copper mixtures it was necessary to separate the copper, and that this was effected by sulphuretted hydrogen; it was much pleasanter to precipitate the copper with sodium thiosulphate. He always used this method in separating copper in the iodide or cyanide assay. With regard to the cyanide assay, which many chemists seemed to think could only yield approximate results, he might say that at some large copper mines in Norway it was the sole method employed for ores, mattes, and metal; at any rate this was the case on the occasion of his visit three or four years ago. If the assay was carried out on strictly defined lines it was capable of giving results of much greater accuracy than was generally supposed.

Mr. SHEPHERD said he had used the titanium method for the estimation of copper in the vats for the electroplating of iron rollers. There was often a fair amount of iron present, which it was not necessary to estimate; excess of ammonia was added to the amount taken, the ferrie hydroxide filtered off and washed with dilute ammonia, the filtrate acidified, and the copper titrated in the usual way with titanous chloride.

Mr. S. B. JATAR, referring to his paper published in the Journal of July 15th last, said that Miss Hibbert mentioned that the "c" method is preferable to the one described as "a" method; the method "a" was mentioned in connection with pure chromium salts, and not chromium and iron together. The indicator was very useful when titanous chloride was to be standardised against bichromate solutions. The "b" and "c" methods could only be used accurately when one was familiar with the delicate colour reactions involved, which required a certain amount of practice. The indicator, therefore, was a great help for one not familiar with the method.

Mr. HOSEASON asked if there was any objection to the use of hypochlorite instead of chlorate as an oxidising agent, since the former was more easy of manipulation.

Mr. LOMAX inquired if the method of estimation had been applied to the analysis of rutile.

Miss HIBBERT, in replying, said the reason why she had brought forward this method of estimating copper, chromium, and iron was, as explained in the paper, for the determination of these metals when they occur together in the ash of mordanted material. The use of hypochlorite for oxidising iron in the presence of chromium would appear to be very suitable, but she had used potassium chlorate and hydrochloric acid because they were more easily obtained in a high degree of purity. Estimations of titanium in rutile, ilmenite, and other minerals, by the methylene blue method, had been very successful. A sample of rutile, analysed by this method, was found to contain 91.0 per cent. of TiO_2 , and this agreed very closely with the iron method, but she had not yet confirmed the result gravimetrically. In reply to Mr. Shepherd, it seemed probable that when the iron was precipitated with ammonia, some copper was carried down also. Methods for the complete separation of these metals were suggested in the paper.

New England Section.

Meeting held at Boston on Friday, January 8, 1909.

MR. F. E. ATTEAUX IN THE CHAIR.

A MATHEMATICAL VIEW OF SAMPLING, WITH REFERENCE TO THE DEGREE OF ACCURACY TO BE OBTAINED.

BY MARTIN L. GRIFFIN.

In a paper read before the New York Section of this Society, entitled, "Standard Methods of Sampling: A Review with some Suggestions,"* I referred to some ideas on sampling that I expected to give at an early date, but which have been delayed until this time.

My subject involves the whole sampling process, whatever the nature of the commodity, substance, or conditions, and the making up of the ultimate sample for assay or analysis, regardless whether the material to be sampled is of such a nature that the separate portions drawn cannot be mixed, as for instance, wood pulp; or whether they can be mixed, as in the case of ores, coals, etc. R. W. Sindall, of London, has done considerable work on one important phase of this subject, namely, the determination of average errors. His methods consist in duplicate sampling and testing, and in this way checking the results or deducing the probable error and showing its commercial significance. So far as I know, this question under the title I have announced has never been dealt with. D. W. Brunton, in a paper, in Vol. 25 of the Transactions of the American Institute of Mining Engineers, entitled "The Theory and Practice of Ore Sampling," in reality enters into it when he says, "In proportion as a sample in preparation diminishes in weight by quartering, it must be re-crushed so that there shall be a constant ratio between the size of the sample and the largest particle." That is, the more nearly uniform or homogeneous any product or substance is, the smaller may be the quantity representing it. His problem is:—Given a quantity of ore composed of particles and pieces of irregular sizes, shapes, and composition, how must it be dealt with so as to arrive at a very small sample of a few grams, which shall represent in true proportion the mechanical condition and chemical composition of all the separate masses of the original pile? He says that the size of the sample in amount must always be in constant proportion with that of the largest particle. In other words—whatever the weight of the sample in preparation, the number of parts or particles must remain constant. In the practice of crushing and grinding there will always be a large proportion of particles smaller than the allowable largest, but this is incidental.

