertilizer have been considered. For mixed fertilizers a separate specification limit is applicable to each component of the mixture and there will be separate risks for each component. Because a producer will have the whole mixture failed if any one of its components fails, the over-all risk of failure is not the same as for any one component. Similarly, because the consumer will accept only a mixture which passes on all its components, the over-all consumer's risk is not the same as the risk of accepting any one component.

Consider a mixture made up of three components. Let α_1 , α_2 , and α_3 be the producer's risk that the first, second, and third components, respectively, fail, these three risks being expressed as fractions. Then, if α is the over-all producer's risk that the mixture fails on any one, two, or all three of its components, and it is expressed as a percentage,

$$\begin{aligned} \alpha &= 100\{1 - (\text{probability that mixture passes on all three components})\}\% \\ &= 100\{1 - (\text{probability that it passes on first component}) \times (\text{probability that it passes on second component}) \times (\text{probability that it passes on third component})\}\% \end{aligned}$$

Table I. Construction of Operating Characteristic Curve

| U, % | U - 95.3, % | t | Prob- ability of Accept- ance, % |
|---------|-------------------|-------|--|
| 89 | -6.3 | -3.15 | 0.08 |
| 90 | -5.3 | -2.65 | 0.40 |
| 91 | -4.3 | -2.15 | 1.58 |
| 92 | -3.3 | -1.65 | 4.95 |
| 93 | -2.3 | -1.15 | 12.5 |
| 94 | -1.3 | -0.65 | 25.8 |
| 95 | -0.3 | -0.15 | 44.0 |
| 95.3 | 0 | 0 | 50.0 |
| 96 | +0.7 | +0.35 | 63.7 |
| 97 | +1.7 | +0.85 | 80.2 |
| 98 | +2.7 | +1.35 | 91.1 |
| 99 | +3.7 | +1.85 | 96.8 |
| 100 | +4.7 | +2.35 | 99.06 |
| 101 | +5.7 | +2.85 | 99.78 |
| 102 | +6.7 | +3.35 | 99.96 |

i.e.,

$$\alpha = 100\{1 - (1 - \alpha_1)(1 - \alpha_2)(1 - \alpha_3)\} \% \quad (9)$$

Similarly, for a two-component mixture,

$$\alpha = 100\{1 - (1 - \alpha_1)(1 - \alpha_2)\} \% \quad (10)$$

To find the over-all consumer's risk, let β_1 , β_2 , and β_3 be the consumer's risks of accepting the first, second, and third components, respectively, these risks being expressed as fractions. Then, if β is the over-all consumer's risk of accepting the whole mixture, and it is expressed as a percentage,

$$\begin{aligned} \beta &= \text{probability that the mixture passes} \\ &\quad \text{on all three components} \\ &= (\text{probability that it passes on the} \\ &\quad \text{first component}) \times (\text{probability} \\ &\quad \text{that it passes on the second com-} \\ &\quad \text{ponent}) \times (\text{probability that it} \\ &\quad \text{passes on the third component}) \end{aligned}$$

i.e.,

$$\beta = 100\beta_1\beta_2\beta_3 \% \quad (11)$$

For a two-component mixture,

$$\beta = 100\beta_1\beta_2 \% \quad (12)$$

Specimen Calculation of Component Risks. Consider a three-component mixture. What will the component producer's risks be for an over-all risk of 1%?

For simplicity, take $\alpha_1 = \alpha_2 = \alpha_3$. Then Equation 9 becomes

$$1\% = \alpha = 100\{1 - (1 - \alpha_1)^3\} \%$$

i.e.,

$$100(1 - \alpha_1)^3 = (100 - 1)\% = 99\%$$

or

$$(1 - \alpha_1)^3 = 0.99$$

so that

$$(1 - \alpha_1) = 0.99666$$

or

$$\alpha_1 = 0.00334 (= 0.334\%)$$

What will the component consumer's risks be for an over-all risk of 5%? Taking $\beta_1 = \beta_2 = \beta_3$, Equation 11 becomes

$$5\% = \beta = 100\beta_1^3 \%$$

therefore

$$\beta_1^3 = 0.05$$

or

$$\beta_1 = 0.3684 (= 36.84\%)$$

This component risk of 36.84% is very high and appears to give little protection to the consumer. This is not true, because the consumer is protected by his over-all risk (5%) of accepting only a mixture which passes on all three components.

