A STUDY OF THE ERRORS INVOLVED IN THE SAMPLING OF SOILS.

A thesis submitted in part-fulfilment of the requirements of the University of South Africa for the degree of Master of Science.

By

W. J. A. Steyn

Rhodes University College,

Grahamstown.

1945.

ACKNOWLEDGMENTS.

Thanks are due to Professor W.F.Barker, B.Sc., Ph.D.,F.I.C., for his enthusiastic guidance and keen interest.

Also to the Librarian of Rhodes University College, Dr. F.G. van der Riet, for his help in obtaining sundry journals and publications.

CONTENTS.

	Page
Introduction	1
A. Review of Sampling Procedures	4
B. Previous Work on Sampling (1) General	10
(11) Soils	14
C. Method of Testing Sampling Efficiency	20
D. Methods for the Determination of Potash (1) General	22
(11) Soils	23
E. Experimental Comparison of the Three Potash Methods.	33
F. Preparation of soil extracts	44
G. Treatment of the hydrochloric acid extract for potash determination	50
H. Sampling procedure and lay-out of plots	57
I. The analysis of the soil samples	63
J. Experimental results	65
K. Statistical treatment of the results.	69
L. Discussion.	82
Literature cited.	90

Introduction.

The importance of representative soil sampling is now beginning to receive more general recognition. The analysis of the sample, and any chemical or physical treatment it may undergo in the laboratory, is of little practical value if it is not known with reasonable certainty that this sample represents fairly the area from which it was taken. It has been said over and over again, that the existence of the world's whole civilization is dependent upon a mere strip of soil, only 9 inches in depth. The study of the soil is therefore of special importance if only for the practical end of replacing any nutrient deficiencies which may be found.

In view of the extent to which soil analysis has been pursued, it is surprising that more attention has not been paid to the problem of the errors involved in sampling. Ideally the sampling procedure must aim at approaching the accuracy of the analytical procedures to which it is to be subjected. In consequence, instructions for sampling abound in statements that proper procedure depends upon the objective. True as this may be, it nevertheless gives little quantitative aid to an investigator faced with the problem of sampling a given soil for a given purpose.

In this study an attempt is made by the author to find experimentally the limits of accuracy involved in sampling three typical South African soils. It is hoped that

the results may be of some value to future workers on this subject.

The object of sampling is to obtain a quantity of soil as nearly as possible identical in properties with the bulk soil over the original area in question. The true value could only be obtained with certainty, by taking all the soil in the area as constituting the sample. This is, of course, quite impracticable and it is therefore important to realise that the true values for the soil are unknown. In practice, only close, and never absolute agreement with this value can be reached.

The first question which arises when considering sampling problems, is the relation between precision in sampling and in analysis. It is clear that the sampling error is commonly much greater than the analytical error for soils, and the limit of accuracy generally is determined by possible variability of the sample rather than by the errors in the laboratory. A value obtained by chemical analysis of a sample of soil defines only a characteristic of a small subsample of the area in question, and only approaches an accurate definition of the soil to the extent that:-

(a) the sample from which it was taken accurately represents the soil in question,

(b) the subsample analysed represents accurately the gross sample, and,

(c) the analysis determines the true value of the characteristic in the subsample under investigation.

A survey of the literature on soil sampling reveals probable errors which are apparently three to six times greater for sampling than for analysis (1).

South African publications, (2) and (3), and other recently published data usually give analytical figures to an accuracy of $\pm$1%, and sometimes even better. The question now arises as to how far this degree of accuracy is justifiable in view of the sampling procedure usually adopted. Experience shows that soils vary considerably over even small areas and unless an exceptionally sound procedure is employed, an analytical accuracy of 1% or below will be entirely out of place. Special attention should therefore be given to the degree of precision justifiable by a given sampling procedure or, alternatively, to the question of the sampling requirements for a prescribed degree of accuracy.

A. REVIEW OF SAMPLING PROCEDURES.

Most of the procedures given in the literature are more or less similar, and only three typical examples will be discussed.

In South Africa all, or at least, most of the sampling of soils is done according to the methods adopted by the Government Division of Chemical Services (3). Stress is laid upon the depth to which the sample is to be taken, never deeper than 1 foot for the top horizon, care being taken to avoid contamination by subsoils. After removal of the vegetation upon the representative spot, a hole is dug with a sharp spade to the necessary depth and one side of the hole trimmed so as to be smooth and vertical. A uniform slice, about 3 inches thick, is then removed by means of the spade and mixed on a clean board with an unspecified number of other samples obtained in a similar way from other "representative" spots in the field.

After mixing, a suitable portion (about 5 lbs) is taken to the laboratory for analysis. Nothing whatever is said as to the number of samples to be taken to give a representative gross sample, or as to what is meant by a "representative spot" in the field.

C.S. Piper in his manual on Soil Analysis (4), gives a more elaborate outline of the principles to be adhered to in soil sampling. He mentions the importance of adopting different procedures for different types of investigation. Composite samples are taken with a 4-inch post-hole auger at a number of sites representative of the plot or area to be investigated. Surface

mulch must be sampled separately from the rest of the soil, especially when nitrates or other soluble salts are to be determined. Six or nine inch depths are sampled. After mixing the samples, small portions are taken at random from the bulk to give a representative sample of about 2 lbs. He also gives a description of the collection of type samples for soil survey studies. Despite the greater degree of detail which is given, the investigator is still left in the dark as to the probable error in any given procedure, which he must apparently choose by instinct.

The most useful information regarding soil sampling procedure was obtained from a paper by Cline, published in "Soil Science" (5) after the commencement of this investigation. Methods are presented for sampling soils,

(a) to represent an area for estimates of mean values only, estimates of variability and estimates of significance and fiducial limits, and,

(b) to represent a soil type.

Instructions for subdivision of areas and selection of sampling sites are included. The relative merits of general types of sampling tools are also pointed out. The paper is of the review type and does not include any experimental data in support of the recommendations which are made. A brief outline of its more important features is given in the next few paragraphs.

The accuracy with which a soil sample represents the population sampled depends upon the soil variability, the

number of sampling units contributing, and the way in which the sample is drawn. The number of samples to be drawn from an area should never be decided upon arbitrarily, but an estimate of the required number should be based on valid statistical treatment. Within a homogeneous soil population, the accuracy of the estimate is a function of the number of sampling units drawn and the variability of the population, as is readily seen from the standard equation

$$S\bar{x} = \sqrt{\Sigma x^2/n(n-1)} \quad \text{----------(1)}$$

where $S\bar{x}$ = the standard error

Σ indicates summation

x = deviation of each sampling unit from the sample mean

n = number of sampling units.

$S\bar{x}$ is a measure of the reproducibility of the sample, and is derived from the usual equation giving the standard deviation S of a sample population, a measure of the population variability, namely

$$S = \sqrt{\Sigma x^2/(n-1)} \quad \text{----------} \quad (2)$$

The interval $\bar{x} \pm S$ includes approximately $^2/_3$ of the sampling units of a normally distributed sample population; the interval $\bar{x} \pm S\bar{x}$ includes approximately $^2/_3$ of the <u>means</u> of similarly drawn samples. The ratio of the difference between the means of two similarly drawn samples (D) to standard error of this difference (Sd) defines "t values"

$$t = \frac{D}{Sd} \quad - - - - - - - (3)$$

from whose frequency distribution for a given size of sample the probability of occurrence in sampling can be estimated.

The standard error of the difference between two means is calculated by the formula.

$$Sd = \sqrt{\bar{S}^2_{xa} + \bar{S}^2_{xb}} \text{ ---------- (4)}$$

Where $\bar{S}_{xa}$ and $\bar{S}_{xb}$ are the respective standard errors of the two means.

When estimating the reproducibility of a sample mean, an investigator wishes to know the error of the difference between means of samples composed of the same number of sampling units and can often assume that the standard errors of the two samples are approximately equal. Under these conditions $Sd = S_{\bar{x}}\sqrt{2} = S\sqrt{2/n}$, by substituting from equation (1) above. Then equation (3) becomes

$$t = D / S\sqrt{2/n}$$

$$\text{or } n = 2t^2S^2/D^2 \text{ - - - - - - - (5)}$$

These relationships should form the basis of sound sampling procedure. Another useful approximation for a sample is the relationship of standard deviation to the range of a normally distributed population:

$$S = (r_n - r_1) / C \text{ - - - - - (6)}$$

Where C = a constant - approximately 3, 4, 5 and 6 for 10,25, 100 and 500 sampling units respectively, r_n and r_1 are the extremes of the range.

Horizontal subdivision, to give sampling areas homogeneous with respect to soil type, plant growth, and treatment, and vertical subdivision into recognizable

horizons of the same soil type, should be observed. A layer in the middle of each horizon should only be sampled.

Three general principles should be kept in mind when selecting sampling units :

(a) A sample composed of few sampling units scattered at random throughout a homogeneous population contains information up to the limits of its size, but even a large sample, confined to a part of the population, contains no information about the excluded parts.

(b) An unbiased estimate of the mean requires that every sampling unit have an equal chance of being drawn.

(c) An unbiased estimate of significance and fiducial limits requires that every sample of n sampling units have an equal chance of being drawn.

Complete randomization is necessary to meet restriction (c). Numbers required for this kind of test are generally great enough so that restriction (a) would automatically be met by a random sample. A small sample, however, should not be ignored for the sake of complete randomization.

For objectives that require only an unbiased estimate of the mean, incomplete randomization by means of a grid superimposed at random, satisfies principle (b). A grid gives every sampling unit, but not every possible combination of n sampling units, an equal chance of being drawn. This method requires special precautions to avoid bias from superimposing the grid parallel to some systematic variation in the soil.

Chemical properties of soil also vary with time, and precautions should be taken to meet this problem.

Compositing of samples is important because it saves the time and expense of analysing each sample separately. Compositing is valid only if

(a) the sampling volume represents a homogeneous population,

(b) equal amounts of each sampling unit contribute to the subsample analysed,

(c) no interactions that would affect the results materially, occur, and

(d) an unbiased estimate of the mean is the only objective.

A sampling tool should provide a sampling unit which is (1) uncontaminated,

(2) approximately uniform in cross-section to the desired depth, and

(3) reproducible.

Cline prefers to use a sampling tube, a 16 inch tiling spade or a parallel-sided , completely sheathed auger.

B. PREVIOUS WORK ON SAMPLING.

(a) General.

A very important work on the sampling of coal was completed by Bushell in 1937 at the Fuel Research Institute, Pretoria (6). Although the mathematical expressions presented in this paper are not applicable to soil conditions unless alterations are made, the outline of the research and the way in which it was tackled, nevertheless provides a sound background for soil sampling studies.

In this paper, a complete study of the best conditions and methods of sampling for use with all commercial grades of South African coal is given and specifications for the sampling of both large and small coal are suggested. A mathematical term, derived from experimental data, to express the relative variability of types of South African coal, is presented. Based on considerable experimental evidence, another mathematical expression incorporating all the variable factors (viz. the probable error, the heterogeneity of the coal, the size of the coal and the weight of the increment) encountered during the taking of random increments from quantities of coal, is also given.

Useful information is obtained from studies made by A. R. Clapham at Rothamsted, England, on the estimation of yield in cereals (7) and (8). Cereal plots were sampled by three different methods - two systematic and one involving a random location of sampling units. The disadvantage of the systematic methods as compared with random sampling, emerged clearly. These disadvantages were

further emphasised by a statistical analysis of earlier data on sampling. Clapham concludes "By the use of a random sampling method, the variance due to sampling errors may be made a satisfactorily small fraction of the total variance of cereal plots 1/40th of an acre in area".

In 1935 Yates and Zacopanay at the Rothamsted Experimental Station, England, published some useful data on the estimation of the efficiency of sampling (9). The estimation of the experimental yields of cereal crops by sampling methods was considered in the light of 18 experiments which were harvested by these methods at Rothamsted and its associated centres. A discussion of the interpretation of the analysis of variance as applied to sampling results is given, and an expression is found for the loss of information arising out of sampling. An important point is that the results of the discussion are applicable to all types of sampling carried out on replicated experiments.

In the main series of experiments the mean loss of information on the main treatment comparisons due to sampling was found to be 3½. The method of determining the optimal percentage of sampling is described. The gain due to subdivision of plots for sampling is considered and it is shown that this is advantageous.

Owing to the fact that most of the statistical treatment discussed in this paper can be found in any good text-book on statistics, it will not be reproduced here.

Arising out of this discussion, however, a few important points should be stressed.

It was found that approximately $\frac{1}{3}$ (31%) of the information was lost by sampling. The authors thought it of interest to see what would be gained by sampling more extensively. By taking double the number of sampling units, the loss of information was found to be 19% and for treble the number of sampling units, 13%. It is clear, therefore, that after a certain number of sampling units has been taken, not much additional information can be gained by increasing the number of samples.