My subject deals largely with the probability and theory of errors. It is not my purpose to enter into all the mathematical refinements of this subject, even if I were able, since it is one dealing almost wholly with higher mathematics. I shall endeavour to pursue the subject only so far as it has a practical value for chemists and not for theoretical considerations.

I may divide the subject as follows:—1. A statement of the problem. 2. The law of errors. 3. The probability curve and the analysis of it. 4. A consideration of the mean value. 5. The relative accuracy obtained by drawing larger or smaller numbers of samples. 6. The determination of results within fixed limits. 7. The number of samples to be drawn.

The problem is not a determination of who is the best marksman from an examination of their shots at a target, neither is it a determination of what shots occupy a mean average distance from the bullseye. It is much simpler than a determination of this, the mean average distance from the bullseye of all the shots. This problem would involve a calculation in the area of the target, while the nature of ours limits the observation to points in a straight line, for instance, those lying on one diameter of the target. Nor is it the determination, which is true in a set of observations, as in determining the atomic weight of some element, or the estimation of the probable error from the truth in the mean of these observations.

Our proposition starts where the degree of truth in these ends, and is by nature susceptible of closer approximation. We assume that the mean of a large number of variations is the truth sought, and we want to discover how few of these observations we may select, the average of which shall not appreciably depart from the mean of the whole number. Let us suppose we have 500 separate packages of any commodity, as for instance, 500 rolls of sulphite pulp which have been run over a drying machine, generally a few points above and below the atmospherically dry limit, to determine the amount of moisture. If we draw a straight line and divide it into two equal parts we may represent the mean variation in moisture by a point at the centre, and from this point lay off in one direction distances representing the departures from the mean of each sample above, and in the other direction, lay off representative distances below the mean. Let

* This Journal, 1905, 183.

us assume that we have tested these 500 rolls of pulp and find the results to be as follows:—

Positive departure.			Negative departure.		
Moisture between.	No. of rolls.	Per cent.	Moisture between.	No. of rolls.	Per cent.
4—5%	10	2	4—5%	10	2
3—4%	20	4	3—4%	20	4
2—3%	40	8	2—3%	40	8
1—2%	80	16	1—2%	80	16
0—1%	100	20	0—1%	100	20

Plotting as ordinates the number of rolls and the corresponding mean variation in moisture as abscissæ, we shall get the following curve:—

In doing so we shall observe: (a) That there are as many samples represented on one side of the origin as on the other. (b) That within equal distances from the origin on each side there is an equal number of samples represented. (c) That by far the greater number will arrange themselves very close to the origin. (d) That small errors are more frequent than large ones. (e) That the greater the variation the less the frequency, and hence very large variations do not occur.

Now any mathematical relation between a variation (X) and the probability of its occurrence (Y) must satisfy these characteristics. When such a function, $Y=f(x)$, is plotted as we have illustrated, it will have a maximum ordinate, OY, corresponding to the mean, that is, no error. It will be symmetrical with reference to this ordinate, the Y axis; and as X increases Y must decrease, until when X becomes very large, Y will become vanishingly small. This corresponds to the fifth observation above, namely, that very large variations from the mean cannot occur. As a matter of actual manufacturing operations they scarcely exist. For example, a manufacturer desires to dry his pulp so as to get the allowable limit of atmospheric moisture as nearly as possible. Obviously it will be his desire to do this, because he does not want to pay freight on water, or if he must he will use wet presses without any attempt to reach this degree of dryness. If any quantity falls below his standard they will be included in the average. If he were punctilious in his orders to his superintendent about uniform conditions of moisture it would mean that if any mishap occurred in drying, resulting in a very few very wet rolls, they would be thrown out, or if the workmen were careless and they were included it could not affect the result because the number (y) was so small.

$$Y = K e^{-h^2 x^2}$$

is the equation which represents this probability curve or curve of variation of any particular roll or average or any given number of rolls from the mean of the whole number. To find the meaning of the constant K, let us solve the equation by putting $X=0$, then $Y=K$, which is the maximum ordinate of the curve. K corresponds to the number of those rolls whose content in moisture coincides with the mean itself. The height at which the curve cuts the Y axis represents the magnitude of the arithmetical mean; K has nothing to do with the actual shape of the curve beyond increasing the length

of the maximum ordinate. It must be borne in mind that it is not the maximum ordinate for any value of X, and only coincides with it when $X=0$. It follows, then, that as K has nothing to do with the curve, the sampling of any of the K rolls has no influence in fixing the result and we may disregard them. Therefore, when $X=0$ and $Y=K$ the whole number of rolls are alike, i.e., any one of them represents the average. Hence the drawing of one sample only will suffice.