Using the component risks, the numbers of samples, the specification limits, and the operating characteristic curves for each component can be calculated by the procedure given in the calculation of the specimen plan above. By putting $\alpha_1 = \alpha_2 = \alpha_3$, $\beta_1 = \beta_2 = \beta_3$, and assigning the same parameters (σ , U_0 , and U_2 as percentages) to each component, the numbers of samples and the specification limits (as percentages) become the same for each component. Then the sampling plan would be: "Take n samples at random from the batch of mixture and analyze these n samples (or a smaller number of good composites) for each component of the mixture; if the mean of the n analyses (or the mean of the composites) is less than $C\%$ of the reputed content for any one of the components, fail the whole batch."

Use of Sampling Plans for Judging Performance of Producer

Derivation of Mathematical Formulas. Consider a manufacturer to have produced over a certain period of time (say about 6 months) a large number of batches of fertilizer. There is no difficulty in talking of batches, because most manufacturers produce fertilizer to fill orders as they arise. Even if the manufacturer had been producing a particular fertilizer continuously during the 6 months, daily lots of production can be regarded as batches.

Suppose the fertilizer is superphosphate and it is required to judge the over-all quality of the superphosphate produced by a manufacturer during 6 months. To do this m batches can be selected at random from the whole production and n samples selected at random from each of these m batches. Of course, the batches will have to be selected and sampled as they are produced, judgment being reversed until after the m th batch is produced.

If σ = over-all standard deviation of the whole production

σ_1 = standard deviation between batches
 σ_2 = average standard deviation within batches

so that

$$\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$$

then the standard deviation of the mean, \bar{x} , of the mn samples from the m batches is

$$\sigma_{\bar{x}} = (\sigma_1^2/m + \sigma_2^2/mn)^{1/2} \quad (13)$$

Suppose that the whole 6 months' production is normally distributed about a true mean value equal to U_0 , then as derived above,

$$\alpha = \{1/(2\pi)^{1/2}\} \int_{-\infty}^{t_\alpha} \exp\left[-\frac{1}{2}t^2\right] dt \quad (3)$$

where

$$t_\alpha = (U_0 - C)/\sigma_{\bar{x}} \quad (2)$$

or

$$t_\alpha = (U_0 - C)/(\sigma_1^2/m + \sigma_2^2/mn)^{1/2} \quad (14)$$

by virtue of Equation 13.

Similarly, if the whole 6 months' production is normally distributed about a true mean value equal to U_2 , then

$$\beta = \{1/(2\pi)^{1/2}\} \int_{t_\beta}^{\infty} \exp\left[-\frac{1}{2}t^2\right] dt \quad (4)$$

where

$$t_\beta = (C - U_2)/\sigma_{\bar{x}} \quad (5)$$

or, by virtue of Equation 13,

$$t_\beta = (C - U_2)/(\sigma_1^2/m + \sigma_2^2/mn)^{1/2} \quad (15)$$

Equations 14 and 15 can be rewritten as

$$U_0 - C = t_\alpha (\sigma_1^2/m + \sigma_2^2/mn)^{1/2}$$

$$C - U_2 = t_\beta (\sigma_1^2/m + \sigma_2^2/mn)^{1/2}$$

Adding these two equations,

$$U_0 - U_2 = (t_\alpha + t_\beta)(\sigma_1^2/m + \sigma_2^2/mn)^{1/2}$$

or

$$n = \sigma_2^2(t_\alpha + t_\beta)^2 / \{m(U_0 - U_2)^2 - \sigma_1^2(t_\alpha + t_\beta)^2\} \quad (16)$$

or

$$m = (n\sigma_1^2 + \sigma_2^2)(t_\alpha + t_\beta)^2 / n(U_0 - U_2)^2 \quad (17)$$

From Equation 14,

$$C = U_0 - t_\alpha (\sigma_1^2/m + \sigma_2^2/mn)^{1/2} \quad (18)$$

Thus if values are fixed for α and β , values for t_α and t_β can be obtained from Equations 3 and 4, or from tables of the cumulative normal distribution. Then, if σ_1 , σ_2 , U_0 , and U_2 are also fixed, the number of samples, n , which must be taken from a given number, m , of batches can be calculated from Equation 16, or the number of batches which should be sampled for a given n can be calculated from Equation 17. The specification limit, C , can then be calculated from Equation 18.

The above formulas apply to straight fertilizers. The same Equations 9, 10, 11, and 12 apply to the component risks for mixed fertilizers when the sampling plan is used to judge a manufacturer's performance.