The authors also determined the optimal amount of sampling as follows : If Q is a number representing the necessary size of the experiment (equal to unity when the whole experiment is harvested) and S a number representing the relative total number of samples (also = 1 when the whole of an experiment of unit size is sampled) so that 100 S/Q is the percentage sampled, the condition that a constant quantity of information is obtained whatever the percentage sampled, is equivalent to

$$Q\,(1 - L) = 1$$

or

$$Q \frac{1}{1 + f\,(Q-S)/S} = 1$$

where L = No. of sampling units.

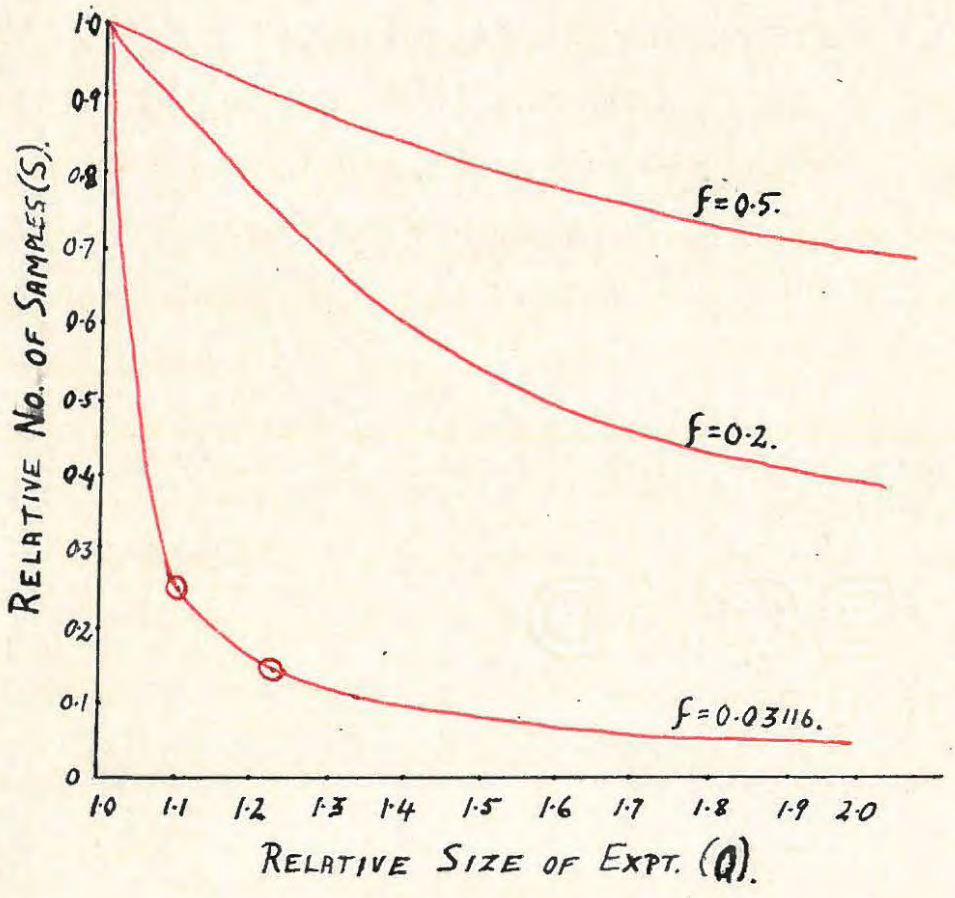
f = error variance due to variation between sampling units when the whole plot is harvested and

= 0.03116 in this particular experiment.

The above equation reduces to

$$\frac{1-f}{Q} + \frac{f}{S} = 1$$

The graph of this function for f = 0.03116 is shown below. The graphs for f = 0.2 and f = 0.5 are also shown for purposes of comparison. The limiting value of S (Q infinite) is in each case equal to f.



For f = .03116 there is a rapid reduction in the required size of the experiment with increasing sampling till S equals about 0.15. Q then equals 1.23 and the

percentage sampled is therefore $100 \times .15 / 1.23$, or about 12%. Beyond this point the rate of reduction in Q rapidly falls off so that there is little further gain after S reaches 0.25 at which point Q is 1.1 and the percentage sampled is 22.5%

It is important not to gloss over the very considerable loss of information which occurs when only a small percentage of an experiment is sampled, as compared with the information obtained when the whole experiment is harvested. As we have seen in this series of experiments $\frac{1}{3}$ of the total information is lost and this implies that as far as the main treatments are concerned the experiments should have been laid down with 50% more replicates than would be requisite if the whole of the plots were sampled.

(b) SOILS :

The literature on soil sampling is so considerable that the treatment of each contribution separately is out of the question, time and space only permitting of the discussion of the more important and significant papers which have been studied. An effort has, however, been made to include in the bibliography references to most of the literature on this problem, as an aid to future workers in this field.

The first extensive and valuable work on Soil sampling appears to be that of Frear and Erb in America in 1920 (10). They tackled the question as to how many sub-samples must be taken from well and symmetrically placed points over respective plots in order that duplicate

composites from the same 1/8th acre plot may agree satisfactorily with respect to the point of composition in question. The soils were sampled in two different ways.
(1) by excavation of holes 9 x 4 inches to subsoil (3-8 inches)
(2) by borings with a $\frac{7}{8}$ inch soil auger, using only the surface soil.

The mechanical analyses of the samples were done and great differences obtained. Chemical analysis (N,P) of the composites also yielded marked differences and the authors concluded that, despite unusual care, the sampling error remains greater than the analytical error. Comparison of the two modes of sampling show no marked difference, and apparently both ways of taking a sample seem to be equally efficient.

In 1927 Mc Call and Mc Kibbin, (11) gave a brief critical review of the methods of sampling soils, with twenty references. This is, however, of historical interest only, and can be neglected in the light of more recent developments. In order to find the best way of sampling garden soils for the determination of nitrates, Blaney and Smith (12) in 1931 took a large number of cores of soil from manured, limed and fertilized garden soils and determined the nitrates in them. Less uniformity of nitrates was observed than has usually been reported for other soil conditions. A minimum of 50 borings was necessary for 1/30th acre areas to reduce the probable error of nitrate to approximately 5% of the mean.

A paper published in New Zealand (13) in 1932, claims that sampling to a depth of 3 inches instead of 9 inches gives more satisfactory information concerning the lime and phosphate status of the soil in relation to pasture production and the chemical composition of the pasture, and is therefore recommended for such studies.

The first apparent use of statistical treatment in soil sampling research is embodied in a contribution due to Youden and Mehlich in 1937 in America, (14). Variations in pH of soil samples taken at different space intervals over a large area were examined statistically and the results discussed in relation to sampling procedure. Their particular object was to select efficient methods of soil sampling for the purpose of soil surveys. Two different soil types were examined.

The sampling procedure adopted by the authors was roughly as follows :- Nine stations, approximately one mile between stations, were sampled. At each station two sub-stations were selected, one thousand feet apart. Two sampling areas, 100 feet apart, were located at each sub-station and, finally in each sampling area, two sample points were taken ten feet apart. 72 samples in all were taken on each of the two types of soils. The pH was determined on each sample by means of a Leeds and Northrup glass electrode.

The maximum difference in pH obtained between

duplicate samples (1-3 miles apart) was 1.37 unit. An analysis of variance of the results shows that statistical significance may be attached to the difference in variation. An interesting point arising out of the data is that four samples taken at intervals of 1000 feet show a smaller variance than that obtained with eight samples, most of which were taken in close proximity to each other. The authors concluded that intervals as low as 10 or 100 feet were too small to constitute an effective method for sampling such big areas.

A much more practical and useful contribution came from two Indian research workers in 1938, Iyengar and Tamhane (15). Four areas of 1/40th acre each were subdivided into 64 plots and the salt content from a sample of each plot determined. Except on very irregular soil, it was found that the plot could be represented by a sample composited from a random boring in each quadrant of the area.

The work was undertaken to determine by experiment the number of samples necessary to represent the soil of a plot of 1/40th of an acre in area, under irrigation conditions. Six inch depths were sampled from the centre of each plot and an additional sample taken at the centre spot of the whole area. After the soluble salt content of each sample had been determined, the results were treated statistically. It was found that in the most variable area a composite sample of 16 cores, each taken to represent 1/16th of the whole area, would have a higher standard error than composites of four cores, each representing a quarter, from

any of the other three areas. Except on such highly irregular soil, a composite made up of four cores selected at random, one from each quarter of the experimental area of 1/40th acre, gave standard errors ranging from 0.066% to 0.117% on the mean values of the salt content of 1.23% to 2.41%. The workers conclude that such samples should be sufficient to represent the salt content of plots in replicated experiments, with the provision that more elaborate samples are needed for very irregular soils. In the present author's opinion, however, a sampling error of 4-6% does not seem to be an indication of efficient sampling unless the analytical determinations show the same inaccuracy and he suggests that more samples should be taken, even to represent regular areas.

In a paper published by Kerr and Stieglitz, (16), in 1938, it is stated that the variability of soils of apparently uniform fields is so great that a representative sample must be a composite from a large number of random borings. Also, where a soil survey project is to extend over a period of years, the time of sampling must be a definite point in the rotation cycle; either at the end of the fallow period, at the beginning or at the end of the crop.

Field variations as a factor in sampling for rapid soil analyses were studied by Collins and Hodgen in 1940, (17). Tests were made on soils from uniform fields in 5 areas of North Carolina, used for growing peanuts. The fields were divided into 144 plots (1/40th acre each) and 9 samples from each plot were composited and tested for K, Mg, Ca, P and pH by a slight modification of Hester's method for rapid

soil tests. The wide variations in the results obtained on the samples from individual fields, suggest the necessity of very careful sampling of soils for rapid-test analyses.

In 1943, in Germany, Hans Riehm, (18), made a study of the most suitable type of sampling for chemical soil tests, without loss of reliability. His conclusions were that the number of samples to be taken to make a good composite sample, increases with the size of the area; the change in plantfood content during the vegetative period is slight so that one sample a year is adequate. Certain precautions must be taken after fertilization. Sampling of the subsoil is as important as sampling the surface soil; the number of samples taken and their arrangement over the area should be the same.

Less important data of work done on soil sampling are given in papers (19) to (31) inclusive.

A point inherent in all these examples on Soil Sampling is that, although all the workers agree on the point of extensive sampling for good representation of an area, nobody seems to give any standards which will be of aid to an inexperienced investigator. Furthermore, no experimental comparison between sampling data and analytical accuracy seems to be given - a relation which will be of immense value to an investigator, irrespective of the object he has in mind. The author hopes to give, with the aid of his experimental data, some discussion of this problem at the end of this thesis.

C. METHOD OF TESTING SAMPLING EFFICIENCY.

An investigator, who aims to do research on soil sampling problems, is immediately faced with the problem of choosing a suitable mode of investigation. This method should have the following vitally important characteristics:-

(a) The results, obtained by this method, should be reproducible as well as accurate so that, when treating them statistically, no doubt will exist as to their analytical precision, and any variance occurring can be confidently ascribed to soil irregularities.

(b) In view of the fact that sampling research involves the analysis of hundreds of samples, time is a very important factor when considering a suitable method of analysis. In addition to being reliable, then, the method must be short and specially adaptable for routine work.

(c) The method should be convenient and easy to perform in any chemical laboratory..

(d)The constituent to be determined should have significantly different values for different soil types.

It is obvious when considering these requirements, that no physical determination will meet the question. Although reliable results can be obtained by pH measurements, the pH value is an intensity factor and therefore not suitable. Work already done on sampling using pH as the method of investigation, (14), shows that for intensive sampling in small areas, soil pH variations are too small to be regarded as significant.

This leaves us to choose from the numerous chemical methods of analysis, and here, the three which immediately sug-

gest themselves, both from the point of view of reliability and fertility value, are those elements commonly sought for when determining nutrient values in a soil, namely nitrogen, phosphorus and potassium (N,P,K). It is readily seen that, with small alterations, the determination of these elements will successfully meet the requirements and restrictions of a suitable method to test the efficacy of soil sampling, as outlined above.

The author started out with the idea of doing all three determinations on sets of samples collected by him, but unfortunately the relatively limited time available allowed of statistical treatment based on determinations of only one constituent, potash, on the samples. It is hoped to continue with the work in 1946.

Potash was chosen as the first constituent to be determined, because preliminary work done on the three types of soil, Karroo, Humansdorp and Grahamstown, showed it to be the most variant of the three, and also, because it was present in much larger proportions than either of the other two, it was thought that it would yield the best data for the preliminary treatment now presented.

The next problem to be considered was, therefore, to choose out of the present known methods for the determination of potash, the one best adaptable and most suitable for routine soil analysis.