The meaning of h is found by making $K=1$ and plotting corresponding values of X and Y. For

$X = \pm \frac{1}{h}, \pm \frac{2}{h}, \pm \frac{3}{h}, \pm \frac{4}{h}, \dots$, when $h=1, \frac{1}{2}, \frac{1}{3}, \dots$ etc.

$$y = K e^{-h^2 x^2} \quad K=1.$$

$h = \frac{1}{4}$			$h = \frac{1}{2}$			$h = 1$		
$x=0$	$y=1$		$x=0$	$y=1$		$x=0$	$y=1$	
$x=\frac{1}{4}$	$y=.98$		$x=\frac{1}{2}$	$y=.94$		$x=\frac{1}{4}$	$y=.778$	
$x=\frac{1}{2}$	$y=.94$		$x=1$	$y=.78$		$x=\frac{1}{2}$	$y=.369$	
$x=\frac{3}{4}$	$y=.87$		$x=\frac{3}{2}$	$y=.56$		$x=\frac{3}{4}$	$y=.105$	
$x=1$	$y=.78$		$x=2$	$y=.38$		$x=1$	$y=.018$	

In this way it will be observed that though all the curves cut the Y axis at the same point, the greater the value of h , the steeper will be the curve in the neighbourhood of the ordinate OY.

The physical significance of this is, that the greater the magnitude of h , the more accurate the results, and the less will be the magnitude of the deviation of individual samples from the arithmetical mean of the whole number. h relates to the number of rolls of pulp approaching in variation the mean; if it is very large, there is very little variation from the mean in the content of moisture; the condition of the rolls is practically the same, and hence very close to the mean average. In sampling the h rolls, where h is large, the possibility of error is greatly reduced, and when we know h is large the necessity for taking a fixed number of samples to keep within an allowable limit of error is much less. Mathematically h has been called "the absolute measure of precision."

At this point some observations regarding the expression "mean average" value should be made. We, as chemists, draw samples from irregular masses and piles of commodities, as coal, limestone, ores, or packages of different sizes and weights, and quite frequently they do not bear a fixed ratio to the mass or weight they represent, yet we grind or mix and average them arithmetically. In so doing we introduce a probable error by the manner of taking the samples. In order that the arithmetical mean may be free from all error, we must draw equal weights from equal quantities by weight. For instance, in the sampling of bales or bundles of wood pulp for moisture, if the determination is to be made from the aggregate weight of the separate samples, they should bear a constant ratio to the weight of the respective packages from which they have been drawn. Referring to our illustration of 500 rolls of moist pulp, we have proceeded on the assumption that each roll of pulp was of equal weight and that the sample represented the condition of the rolls, and that equal weight samples had been drawn. Under these conditions the arithmetical average of the samples would give correct results. In other words our samples might all be weighed together in one weighing. The general statement for this is:—The best value to represent a number of observations of equal weight is their arithmetical mean; while the best value of different weights is obtained by multiplying each observation by its weight and dividing the sum of the products by the sum of their different weights.

It has been demonstrated that the probable error of the arithmetical mean of a series of observations is

inversely as the square root of their number. From which we see how easy it is to over-estimate the effect of largely increasing the number of observations or samples. If E denotes the probable error of the mean of ten samples, in order to reduce this error one-half, or one-half E , we must draw forty samples, and to obtain one-third E we would have to draw ninety samples. The converse of this is that the probable error is increased directly as the square root of the number of observations is diminished, that is the reduction by one-fourth in the number of samples taken doubles the error.

I have made use of this illustration in which it appears that each roll of pulp has been tested, for the purpose of analysing the problem mathematically, and drawing the resulting conclusions. It is, of course, an ideal illustration, and the results of such a sampling and testing, if it were possible, would be free from error.