Specimen Plan for Judging Performance of Manufacturer. How many samples should be taken from each of six batches (spread over 6 months, say) of a straight fertilizer and what should the specification limit be for a sampling plan based on the following parameters?

$$\alpha = 1\% \quad \beta = 1\%$$

U_0 = long term reputed content, or guaranteed analysis

U_2 = 92% of reputed content

σ_1 = 3% of reputed content

σ_2 = 4% of reputed content

Because $\alpha = \beta = 1\% = 0.01$, from tables of the cumulative normal distribution, $t_\alpha = t_\beta = 2.326$. Thus from Equation 16, since $m = 6$,

$$n = \frac{(0.04U_0)^2(4.652)^2/16(U_0 - 0.92U_0)^2 - (0.03U_0)^2(4.652)^2}{}$$

$$= \frac{(0.04)^2(4.652)^2/16(1 - 0.92)^2 - (0.03)^2(4.652)^2}{}$$

$$= 1.83$$

Rounding off to the nearest whole number, $n = 2$. From Equation 18,

$$C = U_0 - \frac{(2.326)\{(0.03U_0)^2/6 + (0.04U_0)^2/6(1.83)\}^{1/2}}{}$$

$$= U_0[1 - \frac{(2.326)\{(0.03)^2/6 + (0.04)^2/6(1.83)\}^{1/2}}{0.0400}]$$

$$= U_0[1 - 0.0400]$$

i.e.,

$$C = 0.96U_0 (= 96\% \text{ of } U_0)$$

The specimen sampling plan would be: "Take two random samples from each of six batches, the selected batches being sampled, over a period of time, as they are produced, and analyze the 12 samples (or a smaller number of good composites); if the mean of the 12 analyses (or the mean of the composites) is less than 96% of the long-term reputed content, the manufacturer is producing material which is not acceptable."

The operating characteristic curve for

the specimen sampling plan can be constructed from the formula

$$t = (U - C)/(\sigma_1^2/m + \sigma_2^2/mn)^{1/2}$$

which is obtained from Equation 14 by regarding U as a variable and expressing it as a percentage of the long-term reputed content.

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ION ASSAYS

Simultaneous Determination of Phosphate and Sulfate Ions in the Presence of Metal Contaminations

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A method is presented for determining phosphate and sulfate ions simultaneously in the presence of calcium, magnesium, aluminum, iron, and fluoride ions as contaminants. The method is suitable for the rapid and simple determination of phosphate and sulfate ion content of phosphorus fertilizers.

A SIMPLE VOLUMETRIC METHOD (5), presented for the determination of phosphate and sulfate ions in the presence of each other, is suitable for the investigation of alkali salts. It is based on the following principle: The dissolved sample is adjusted with an ammonium hydroxide-ammonium chloride buffer to pH 10, ethyl alcohol is added, and the mixture is titrated with a standard solution of magnesium chloride and Eriochrome Black T as indicator. During the course of titration, crystalline magnesium ammonium phosphate is precipitated (2). At the equivalence point the excess magnesium ions react with the indicator to produce a color change from blue to purple-violet. Then the original blue color of the reaction mixture is recovered by adding a few drops of EDTA [(ethylenedinitrilo)tetraacetic acid, complexone III] and the sulfate ions are titrated with standard barium chloride solution

(4). During this titration barium sulfate precipitates and, after the equivalence point is reached, magnesium ions are liberated from their complexonate bonds by the excess barium ions; this is indicated again by a color change from blue to purple-violet as in the first titration.

In a previous communication (4) an analogous measurement of arsenate ions with a standard solution of magnesium sulfate was suggested and was also applied to the determination of calcium arsenate (6). Essentially the same principle was utilized to mask certain ions which interfered in the investigation of phosphate fertilizers (3), as the earlier method suggested for the simultaneous determination of alkali sulfates and phosphates in the presence of Mg^{+2} , Ca^{+2} , Fe^{+3} , and Al^{+3} (7) was unsatisfactory for this purpose. Therefore, in the presence of these ions, as in the analysis of phosphorus ferti-

lizers, the simultaneous determination of phosphates and sulfates was completed as follows:

Ferric and aluminum ions were masked with DCTA (1,2-diaminocyclohexanetetraacetic acid or complexone IV) in a solution whose pH was buffered between 2 and 3; then EDTA was added and the solution was adjusted to pH 10.0 to 10.5 with ammonium hydroxide, and with a buffer mixture of ammonium chloride and ammonium hydroxide solutions. EDTA formed stable complexes with Ca^{+2} and Mg^{+2} and the complexes of DCTA formed with iron and aluminum between pH 2 and 3 did not decompose either, if the pH of the medium was adjusted to 10 (7, 8). Although Ca^{+2} and Mg^{+2} may be masked with DCTA, this technique was abandoned because of the expense.

After the metal ions were masked, Eriochrome Black T was added as indicator and the solution was titrated