D. METHODS FOR THE DETERMINATION OF POTASH

(1) General :

There are three standard general procedures for the determination of potash, namely

(I) gravimetric determination as potassium chloroplatinate,

(2) gravimetric determination as potassium perchlorate, and

(3) gravimetric determination as dipotassium sodium cobaltinitrite. In the latter procedure the nitrite in the precipitate can also be determined, either volumetrically with permanganate or ceric sulphate, or colorimetrically; or the cobalt in the precipitate can be determined colorimetrically.

From the point of analytical accuracy, method (I) seems to be the best of the three, its only drawback being the expensiveness of the chloroplatinic acid used in the procedure, and the fact that all metals except sodium and all radicals like sulphate, phosphate, etc. must be absent - in fact, the precipitation can only be carried out if the potash exists as potassium chloride.

Perchloric acid, used as the precipitating agent in method (2), on the other hand, is relatively inexpensive as compared with chloroplatinic acid. Furthermore, the accuracy obtainable with this method is comparable with that of method (I), with the result that today it has come to be regarded as the standard method. Here again, the restriction that all metals and ammonium, except the alkali metals, and that all

anions except chloride should be absent,, is of practical importance.

Recently, considerable work has been done on method (3) and chemists have come to the conclusion that, with some care, results comparable in accuracy with those obtained by methods (I) and (2) may be yielded by this procedure. The precipitating agent, sodium cobaltinitrite, is fairly inexpensive, but can be obtained today in a high state of purity. Furthermore, the method can be applied in the presence of moderate amounts of other metals and radicals, the only radical which must be absent being ammonium.

A detailed outline of procedure for any of the above methods can be obtained in any modern standard text on Quantitative Analysis.

(ii) Soils :-

Method (I) described in the previous section, has become almost obsolete in modern soil analysis, due to its expensive nature and the restrictions involved by its use. Method (2) is still being used for the determination of potash in soils, but mostly for comparison tests. The fact that soils contain most of the elements in whose presence the method is valueless, makes its use rather tedious and cumbersome, as such elements have to be removed. Moreover, recent work by Mitchell and Ford in America in 1945 (32) shows that the presence of phosphate causes low results in the

potash content of fertilizers analysed by this method, and phosphates, which are invariably present in soils are difficult to remove.

Method (3), on the other hand, is extensively used in soil analysis today, and its pliable nature has many advantages over the above two when applied to routine work. Because soils are generally low in potash content, the volumetric or colorimetric analysis of the precipitate is usually preferred to the gravimetric procedure, and of these two the volumetric estimation will obviously be the safest and more accurate. The author, therefore, chose the volumetric determination of potash by sodium cobaltinitrite as his subject for critical preliminary study and for special development, for ultimate use as a means for testing the efficacy of soil sampling.

Various modifications of the cobaltinitrite method have been suggested for use in soil potash estimations, the main three having been developed,

(a) in 1934 in Australia by Piper (33),

(b) in 1937 in America by Wilcox (34), and

(c) in South Africa by Steenkamp, (3).

Each claims quantitative accuracy for his method, and the choice of any one of these methods as the most suitable was impossible before an experimental comparison of the three methods had been made. The experimental procedure for each method as outlined by the respective author, is as follows :-

(a) Piper :-

To the neutral aqueous solution containing potash (± 5 mgs. K_2O), add 6 drops of concentrated hydrochloric acid and evaporate to dryness on the waterbath. When cold take up the evaporated residue in 1.5 ml. of glacial acetic acid and 10 ml. of saturated pure sodium chloride solution, added in that order. Stir, and after 3 - 4 minutes add 5 ml. of 35% sodium nitrite (K-free). AFTER 5-10 MINS. ADD 5 ml. 20% COBALT NITRATE (K & NH_4- FREE) solution from a dipping pipette with an enlarged aperture. This addition must be made rapidly (taking not more than 2 - 3 seconds) and with constant stirring, since the desired composition of the precipitate formed depends on the rapid addition of the precipitant. Stir for 40 - 60 seconds, cover, and allow to stand overnight in a cool place.

Filter through a small gooch crucible charged with asbestos, previously digested with acidified permanganate followed by an excess of oxalic acid and then washed thoroughly with water. Transfer the precipitate to the crucible and wash, four times in all, with 8 - 10 ml. portions of 35% alcohol. Finally wash the sides of the crucible with 3 very small lots (about 2 ml. each) of cold water to remove the alcohol.

Pipette a suitable amount of 0.05N potassium permanganate into a 400 ml. beaker, dilute to about 150 ml. and add 5 ml. of concentrated sulphuric acid. Then add the

crucible and precipitate to this acidified permanganate, stir to keep the precipitate beneath the surface of the liquid and warm gently. If the colour appears likely to be discharged, remove the beaker from the flame and add a further measured amount of standard permanganate, to ensure an excess. Heat nearly to boiling, remove, and rinse the crucible and continue heating to boiling. Remove from the flame and after a few minutes add a small excess of 0.05N oxalic acid. Warm until all oxides of manganese have been dissolved and titrate the excess oxalic with standard permanganate. From this titration value the amount of K_2O present can be calculated from the formula.

$$K_2O \text{ (in mg)} = 0.354 \times \text{vol. of .05N } KMnO4 + .00034 \times (\text{vol. of .05N } KMnO_4)^2.$$

This formula was developed by Piper because the cobaltinitrite precipitate obtained in this manner is not constant but changes with change in potash concentration. If a graph of titration value is plotted against amount potash present, a curve is obtained, illustrating this fact.

(b) Wilcox :

The aliquot for analysis should contain between 2 and 15 mg. of potassium in a neutral aqueous solution of 10 ml. volume. Add 1 ml. of a normal nitric acid solution and 5 ml. of the sodium cobaltinitrite solution (containing 1 gram of A.R. Trisodium Cobaltinitrite per 5 ml., filtered and prepared fresh before use) mix, and allow to stand for

two hours. (The temperature of the solutions before mixing should be about 20°C and this temperature should be maintained during the precipitation period). Filter in a porous-bottomed porcelain filtering crucible, using 0.01N nitric acid in a wash-bottle to make the transfer. Wash 10 times with 2 ml. portions of the dilute nitric acid. Wash the precipitate into a 250 ml. beaker, place the crucible in the beaker, and make to about 100 ml. with water. Add 20 ml. of 0.5N sodium hydroxide and boil for 3 minutes. Withdraw into another beaker a slight measured excess of standard potassium permanganate (.02N), make to 50 ml. with water, and add 5 ml. of concentrated sulphuric acid. Pour the hot cobaltinitrite solution into the cold permanganate solution, transfer the crucible, and wash the beaker with a small amount of water. Add an excess of standard .02N sodium oxalate solution, heat to boiling, and complete the titration with potassium permanganate.

K_2O (in mg) = ~~17.13~~ 8.563 x ml.K MnO_4 x normality of $KMnO_4$.

The normality of the $KMnO_4$ bears a stoichiometric relation to the potash in the precipitate, $K_2NaCo(NO_2)_6.H_2O$. The reaction can be represented as follows : -

$$5K_2NaCo(NO_2)_6 + 11KMnO_4 + 14H_2SO_4 = 5CoSO_4 + 9MnSO_4 + 2Mn(NO_3)_2 + 5NaNO_3 + 21KNO_3 + 14H_2O$$

Here, 30 NO_2 or 60 reducing equivalents are balanced by 11 KMnO4 or 55 oxidising equivalents plus 5 oxidising equivalents from the cobaltic - cobaltous couple.

Therefore, 11 $KMnO_4$ or 55 equivalents are required for 10K or $\frac{10K}{55} = \frac{390.96}{55}$ = 7.1084 grams of K per equivalent of $KMnO_4$. = 8.563 grams K_2O per equivalent of $KMnO_4$.

In addition the resulting precipitate is granular, heavy, and easily filtered and washed.

(c) Steenkamp : The aliquot for analysis should be a neutral aqueous solution containing .5 - 5 mgs. K2O. Evaporate to dryness on a waterbath and add 1 ml. water to the cold residue in the beaker. Add 1 ml. of cobaltinitrite reagent (20g. sodium cobaltinitrite + 20 g. sodium acetate in 100 ml. water, filtered before use) and leave to stand for about half an hour. Insert the beaker into a Freas oven (100°c) and evaporate to dryness (40 mins). When cold add 5 ml. of 5% acetic acid, shake to completely disintegrate the precipitate and filter through a Gooch crucible well packed with specially treated asbestos; wash four times with water and replace gooch in original beaker.

Add 10 ml. of a saturated solution of sodium bicarbonate and dissolve the yellow precipitate, effecting solution as rapidly as possible on a hot plate. Rapid dissolving prevents any cobalt hydrate from precipitating, which generally happens when K_2O content is in excess of 1 mg. and the yellow precipitate is dissolved slowly. (10 ml. saturated sodium bicarbonate will dissolve 3 mg.K_2O as sodium potassium cobaltinitrite; in excess of this

quantity, relating more sodium bicarbonate must be used). A complete solution of the yellow precipitate is essential, otherwise low results are obtained.

The resulting green solution is diluted to 50 ml and allowed to cool. A slight excess of N/50 $KMnO_4$ is added (1 - 2 ml)in excess) and then slowly 10 ml. of 20% H_2SO_4 and left to stand for 20 minutes. Heat to 40°C, add 5 ml. of a 10% iodine-free potassium iodide solution and immediately titrate the liberated iodine against N/50 sodium thio-sulphate, using starch as an indicator.

In the calculation an empirical factor has to be determined owing to the fact that slight changes in the composition of the potassium precipitate occurs under different conditions. It is found from the average of several determinations carried out as above on standard potassium chloride solutions of different concentrations.

Under local conditions it was found that the true potash value is given by the following formula :-

K_2O (mg) = 8.10 x ml.$KMnO_4$ x Normality of $KMnO_4$.

A brief comparison of the three methods will now be given, pointing out the main advantages and disadvantages of each.

Points of difference between the three methods :

(1) Precipitating agent : Piper uses separate solutions of sodium nitrite and cobalt nitrate whereas Wilcox and Steenkamp each use a solution of sodium cobaltinitrite.

While the separate solutions are more stable, the author found this to be of minor importance since little time is consumed by making up the required amount of precipitant each day and filtering before use.

A much more substantial difference, however, arises from the acidifying agent which the three workers use in conjunction with the precipitant. Nitric acid, used by Wilcox rather than acetic acid (Piper and Steenkamp) maintains the nitrate-nitrite equilibrium and thereby prevents nitrite decomposition. This is a point of great value, especially in routine work, where the precipitate has often to be left in contact with the mother-liquor for some time before it can be analysed.

(2) Nature of precipitate. In contrast to the extremely fine precipitate obtained by using Piper's method, a heavy, granular and easily filtered precipitate is obtained by using either of the other two methods. This is due to the addition of nitric acid in Wilcox's procedure, and to the evaporation to dryness after precipitation in Steenkamp's procedure.

Piper's precipitate has a variable composition which depends upon the potash concentration, whereas there is a definite stoichiometric relationship between the potash in Wilcox's and the normality of the permanganate used to titrate it. Steenkamp's precipitate also has a variable composition; its composition varies, however, not with the

potash concentration, but apparently with locality and with the actual reagents used. Wilcox's calculation for potash is therefore extremely simple as compared with the other two, where empirical factors have to be checked frequently. For routine analysis carried out over a considerable period of time, as will necessarily be the case when tackling sampling problems, the method of Wilcox would therefore seem to be much more reliable and quicker in use than either of the other two.

(3) Volumetric analysis of precipitate : The iodometric method of titration used by Steenkamp has been found to be much simpler and more reliable in actual use than the methods used by either of the other two. This is probably due to the very sensitive endpoint which can be obtained and to the atmosphere of carbon dioxide present during the titration. Furthermore, on dissolving the precipitate in saturated sodium bicarbonate, a green solution is obtained whose stability is of special importance in routine work where solutions have to be left standing for various periods before titration.

(4) Time factor : The time of precipitation by Piper's method is approximately 12 hours, by Wilcox's method 2 hours, and by Steenkamp's method about 1½ hours (including the time of evaporation). A big difference, therefore, exists between the length of Piper's procedure and that of the other two, a difference which is a real drawback for routine work where time is of paramount importance.

(5) Economy : The only disadvantage of Wilcox's method is that rather a lot of sodium cobaltinitrite reagent is used (1 g. per determination).

It therefore appeared that the method of Wilcox should be the obvious one for the work which the author had in mind. It remained to be seen, however, how it compared experimentally with the other two and this will be reported upon in the next section.