The fundamental preliminary to sampling a mass of any commodity which may be mixed and quartered down is that it shall be mixed and crushed and quartered down successively mechanically in the abstract, and that the weight of each successive quarter shall bear a direct relation to the size of the mesh of a corresponding screen, and that it shall all pass through this screen. A set of standard screens corresponding to a set of weights diminishing proportionally in the quartering process would be very valuable to chemists. In sampling commodities which cannot be mixed, the theoretical fundamental conception is that in the process by which they have been produced there is a certain cycle of varying conditions which repeat themselves. This is inevitably so. The cycle may be large and the frequency small, and if so the sampling must be extensive. If the cycle

is small and the frequency large the sampling may be trifling. But all of this is included in the main argument of this paper.

From the discussion of the subject thus far we see that the number of samples within certain limits to be drawn does not play as important a part as is generally supposed, however, its importance is greatly dependent upon the representative value of each sample. This, of course, pertains to the sampling. The sampler must be free from all bias and personal errors in his work, or there will be an added error. My paper, therefore, becomes an argument also for greater knowledge of the product to be sampled, how it has been produced, etc., and greater care and diligence in the mode of sampling. The commercial value of the products sampled will also play a very important part in determining what the allowable limit of error should be, and this will affect the number of samples and the mode of sampling.

We may therefore conclude that if a chemist is conversant with the history of the product which he is about to sample and knows how to draw proper samples, the number may be very limited, perhaps ten and not more than 20 or 25. If he lacks the knowledge and ability to do this part of the work, the drawing of almost any number of samples will not be trustworthy.

New York Section.

At a meeting of the Section on Nov. 20th, 1908, held at the Chemists' Club, Mr. Frederick Klein read a paper on "Selenium."

Journal and Patent Literature.

PATENT SPECIFICATIONS may be obtained by post by remitting as follows:—

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I.—PLANT, APPARATUS, AND MACHINERY.

PATENTS.

Separating subdivided solid matter from a liquid, particularly applicable for thickening ore pulp and for feeding or measuring the pulp or solid. F. E. and A. S. Elmore, London. Eng. Pat. 26,821, Dec. 4, 1907.

THE mud or pulp to be separated is fed into a conical vessel known as a "spitzkasten" and the separation takes place in the known manner. The invention relates to the provision of a chamber at the apex of the cone through which the separated solids are discharged. This chamber has an upper valve opening upwards and a lower valve opening downwards, and forms a kind of lock for the passage of the solids. The valves are operated alternately by concentric rods which pass up through the vessel and are actuated by mechanism situated on the cover. In order to sweep the solids into the apex of the cone, slowly rotating rakes are arranged within the tank, supported by a frame having wheels which run on a track situated, in order to avoid clogging by deposited solids, in the overflow gutter which extends round the upper edge of the tank.—W. H. C.

Evaporating or concentrating apparatus. J. and C. McNeil, Govan. Eng. Pat. 5069, March 6, 1908.

THE claim is for improvements in the apparatus described in Eng. Pat. 8763 of 1900 (this J., 1901, 400). The chamber or box forming the steam space has the top and bottom plates dished upwards parallel to each other. The upper plate is of greater diameter than the lower one,

so that the chamber has the shape of an inverted truncated cone. The tubes are set at right angles to the plates, and are consequently inclined to the vertical, but parallel to the side of the steam chamber. A circulating space is left between the chamber wall and the wall of the evaporator, and the liquid is introduced by a perforated ring fixed either centrally over the tube chamber or above the circulating space.—W. H. C.

Mixing and pulverising apparatus for liquids. A. Martin, Paris. Eng. Pat. 6552, March 24, 1908.

THE liquid to be pulverised is pumped by a set of three pumps driven from the same shaft by cranks set at an angle of 120° to one another, so that one pump is always working into a pressure chamber. From this chamber the liquid is allowed to escape under strong pressure controlled by a piston, actuated by a spring, into a system of narrow passages. The thin streams of liquid are broken up and united again in these passages and finally discharged from two opposite nozzles, whereby the liquid is atomised.

—W. H. C.

Recording the quantity of water or other liquid evaporated in a boiler or the like. J. Stratton and E. A. Claremont, Manchester. Eng. Pat. 10,588, May 15, 1908.

TWO calibrated tanks, A, A', of equal capacity, and provided with an overflow, F, are fixed side by side at the same level. They are alternately filled with the liquid to be measured by the pipes, B, B, which are connected by a three-way tap, behind the tap, D, shown in the figure, to the supply main, G. They are alternately emptied by the pipes, C, C, connected by the three-way