The author has introduced a few useful alterations into Wilcox's method. He dissolves the precipitate, not in caustic soda, but in 20 ml. saturated sodium bicarbonate and continues the subsequent titration as described by Steenkamp. Also, instead of using 20% sulphuric acid for acidifying the bicarbonate solution, he uses 10 ml. 50% H_2SO_4 which has been freed from SO_2. This is made by treating 50% H_2SO_4 with dilute permanganate drop by drop till a faint pink colour persists in the solution. It was found that strong sulphuric acid contains a fair amount of SO_2 which may cause an error in the potash value unless it is removed. A few improvements in general practical manipulation have also been introduced and will be later mentioned/in the full description of the procedure as applied to soils. It is to be borne in mind that, from this stage onwards, wherever mention is made of the Wilcox method, the method as modified by the author is being referred to.

E. EXPERIMENTAL COMPARISON OF THE THREE POTASH METHODS.

The three methods were tried out, side by side, on standard potassium chloride solutions of ten different concentrations ranging from 0.5 to 5 mg. K_2O per aliquot. It was considered essential that the potash content of the standard solutions should be known as exactly as possible if valid comparisons of reproducibility of the methods were to be made. The methods employed were as follows : A sample of potassium chloride (A.R.), recrystallised six times, was available. A suitable quantity of this was fused in a platinum crucible and kept in a desiccator. A weighed quantity (1.583g.) of this potassium chloride was dissolved in water and made up to 1 litre (in duplicate). The potash content of these two solutions was next estimated by three standard methods :

(1) Gravimetric estimation as silver chloride (35). It is essential to exclude light while doing the experiment because of the light-sensitivity of silver chloride.

(2) Volumetric estimation by titration with silver nitrate using dichlorofluorescein as adsorption indicator (36).

(3) Potentiometric estimation by titration with silver nitrate (37).

The means of a number of determinations by each method are given below :

Method	K$_2$O/litre(g)	Mean
Weighing (KCl)	1.5827	
Gravimetric (AgCl)	1.580	1.583
Volumetric (Ads.Ind.)	1.583	≡ 1.000 g.K$_2$O
Potentiometric	1.584	

125 ml. of this stock standard potash solution was then run into a 500 ml. volumetric flask and made up to the mark with distilled water. 10 ml. of this diluted solution contained 2.5 mg.K_2O and was used in the comparative tests of the three potash methods.

The next important question to be considered was the standardisation of the volumetric solutions to be used in the experimental procedure, viz. potassium permanganate sodium thiosulphate and sodium oxalate. Stock solutions of approximately N/50 strength were made up of each and kept in dark coloured glass aspirators. It was found that the addition of 2 ml. of chloroform per 5 litres of the thiosulphate solution so far retarded its decomposition that it maintains its effective strength even up to 1 month. The solutions were standardised as follows :-

N/50 $KMnO_4$:- Dried sodium oxalate (British Chemical Standards : purity 99.97%) was used as primary standard and the method followed was as supplied by the Bureau of Analysed Samples :-

15 ml. oxalate solution is run into a titration flask containing 20 ml. "SO_2-free" 50% H_2SO_4, heated to 80°C, and

and permanganate run in at the rate of 12 to 14 ml. per minute, swirling vigorously all the time. Near the end-point the titration is continued drop by drop till a faint pink persists for 30 seconds. The final temperature should not be below 60°C. Repeat every fortnight.

N/50 Sodium Oxalate: Standardised against standard permanganate using the above procedure.

N/50 Sodium Thiosulphate : The standardisation was carried out using the procedure of Scully (38), by means of dried (140°C) potassium dichromate (A.R. Grade). Copper is employed as a catalyst and the use of a mineral acid with potassium iodide is avoided. The method, which is more rapid and accurate than the customary procedure, is as follows :

To 20 ml. of standard $K_2Cr_2O_7$ solution in a titration flask add 5 ml. each of glacial acetic acid and N/1000 $CuSO_4$, and wash down the sides of the flask with 20 ml. water. Add 15 ml. of 10% potassium iodide and titrate the iodine as it is liberated with sodium thiosulphate, adding a little freshly-made starch towards the end. The temperature should be about 20°C and in any case not higher than 25°C so that oxidation of the I^- by atmospheric oxygen may be minimised. The endpoint, when once reached, is stable for a long time and no difficulty is experienced in working to a fraction of a drop if a second flask

containing the previous titration with an excess of $Na_2S_2O_3$ is used for comparison. A blank of 0.05 ml. must be subtracted from the titration reading ($Na_2S_2O_3$) to allow for the iodine liberated by the $CuSO_4$ catalyst. The colour at the endpoint is slightly greenish, that of the copper acetate complex. The normality is checked against the standard permanganate. Repeat every fortnight.

The figures for the solutions used are as below :

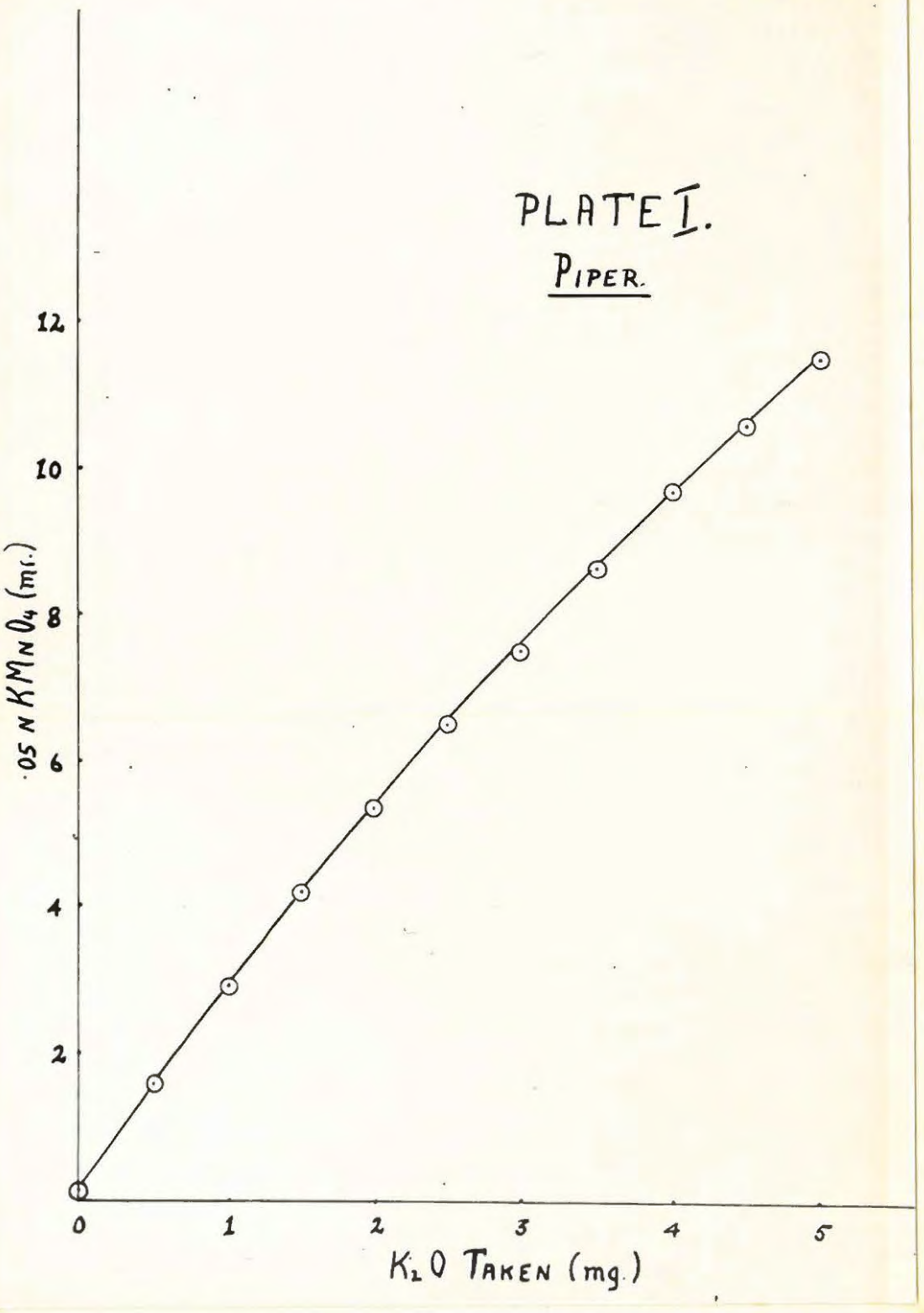
Solution.	Complete duplicate standardisation		Mean Normality.
	Normality A.	Normality B.	
$KMnO_4$(1)	0.02030	0.02029	0.02029 N
$KMnO_4$(2)	0.02234	0.02236	0.02235 N
Sodium Oxalate	0.02005	0.02005	0.02005 N
$Na_2S_2O_3$	0.01963	0.01965	0.01964 N

Two different solutions of permanganate were used at different stages of the work.

The comparison trials were next carried out on the three methods for the determination of potash. In each case a few blank controls were run to correct for the minute quantities of potash invariably present in the reagents. Potash on 10 different concentrations of the standard Kcl solution (10 ml. = 2.5 mg. K_2O) was determined, ranging from 0.5 - 5.0 mg. K_2O. Ten replicates were done on each concentration for each method, giving 300

PLATE I.

PIPER.



determinations, 100 for each method. Special care was taken to keep strictly to detail, and, as far as possible, conditions for each method were kept the same.

In tables I, II, and III are given the means of each set of ten titration values for each concentration.

TABLE I. (PIPER)

Normality of ± N/50 $KMnO_4$ = .02029 from 1-7
(Blank = .016 mg.K_2O)
and = .02292 from 8-11 (Blank = .016 mg.K_2O.

No.	K_2O taken (Mg.)	$\pm N/50$ $KMnO_4$ (ml.)	$=N/20 KMnO_4$ (ml.)
1.	0.00	0.12	0.05
2.	0.50	4.01	1.63
3.	1.00	7.15	2.90
4.	1.50	10.42	4.23
5.	2.00	13.01	5.28
6.	2.50	16.07	6.52
7.	3.00	18.59	7.54
8.	3.50	18.78	8.61
9.	4.00	21.13	9.69
10.	4.50	23.15	10.61
11.	5.00	25.16	11.53

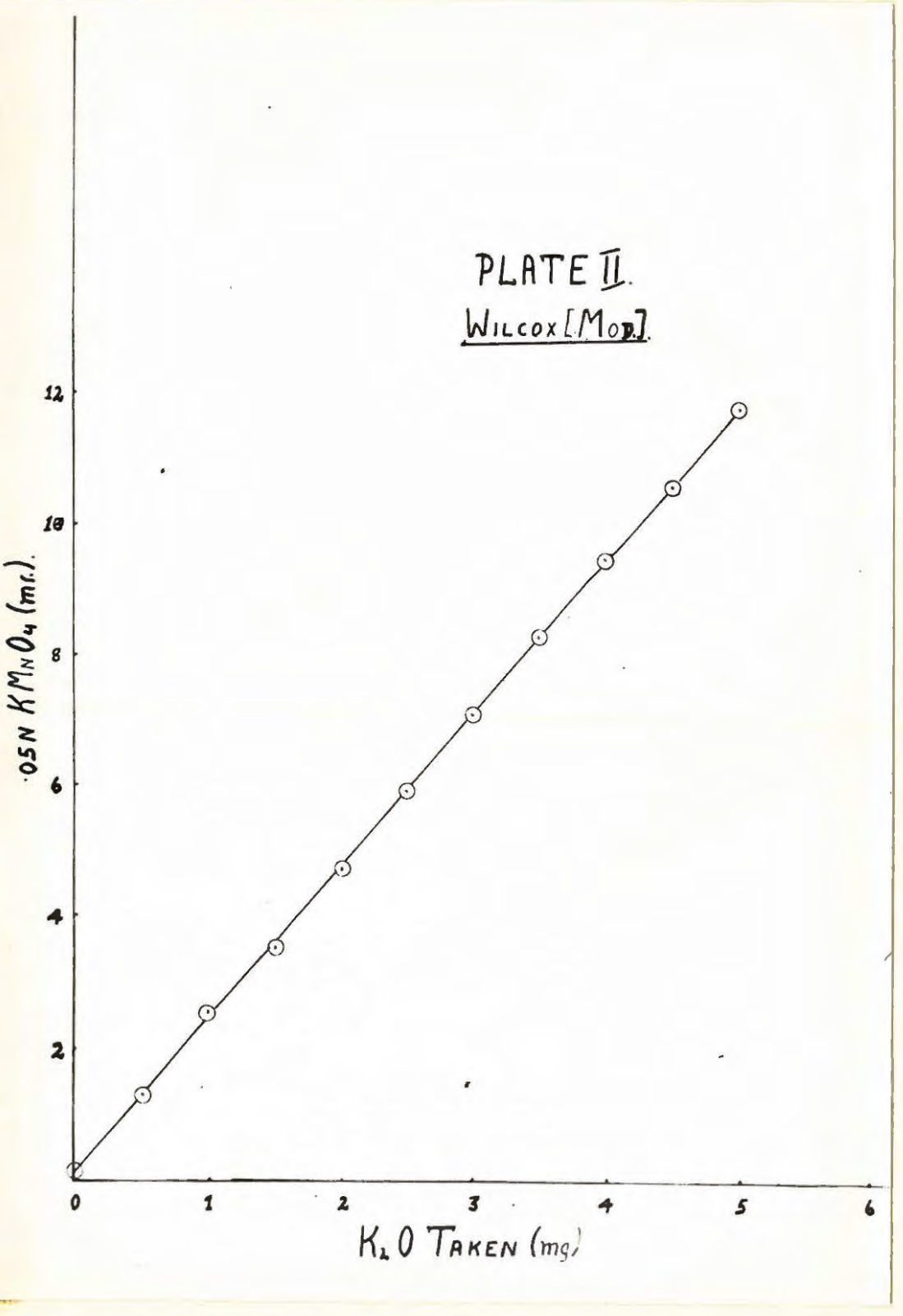
When a graph of K_2O taken (Mg.) is plotted against ml.05N $KMnO_4$ a curve is obtained as shown in Plate 1. This curve can be fitted with the general equation $y = ax^2 + bx$ and Piper obtained, for conditions under which he worked, values of a = .00034 and b = .354, giving the equation for the potash content as

K_2O (Mg.) = .00034 (Permanganate value)^2 +.354 (perm.value)

(Permanganate value = volume of .05N $KMnO_4$ required to oxidise the precipitate).

PLATE II.

WILCOX [Mod.]



It was found that this equation does not hold for the above results although the smoothness of curve I proves the author's experimental work to be correct, but suggests another equation. On this assumption, another equation was developed by the method of Least Squares, giving a = .009 and b = .3305. On calculating the potash content by the equation

K_2O (Mg.) = .3305 (Perm.value) + .009 (Perm. value)^2

accurate results were obtained (See Table IV).

TABLE II (Wilcox,Mod.)

Normality of ± N/50 $KMnO_4$, 1-4, 8-11 = .02029N } (Blank
5 - 7 = .02292N } = .048Mg.K_2O)

No.	K_2O Taken (Mg.)	± N/50 $KMnO_4$(Ml)	= N/20 $KMnO_4$(ml)
1.	0.00	0.28	0.11
2	0.50	3.29	1.34
3	1.00	6.30	2.56
4	1.50	8.73	3.54
5	2.00	10.26	4.70
6	2.50	12.83	5.88
7	3.00	15.48	7.09
8	3.50	20.42	8.29
9	4.00	23.48	9.55
10	4.50	26.26	10.65
11	5.00	28.99	11.77

Graph II of K_2O taken (mg) vs. ml. .05N $KMnO_4$ shows a straight line and proves the consistent composition of the precipitate. The potash is calculated by the equation,

K_2O (mg) = 8.563 x ml. $KMnO_4$ x normality of $KMnO_4$.

PLATE III.

STEENKAMP.

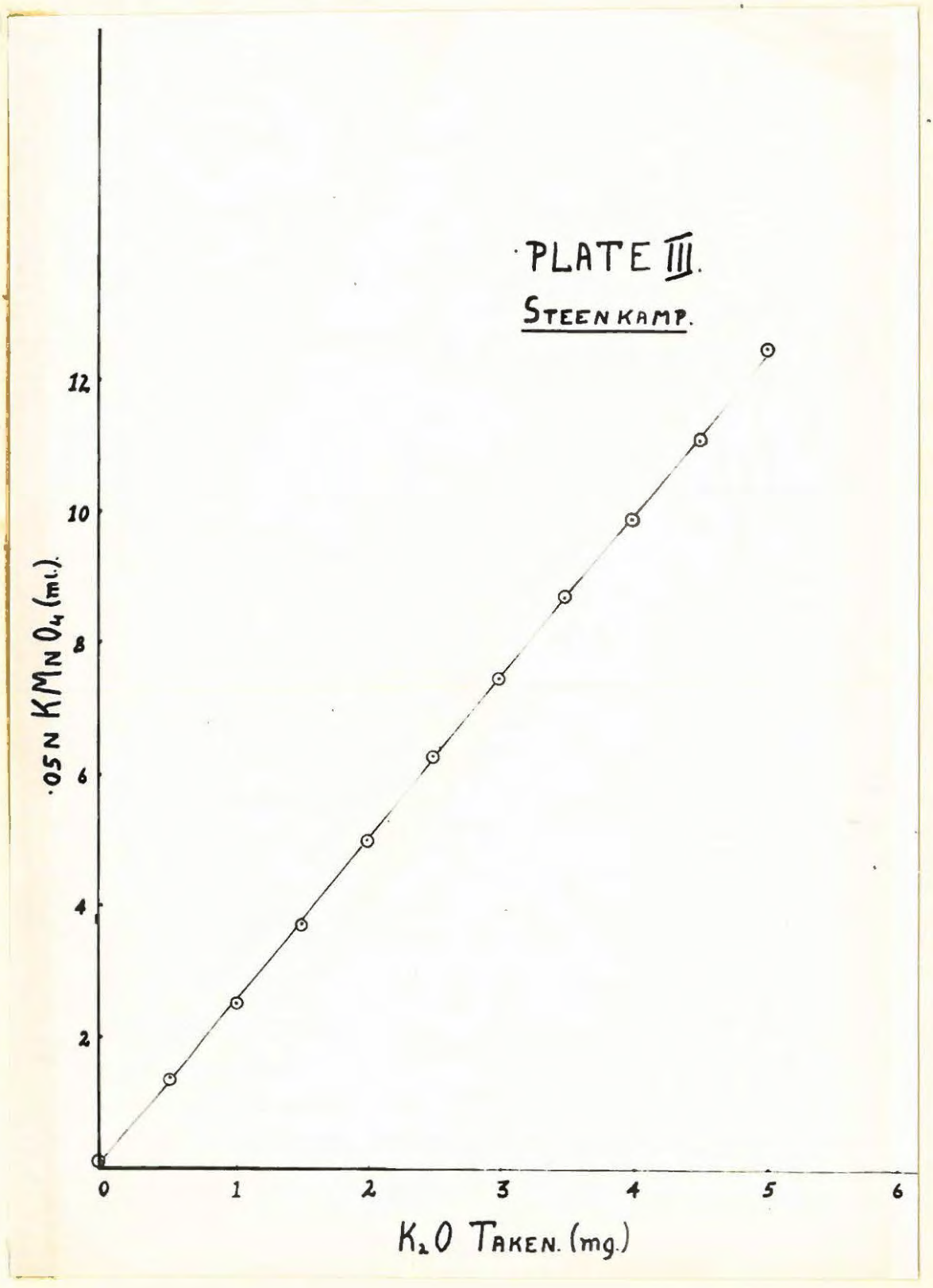


TABLE III (Steenkamp)

Normality of ± N/50 $KMnO_4$, 1 - 4, 8 - 11 = .02029N -
5 - 7 = .02235N

(Blank=.035mg.K_2O)

No.	K_2O Taken (mg)	±N/50KMn04(ml.)	= .05N Kmn04 (ml)
1	0.00	0.20	0.10
2	0.50	3.43	1.39
3	1.00	6.31	2.56
4	1.50	9.20	3.73
5	2.00	12.25	4.97
6	2.50	14.00	6.26
7	3.00	16.71	7.47
8	3.50	21.36	8.67
9	4.00	24.37	9.89
10	4.50	27.48	11.15
11	5.00	30.77	12.48

Graph III being also a straight line shows that the composition of the precipitate is constant. An empirical factor has, however, to be introduced because the precipitate has a composition which is slightly different from that corresponding to the formula K_2 Na CO $(NO_2)_6H_2O$. Steenkamp found the value of the empirical factor to be 7.69 for the conditions under which he worked,

i.e. K_2O (mg) = 7.69 x ml. $KMnO_4$ x Normality of $KMnO_4$

To determine the empirical factor the average of several determinations on standard potassium chloride solutions is taken. Under local conditions the author found the value of the factor to be 8.100,

i.e. K_2O (Mg) = 8.100 x ml.$KMnO_4$ x Normality of $KMnO_4$.

In Tables IV, V and VI the means of the potash found

for each concentration, for the three methods, are given, as well as the standard error and the standard error of the mean.

A = Arithmetic mean of the potash found (10 replicates)

S = Square root of the sum of the squared deviations of potash found from potash taken (10replicates).

= Standard Error for each determination.

S.M. = Square root of the sum of squared deviations of potash found, from the mean (A) (10 replicates)

= Standard error for the deviation from the mean.

TABLE IV (PIPER)

No.	K_2O Taken(mg.)	A (mg)	S	S.M.	%S	%S.M
1.	0.50	0.545	.04995	.02128	10.0	4.0
2.	1.00	1.009	.03361	.03241	3.5	3.0
3.	1.50	1.542	.05590	.03617	3.3	2.3
4.	2.00	1.979	.04906	.04430	2.5	2.2
5.	2.50	2.521	.04679	.04159	1.8	1.6
6.	3.00	2.992	.06090	.06650	2.0	2.2
7.	3.50	3.496	.05530	.04715	1.6	1.4
8.	4.00	4.024	.03614	.02641	0.9	0.7
9.	4.50	4.501	.08090	.08080	1.8	1.8
10.	5.00	4.994	.09330	.07850	1.9	1.6
Mean			.05618	.04751	2.25	1.90

S.

PLATE IV.

REPRODUCIBILITY.

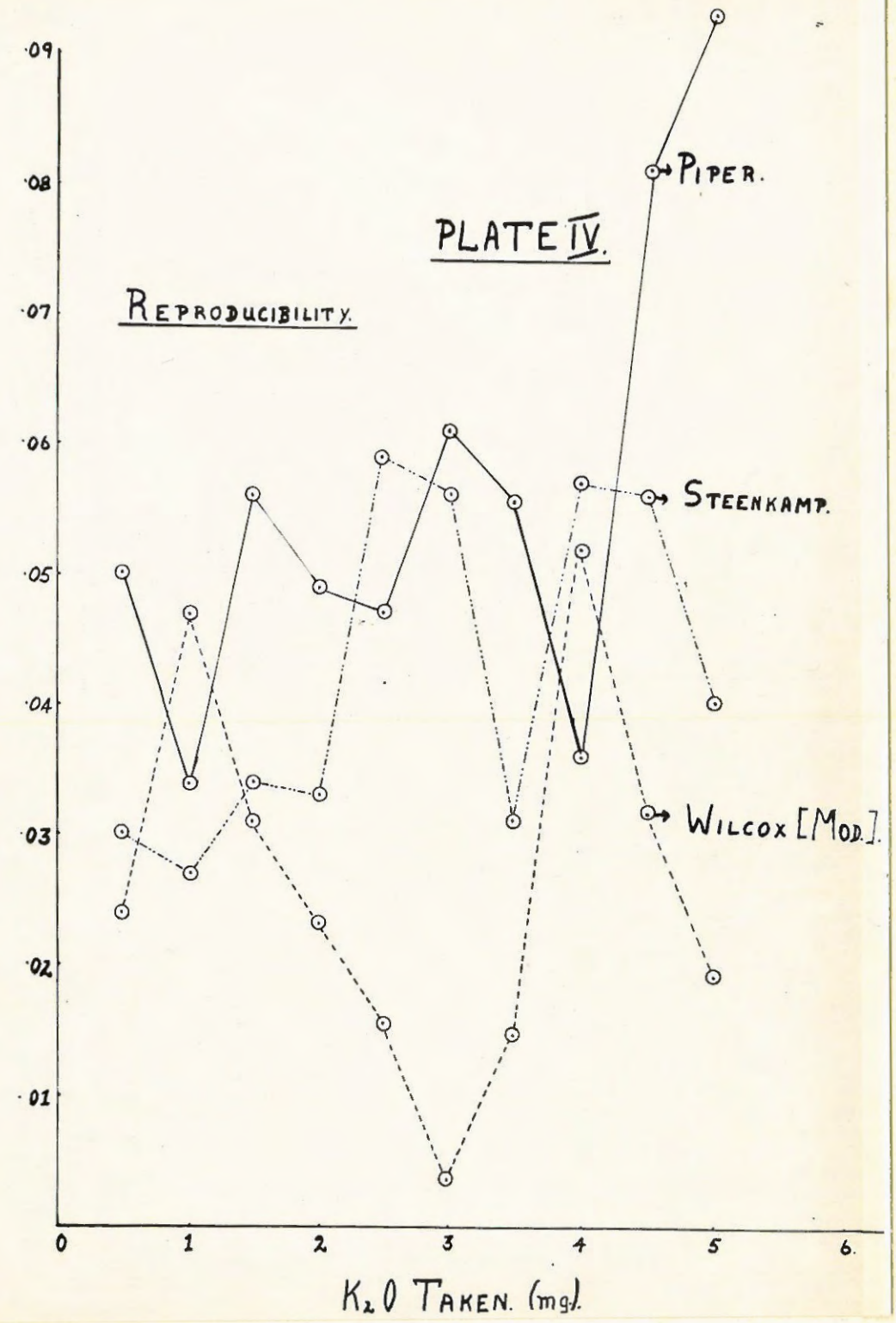


TABLE V (WILCOX MOD.)

No.	K_2O taken (mg)	A (mg)	S	S.M.	% S.	% S.M.
1	0.50	0.523	.02384	.00610	4.7	1.2
2	1.00	1.047	.04711	.00403	4.7	0.4
3	1.50	1.469	.03124	.00678	2.1	0.4
4	2.00	1.977	.02324	.00448	1.1	0.2
5	2.50	2.490	.01569	.01230	0.6	0.5
6	3.00	3.002	.00353	.00324	0.1	0.1
7	3.50	3.512	.01463	.00719	0.4	0.2
8	4.00	4.046	.05185	.02244	1.3	0.5
9	4.50	4.528	.03174	.01476	0.7	0.3
& 10	5.00	5.002	.01885	.01872	0.4	0.4
	Mean		.02617	.01000	1.05	0.4

TABLE VI (STEENKAMP)

No.	K20 Taken (Mg.)	A (mg)	S	S.M.	%S	%S.M.
1	0.50	0.528	.02980	.00785	6.0	1.6
2	1.00	1.002	.02707	.02699	2.7	2.7
3	1.50	1.478	.03411	.02671	2.3	1.8
4	2.00	1.979	.03324	.02560	1.6	1.3
5	2.50	2.499	.05910	.05950	2.4	2.4
6	3.00	2.990	.05625	.05590	1.9	1.8
7	3.50	3.476	.03081	.01945	0.9	0.6
8	4.00	3.970	.05695	.04864	1.4	1.2
9	4.50	4.482	.05600	.05320	1.2	1.2
10	5.00	5.023	.03990	.03131	0.8	0.6
	Mean		.04232	.03551	1.70	1.42

In Table VII the results of the means of the three methods are given.

TABLE VII.

No.	Method	S	S.M.	%S	%S.M.
1.	Piper	.05618	.04751	2.25	1.90
2.	Wilcox (mod)	.02617	.01000	1.05	0.40
3.	Steenkamp	.04232	.03551	1.70	1.42

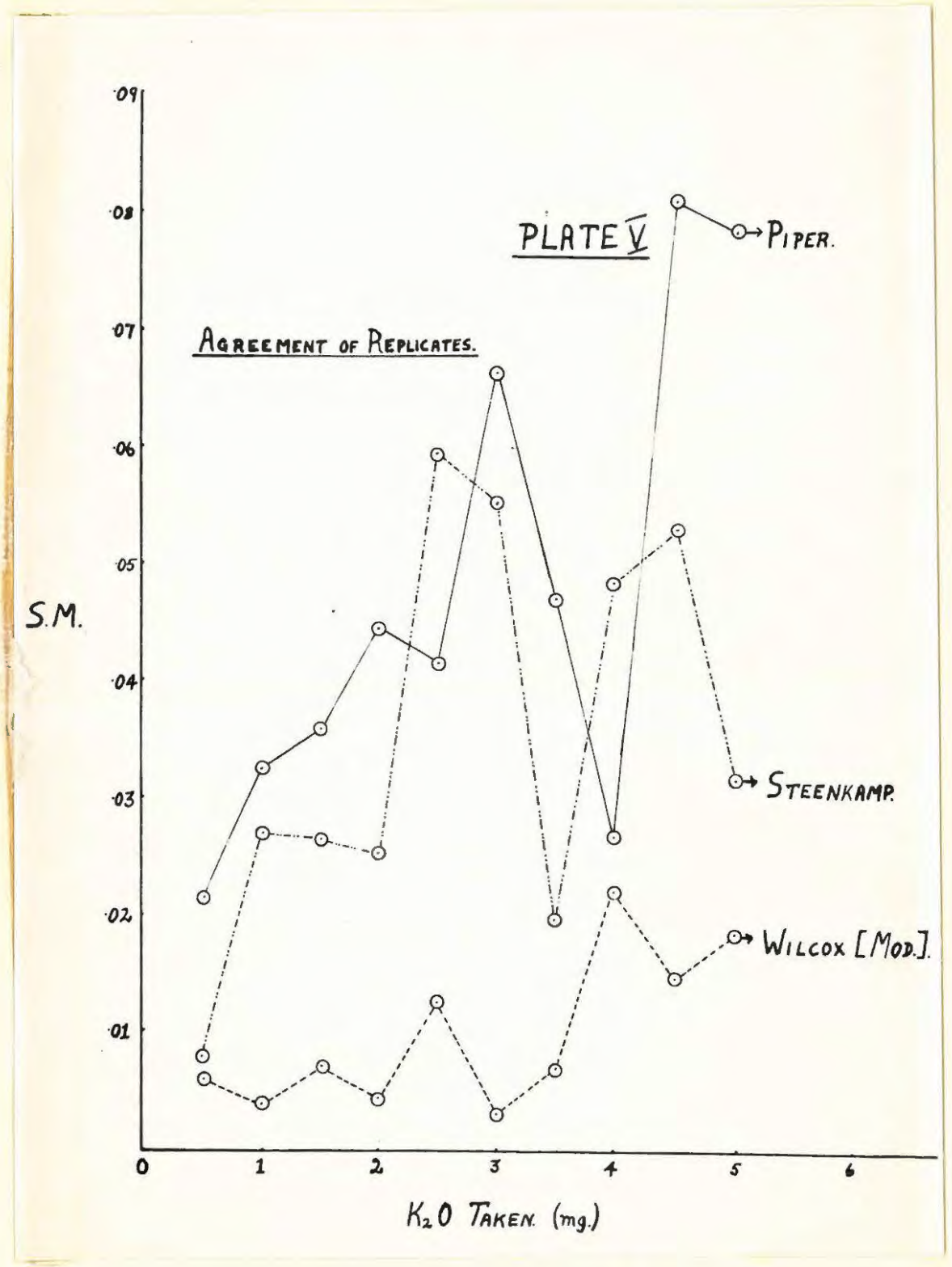


PLATE V
AGREEMENT OF REPLICATES.
PIPER.
STEENKAMP.
WILCOX [MOD.].
S.M.
·09
·08
·07
·06
·05
·04
·03
·02
·01
0
1
2
3
4
5
6
K₂O TAKEN. (mg.)

DISCUSSION : In the foregoing tables the values of S also give the reproducibility of the results, while S.M. is an indication as to the agreement between replicates. Graphs IV and V are curves of S. and S.M. plotted against the concentration of potash in milligrams and serve as good illustrations of the differences between the methods.

It is clear from Table VII that the modified method of Wilcox is much superior to the other two, both from the point of reproducibility as well as from the agreement of replicates. In fact, the standard error of .4% in the difference between replicates when the total potash content is only .0025 grams shows that the method can hold its own in comparison with other general analytical procedures of high precision. The fairly large error when the potash concentration was low, is not surprising when it is remembered that the total potash content is only .0005 grams as K_2O.

In the light of the theoretical consideration of the methods and on the grounds of the experimental evidence summarised in the preceding tables, the method of Wilcox, as modified by the author, was definitely chosen as being the best of the three for use in tests of sampling efficacy.

To show that a similar order of accuracy is obtainable on actual soils, some experimental data of analyses done on soils of different types will be reported.

(See end of section G.)

The only question which still remained to be

settled before tackling the actual samples and sampling procedure, was the preparation of soil extracts and the choice of the method of extraction of the potash. This problem will be dealt with in the next section.

F. PREPARATION OF SOIL EXTRACTS.

There are two widely different methods whereby the constituents for analysis can be extracted from a soil, viz.

(I) Hydrochloric acid extraction.

(2) Fusion with sodium carbonate in a Lawrence Smith platinum crucible.

Method (I) only gives a fraction of the total potash present, because some of the potash in soils exists in insoluble complex silicate forms, whereas method (2) gives the total amount of potash in the soil. From the point of view of plant-food value, the extraction of potash by method (2) is of little or no real value to the soil scientist and this procedure is mostly used for the purposes of soil surveys. Moreover, the present-day cost of Platinum crucibles is high and since for any satisfactory speed of working to be obtained, at least ten crucibles were considered to be necessary for this work. This raised an economic obstacle which was more than enough to dissuade the author from further considering this method as a possibility for his work. Some tests were therefore made on the hydrochloric acid method of extraction.

HYDROCHLORIC ACID EXTRACTION : At one time a lot of controversy existed with regard to the hydrochloric acid extraction of soils, and it was thought that the method could discriminate between the weathered and unweathered minerals present. However, it is realised today that

potash values obtained by hydrochloric acid extraction are entirely empirical ; it does not differentiate between the different categories of minerals present and the amounts brought into solution depend on such factors as the strength of the acid, the time of digestion, and the degree of sub-division of the soil. Except for the determination of potash and phosphoric acid, this method is now used only occasionally.

The amount of potash extracted varies considerably with the time of the digestion and increased amounts are still obtained after five days of digestion. Even this prolonged digestion does not give the total potash present. However, after 24 hours digestion, the amounts of potash remaining to be extracted are small and seem to have a fairly constant relation to the total. Most text-books recommend 48 hours of digestion because nearly all the early experimental data were based on this period of digestion. The author considers this to be a point which must be arbitrarily decided upon by the investigator with a bearing upon the object he has in mind. If anything like consistent values are obtained with 24 hours digestion, the author will definitely choose this much shorter period, since his research is concerned less with the total potash in the soil than with the variation of the potash in the samples.

With this object in mind, the following experiment was carried out :-

Three samples, all of distinctly different soil types, were digested with constant boiling-point hydrochloric

acid for 24 hours and 48 hours respectively in a boiling waterbath. Five replicates were done in each case on fresh subsamples of each soil type. Potash was determined in the extracts using the procedure to be fully described later in this thesis. The results are given in Table VIII: -

TABLE VIII

No.	Time of Digestion	% K_2O Humansdorp	Grahamstown	Venterstad
1	24 hours	.0555	.138	.514
2	- -	.0550	.137	.514
3	- -	.0550 .0552	.139 .138	.516 .5154
4	- -	.0555 ±0.0002	.138 ±0.0002	.515 ±0.0010
5	- -	.0550	.138	.513
6	48 hours	.0680	.165	.600
7	- -	.0685	.164	.602
8	- -	.0685 .0683	.164 .164	.603 .602
9	- -	.0680 ±0.0002	.165 ±0.0005	.601 ±0.0011
10	- -	.0685	.164	.602
Increase in K_2O after 24 hrs.		.013	.026	.088
Increase in K_2O as % of total.		19%	16%	15%

It is evident from the above table that, although much less potash is extracted in a period of 24 hours as compared

with a digestion period of 48 hours, the closeness of agreement between replicate extractions is of the same order for both periods. This is obvious, considering that less than 1% of the total potash comes into solution for every extra hour of digestion continued after a period of 24 hours, and no serious error in replicate samples can be encountered if conditions are kept the same throughout the procedure. Based on the experimental evidence presented in Table VIII, and also because of the appreciable amount of time to be saved thereby, the author decided to use the shorter period of 24 hours as the time of digestion for the soil samples in the research to follow.

Another point of importance arising out of the preparation of the hydrochloric acid extract of soils, is the washing of the soil after removal of the extract by filtration. Personal experience showed that after four washings enough potash still remained in the soil to cause serious errors. Six washings, with ±10ml. boiling water each, were found by experiment to be ample for three different soil types. To determine if any potash remained in the washed sample, it was boiled with water for 10 minutes, filtered, and potash estimated in the filtrate.

In Table IX the results of some of the tests performed on different soils by the author, are given. The three soil types are widely different in physical texture and general character and are generally representative of

soils which may be encountered in South Africa.

TABLE IX

Soil type	Sample No.	Times of washing	%K_2O left	%age error
Humansdorp	1	4 times	.00420	8%
Clayey with lot of fine silt.	2	5 "	.00072	1
	3	6 "	.00024	0.5
Grahamstown	4	4 "	.0045	3
Medium to	5	5 "	.0015	1
heavy	6	6 "	.0003	0.2
Venterstad	7	4 "	.0060	2
Light, rather	8	5 "	.0028	1
sandy	9	6 "	.0006	0.1

The difference between the Humansdorp soil and the other two is probably due to the fact that it is heavier and filters much more slowly. It therefore tends to cling to the potash. The weight of the samples used in the extractions was 12.5 grams in each case with 100 ml. hydrochloric acid. If bigger soil weights are used more washing will be necessary. The ratio of soil weight to volume hydrochloric acid should always be roughly 1:10. Below is the detailed procedure for the hydrochloric acid extraction method as used by the author :

Weigh out 12.5 grams of soil in a 250 ml. erlenmeyer flask. Add 100 ml. concentrated C.P. hydrochloric acid, cover with a glass-bulb or watch-glass and boil for 5 minutes on a hotplate in the fume chamber to bring the hydrochloric

acid to constant boiling point. Then stand the flask on a tray in a boiling waterbath for 24 hours continuously. The level of the water in the bath must be a little above that in the flask. After the required time of digestion has elapsed, cool and add 20 ml. cold water to dilute the acid for filtration. Filter through a Whatman No.40 filter paper into a 250 ml. beaker. Wash the soil once by decantation with hot water and then transfer the whole onto the filter paper. Wash the soil six times with $\pm$ 10 ml. portions of boiling water, allowing the filter to drain completely before each washing. (In some soils during washing, when the HCl concentration in the soil has dropped almost to zero, deflocculation of the small particles may occur with the result that they may pass through the filter. In such cases use a wash-liquor of 0.01N HCl.) Cool the filtrate and make up to 250 ml. with distilled water in a volumetric flask. Aliquots of this filtrate are used for the determination of potash.

G. TREATMENT OF THE HCl EXTRACT FOR POTASH DETERMINATION.

The hydrochloric acid extract, as prepared in Section F, cannot be directly treated with sodium cobaltinitrite for the precipitation of potash, due to interference from the relatively high proportions of iron, aluminium and silica which may be present. These three constituents do not, however, present any great difficulty in removal, for they are easily rendered insoluble on conversion to the oxide by heating. Organic matter also interferes.

The usual method given in textbooks (e.g. Piper,(39)) is to ignite the residue to dull red heat over a flame, after evaporation of the required aliquot to dryness on the water-bath. Personal experience showed this procedure to be quite unsafe and unsatisfactory in respect of reproducibility. Apart from the fact that no two samples can be heated to the same temperature, the danger always exists that some samples may be overheated, potash then being lost by volatilisation. Furthermore, it was found that for most samples heating to dull-redness was not sufficient because in numerous cases, when the residue, after ignition, was extracted with water and filtered, the filtrate still came through coloured and cloudy, a condition entirely unsuitable for satisfactory precipitation with cobaltinitrite.

The author overcame this difficulty by using an electric muffle furnace for ignition of the residue. It was found that by heating to $\pm 400^{\circ}C$ for 10 minutes, the iron and aluminium salts are rendered insoluble in water and the organic matter is completely destroyed. This temperature

is still a considerable distance from dull-red heat, but the evenly-distributed heat is far more effective than the localised heating of a burner. Furthermore, no measurable amount of potash volatilises at this temperature. It was also found advisable to dry the residue in an electric oven at 120-140 C for about one hour before putting it into the furnace. This dehydrates the silica and prevents it from going into solution.

Most textbooks advise the destruction of the organic matter in the extract by adding a few drops of concentrated nitric acid before the evaporation on the waterbath is complete. This, however, gives rise to much spluttering, and when the residue is ignited, it froths up in a spongy mass which is very difficult to heat to the correct temperature. It was found by experiment that this addition can, with advantage, be neglected if the residue is ignited in a furnace at 400 C for 10 minutes, the organic matter being destroyed or rendered insoluble at this temperature.

The advantages of the furnace over an ordinary burner are that the heat is evenly distributed over the whole area, and that in routine analysis every sample can be ignited for the same time under the same conditions and at a safe temperature.

Another important point in the subsequent extraction of the potash from the residue with water, is that enough calcium salts must be present to prevent any potash from remaining in the residue in an insoluble form. Sufficient washing of the residue during filtration is also important and it was found by experiment that six washings with $\pm$ 4ml. of boiling water were sufficient.

A detailed description of the complete analysis of a hydrochloric acid extract of a soil sample, as used by the author, can now be given.

Volumetric Determination of Potash in Soils:

Reagents :

(1) Sodium Cobaltinitrite : Prepare an aqueous solution, containing 1.0 g. trisodium cobaltinitrite of reagent quality per 5 ml. of solution. Filter before use. A fresh solution should be made for each set of determinations.

(2) Sodium Bicarbonate (about saturated) : Dissolve 96 grams C.P. $NaHCO_3$ in 1 litre of distilled water. Filter.

(3) Potassium Iodide (10%) : Dissolve 100 grams KI in water and dilute to 1 litre. Before use, remove any trace of free iodine with a drop or two of thiosulphate.

(4) Sulphuric Acid (50%), SO_2-free : Add carefully, with stirring, 500 ml. concentrated H_2SO_4 to 500 ml. water. Cool and bring to faintly pink with N/50 $KMnO_4$ solution.

(5) Starch (0.1%) : Bring 500 ml. distilled water to the boil. To 0.5 g. soluble starch in another beaker, add sufficient cold water to make a thin paste. Add to the boiling water with stirring and continue to boil for a few minutes. Cool to $\pm$ 60°C and pour into a dark-coloured, rubber-stoppered bottle. This can be used for 1 month if kept in a cool, dark place.

(6) Asbestos : Place a suitable quantity of gooch asbestos (Merck or Kahlbaum was used) in a large porcelain basin. Add a few permanganate crystals and enough 20%

H_2SO_4 to cover the lot. Digest on a boiling waterbath for ± 3 hours. Wash the brown mass with water to remove the excess $KMnO_4$, add excess oxalic acid and dilute HCl and heat on the waterbath till the mass is white. Wash the asbestos thoroughly with hot water until free from acids, using a Buchner funnel and suction pump. It can be used repeatedly.

(7) Standard Thiosulphate (N/50) : Dissolve 3.25 g. $Na_2S_2O_3.5H_2O$ (A.R. grade) in water and make to 5 litres. Add 1 ml. chloroform which keeps the solution stable. Standardise by two different methods and check the normality every fortnight.

(8) Standard Permanganate (N/50) : Dilute a normal solution of $KMnO_4$ to N/50. Standardise by two different methods, repeating fortnightly.

Analytical Procedure : Pipette an aliquot of the HCl extract, containing ± 2.5 mg. K_2O, into a 100 ml. porcelain basin. Add 10 drops of a 4% solution of $CaCO_3$ (A.R.) in dilute HCl, to assist in the subsequent potash extraction. Evaporate the contents of the basin to complete dryness on a boiling water-bath in a fume chamber. Place the basin in an electric oven at 140°C. and dry further for about one hour, to dehydrate the silica. Transfer to an electric furnace at 400°C. and ignite for 10 minutes. Cool, and grind the residue to a fine powder with a glass rod. Add 10 ml. hot water, stir well and finally rinse the rod into the basin with 1 or 2 ml. hot water. Bring the contents of the basin to incipient boiling on a hot-plate, filter into a 150 ml. beaker, (ordinary filter paper may be used) transfer the residue to the filter with hot water

from a wash-bottle, and finally wash the residue six times with 4 ml. portions of boiling water, giving about 60 ml. of filtrate.

Evaporate the filtrate carefully to dryness on a hotplate, cool, add 10 ml. water and 1 ml. N. Nitric acid (A.R.) and mix well by swirling. Bring the contents of the beaker to ± 20°C, add 5 ml. sodium cobaltinitrite reagent (20°C) / mix and leave to stand for two hours. Filter through a gooch crucible, well-packed with specially treated asbestos, using 0.01N nitric acid in a wash-bottle to make the transfer. Wash 10 times with 2 ml. portions of the dilute nitric acid. With the help of a glass-rod, transfer the asbestos with the precipitate to the original beaker. Wash the gooch with 20 ml. hot saturated sodium bicarbonate solution, allowing the washings to drip into the beaker. Leave the glass-rod in the beaker. Immediately bring the contents of the beaker to the boil on a hotplate so as to dissolve the precipitate as quickly as possible, preventing any cobalt hydrate from forming. Dilute the resultant green solution to 50 ml. with water and cool.

Add a slight excess of N/50 potassium permanganate (± 15 ml. for 2.5 mg. K20) from a burette, and, slowly, 10 ml. 50% H_2SO4 (Be careful to avoid excessive frothing.) Leave for about 20 minutes, heat to 40°C, add 5 ml. 10% KI solution and immediately titrate the liberated iodine with N/50 sodium thiosulphate, using a micro-burette. Add starch near the end-point. The "flashing back" of the

blue colour after the endpoint has been reached is considerably retarded, owing to the carbon dioxide atmosphere present.

The potash in the aliquot is found from the equation K_2O (mg.) = 8.563 x ml. $KMnO_4$ required to oxidise the ppt. x normality of $KMnO_4$. Before proceeding to the analysis of the actual samples taken for sampling research, the above method was finally put to the test on four soil samples collected at Grahamstown and neighbouring vicinities. The experimental results are given in Table X. The potash in each sample was first determined (in duplicate) by the standard perchlorate procedure (39) and then 5 replicates on each sample were done according to the cobaltinitrite method.

TABLE X

Soil type	Expt. No.	A. % K_2O by Perchlorate (Mean of duplicate.	B. %K_2O by Cobalti-nitrite.	C. Mean %K_2O	D. Deviation A - C
I. Grahamstown Light grey sandy Loam	1	.1615	.1607	.1613	.0002 = .1%
	2		.1614		
	3		.1612		
	4		.1617		
	5		.1614		
II. Grahamstown (West Hill) Light grey sandy loam	1	.1750	.1722	.1728	.0022 = 1%
	2		.1735		
	3		.1722		
	4		.1730		
	5		.1731		
III. Riebeeck E. (Mitford Pk) Dark, grey-brown loam	1	.2240	.2242	.2237	.0003 = .1%
	2		.2242		
	3		.2235		
	4		.2237		
	5		.2230		
IV. Riebeeck E. Brownish red sandy loam.	1	.4310	.4316	.4312	.0002 = .05%
	2		.4308		
	3		.4308		
	4		.4315		
	5		.4312		

It is evident that the cobaltinitrite method compares very favourably indeed with the standard gravimetric perchlorate procedure, and it can safely be substituted for this tedious method.

Having now accumulated all the necessary experimental evidence to satisfy the author that this method for potash could be used safely and efficiently to test sampling variance, he proceeded with the sampling research.

H. SAMPLING PROCEDURE AND LAY-OUT OF PLOTS.

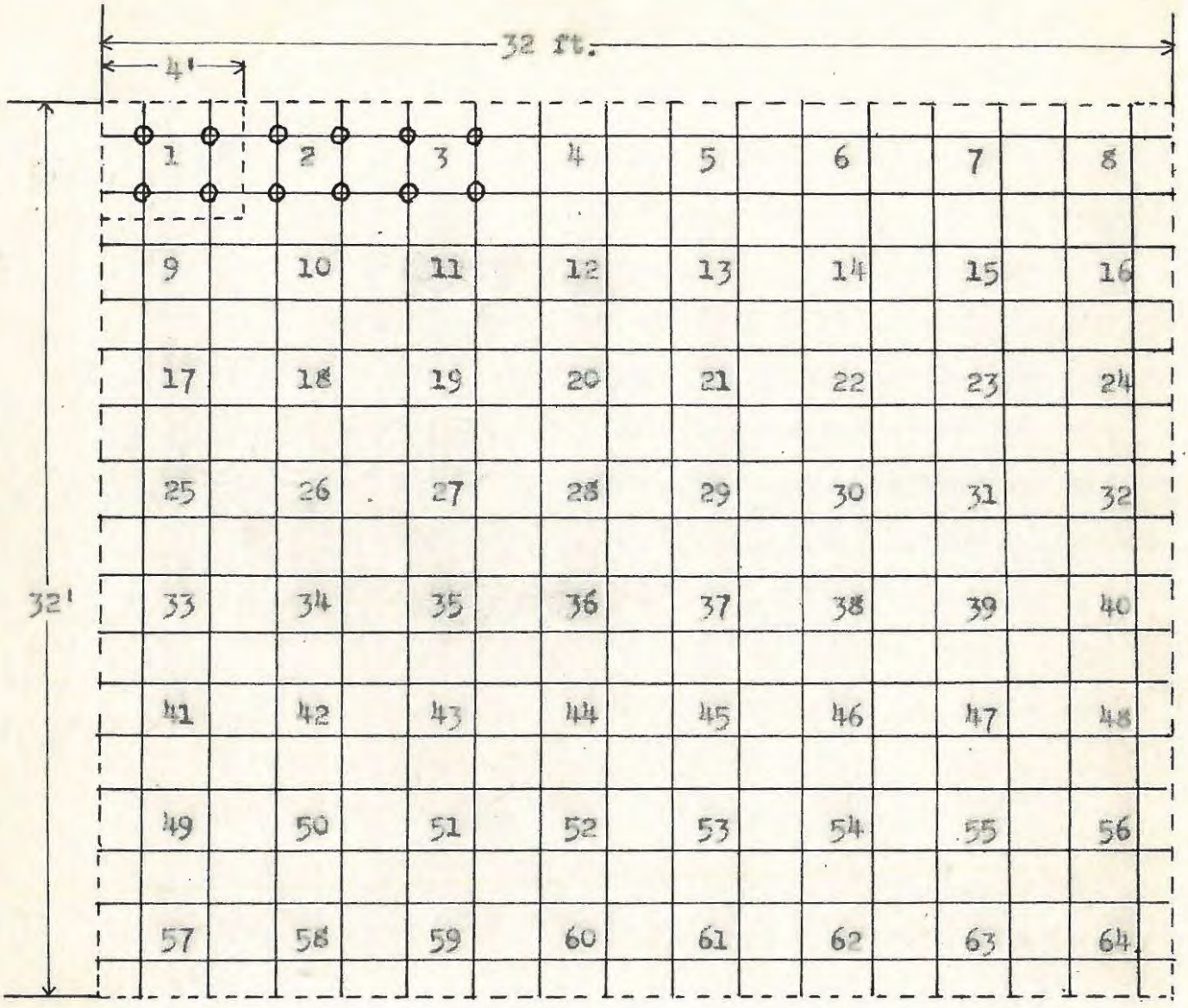
As has been pointed out earlier in this thesis, an investigator can never obtain the absolute value of a constituent in a soil to represent a certain area, by sampling - a close approach can only be made to this value in practice by taking a large number of samples. For comparative purposes when testing soil sampling efficacy, it is essential to approach this value as closely as possible, and an investigator, faced with this problem, should sample the chosen area almost completely. Furthermore, all possible interfering factors must be eliminated and the area to be sampled must be homogeneous and representative of the soil type under which it falls. Special attention should be given to the visible physical characteristics like vegetation, slope, degree of erosion and, for cultivated fields, time of fertilization.

The author decided to sample small areas only, 1/40th of an acre in size (usual size of experimental plots) as such areas can be treated much more efficiently and economically, and conclusions in relation to larger areas can be drawn from the results. Areas of three distinctly different soil types in the Union were sampled, viz. in (1) Humansdorp district, (2) Venterstad district, and (3) Grahamstown commonage.

By looking at the soil map published in Dr. van der Merwe's book on Soil Classification in South Africa (2) it will be seen that (1) lies in the Winter Rainfall area and consists of grey sandy soil, (2) falls under desert soils, usually alkaline in nature, and (3) is one of the Grey-like Podsolic soils of the Eastern Province semi-coastal belt. The latter two both fall in the Summer Rainfall area.

The three areas were sampled in exactly similar manner as follows :-

Bearing in mind all the facts mentioned at the beginning of this section, a suitable area was chosen on virgin land. A square-shaped area of 32 x 32 feet was measured off. This was divided into plots of 4 x 4 feet. A grid was then superimposed on this area having lines 2 feet apart as shown in the diagram below :-



———— = Grid of 2 x 2 feet.

o = Boring site.

The area of 1/40th acre was thus divided up into 64 similar plots, each 4 x 4 feet. From each plot one representative sample was taken. This sample was obtained by taking 4 borings (6 inch depths) with a soil auger at the intersection of each of the grid lines in the plot, as illustrated in the diagram above, in which each boring site is marked with a circle (0). A 60 ml. beaker, used as a convenient measure, was separately filled with the material from each of the 4 borings and emptied on to a clean metal tray. The four equal volumes from each 4 x 4 feet plot were well mixed and placed in a labelled bottle. The other 63 samples were taken in exactly the same way, taking care to wipe the auger, beaker and tray with a cloth before sampling the next plot. 64 samples, resulting from 256 borings, were thus taken in the small area of 1/40th acre and it was considered that the mean of all these should give a fair representation of the area. It should be mentioned that, before a boring was made, the site to be sampled was cleared of vegetation and about ½ - 1 inch of the top-soil removed with a sharp spade. This was done to prevent any surface contaminations from affecting the samples.

The depth of the soil in each area was also taken, as well as the usual physical characteristics. A description of these are given for each area in the next few paragraphs.

(I) HUMANSDORP : The samples were taken on Professor W. F. Barker's land at Robbe Hoek, near Witte Els Bosch. The area chosen was situated about 70 yards North East of the house and about 800 yards from the sea, with a gentle slope of approximately 2°. The whole area had been burnt over about 3 months prior to sampling and, in addition, after a severe drought of several months, 5 inches of rain had fallen on the area, one week before the samples were taken. Vegetation consisted mainly of sour grass and "biesies". A slight degree of sheet erosion was apparent.

A deep boring in the centre of the area gave the following data : -

Horizon A - 0 - 9". Dark grey, sandy soil

Horizon B - 9 - 14". Yellow clay, mixed with sand.

Horizon C - 14" - ∝ . Red gravel and stones.

(2) GRAHAMSTOWN. The samples were taken on the flat of a hill, next to the National Road between Grahamstown and Port Elizabeth, about one mile out of town. The slope was about 2° and the area, well-covered with grass, seemed physically to be the most homogeneous of the three. About half an inch of rain had fallen on the area, one week before sampling. No visible erosion was noticed.

Horizon A - 0 - 12". Grey sandy loam

Horizon B - 12 - 16", Clay mixed with gravel.

Horizon C - 16" - ∝ Gravel.

(3) VENTERSTAD : Samples were taken on Mr. D. G. Steyn's

farm, Broedersbank, about 12 miles out of Venterstad to the South. The area was situated in a gently sloping (about 1°) field which had been lying fallow for a couple of years prior to sampling. A small amount of rain had fallen before samples were taken. No visible erosion was evident.

Horizon A - 0 - 13". Reddish brown, sandy loam.

Horizon B - 13 - 18". Sand, mixed with gravel.

Horizon C - 18" - ∞ Gravel and stones.

I THE ANALYSIS OF THE SOIL SAMPLES.

After the samples had been collected, they were brought to the laboratory, spread out on clean pieces of paper and air-dried away from gas fumes and dust for 3 days. Each sample was then passed through a 1 m.m. sieve with round holes, the larger particles being broken with a wooden pestle and mortar. Stones and plant-roots remaining on the sieve were discarded. Only a few stones were encountered, and most of the soil passed through the sieve. Each sample was replaced in the original labelled bottle, well shaken, and put aside for analysis. The weight of each sample was approximately one kilogram.

Potash was determined in each of the 64 samples obtained from each of the three areas, by the volumetric cobaltinitrite method as described in Section G. Batches, of 12 determinations each, were analysed at a time, and it was found that one batch could easily be completed in a day. Duplicates were done on each sample. Blank controls were often run during the analyses to correct for any potash in the reagents. (In most cases it was found that this blank was negligible). It was found expedient and time-saving to have a batch of 12 soils digesting on the waterbath while analysing the extracts from the previous day. In this way no time was lost and approximately 400 estimations were carried out in seven weeks. Before

each sample was weighed out for extraction, the bottle was shaken well, because soil tends to separate into layers on standing.

J. EXPERIMENTAL RESULTS.

It will be inconvenient and space-consuming to reproduce all the individual potash results and only the mean for each sample will be given. Suffice it to say that duplicates were seldom more than 1% out and wherever this difference was exceeded, the determination was repeated.

In Tables XI, XII, and XIII, the data for the areas as sampled at Robbe Hoek, Grahamstown and Broedersbank are reproduced and the potash value for each plot is given as a percentage of the air-dry soil.

TABLE XI

ROBBE HOEK

(g. K_2O per 100g. air-dry soil)

1. .050	2. .056	3. .046	4. .053	5. .050	6. .045	7. .052	8. .056
9. .054	10. .046	11. .051	12. .056	13. .046	14. .055	15. .059	16. .057
17. .050	18. .050	19. .060	20. .057	21. .058	22. .062	23. .061	24. .065
25. .050	26. .050	27. .053	28. .052	29. .051	30. .050	31. .075	32. .071
33. .069	34. .068	35. .068	36. .064	37. .062	38. .062	39. .062	40. .061
41. .063	42. .063	43. .060	44. .063	45. .061	46. .065	47. .062	48. .059
49. .065	50. .058	51. .060	52. .060	53. .056	54. .059	55. .060	56. .061
57. .059	58. .056	59. .058	60. .061	61. .070	62. .070	63. .069	64. .072

Mean of the total = 0.058% K_2O

TABLE XII

GRAHAMSTOWN.

(g. K_2O per 100 g. air-dry soil.)

1. .135	2. .132	3. .148	4. .134	5. .130	6. .138	7. .150	8. .137
9. .133	10. .133	11. .137	12. .138	13. .137	14. .136	15. .155	16. .147
17. .139	18. .131	19. .131	20. .122	21. .130	22. .139	23. .150	24. .137
25. .126	26. .130	27. .124	28. .134	29. .127	30. .128	31. .144	32. .142
33. .122	34. .132	35. .139	36. .129	37. .132	38. .136	39. .142	40. .137
41. .129	42. .140	43. .133	44. .126	45. .125	46. .148	47. .129	48. .131
49. .123	50. .133	51. .136	52. .133	53. .129	54. .135	55. .139	56. .140
57. .119	58. .131	59. .133	60. .125	61. .117	62. .124	63. .128	64. .133

Mean of the Total = 0.134 % K_2O

TABLE XIII

BROEDERSBANK

(g.K_2O per 100 g. air-dry soil)

1. .387	2. .382	3. .379	4. .379	5. .371	6. .397	7. .429	8. .417
9. .486	10. .456	11. .388	12. .399	13. .365	14. .376	15. .395	16. .421
17. .423	18. .390	19. .410	20. .408	21. .429	22. .449	23. .461	24. .459
25. .460	26. .452	27. .448	28. .448	29. .432	30. .448	31. .406	32. .409
33. .444	34. .426	35. .397	36. .393	37. .384	38. .395	39. .403	40. .400
41. .401	42. .411	43. .412	44. .405	45. .408	46. .429	47. .417	48. .437
49. .381	50. .347	51. .409	52. .408	53. .423	54. .399	55. .466	56. .447
57. .451	58. .441	59. .445	60. .440	61. .383	62. .379	63. .379	64. .385

Mean of total = 0.414 % K_2O

K. STATISTICAL TREATMENT OF RESULTS.

It is quite obvious that these results must be treated statistically before it can be said whether any degree of significance may be attributed to the variance of the potash values. Data on statistical treatment have mainly been obtained from the texts on statistics by Fisher (40) and by Saunders (41).

A three-stage analysis was performed on the results of each of the areas :-

(a) The standard error, if only one sample is taken from the whole 1/40th acre, was found :- The total sum of squares of the deviations was assigned to 63 degrees of freedom representing the average differences within the 1 block of 64 plots. The square root of the mean square gives the standard error per sample.

(b) The area was divided symmetrically into quarters of 16 plots each, and the sum of the squares of the deviations was assigned to 60 degrees of freedom representing the average differences within the 4 blocks of 16 plots each, and to 3 degrees representing the differences between these blocks of 16 plots each. The square root of the mean square gives the standard error per sample and when divided by the square root of the number of blocks ($\sqrt{4}$) gives the standard error of a single composite obtained by bulking together 4 samples, taken one from each block.

(c) In the third stage the area was divided into

sixteen blocks of 4 plots each and the sums of squares assigned to 48 degrees of freedom within the 16 blocks and to 15 degrees between the blocks of 4 plots each. The standard error of a single composite of 16 soil samples, one from each of the 16 blocks, will be the square root of the mean square divided by $\sqrt{16}$.

In the following tables the results of the treatments are given separately for each area.

I. ROBBE HOEK

TABLE XIV

(a) 1 Block of 64 plots

Plots	1	2	3	4	5	6	7	8.	Total	
1.	.050	.056	.046	.053	.050	.045	.052	.056	.408	
2	.054	.056	.051	.056	.046	.055	.059	.057	.424	
3	.050	.050	.060	.057	.058	.062	.061	.065	.463	
4	.050	.050	.053	.052	.051	.050	.075	.071	.452	
5.	.069	.068	.068	.064	.062	.062	.062	.061	.516	
6	.063	.063	.060	.063	.061	.065	.062	.059	.496	
7	.065	.058	.060	.060	.056	.059	.060	.061	.479	
8	.059	.056	.058	.061	.070	.070	.069	.072	.515	
Total	.460	.449	.456	.466	.454	.468	.500	.503	3.754	Grand Total
Mean	.057	.056	.057	.058	.057	.058	.062	.063	.058	General Mean

Sum of squares of all plot yields = $(.050)^2+(.056)^2+(.072)^2$
= 0.22320

Subtract product of grand total
and general mean, 3.754 x .058 = 0.21770

i.e. sum of squared deirations for all yields = 0.0055

TABLE XV

(b) 4 blocks of 16 plots each

Plots	Blocks			
	I	II	III	IV
1	.050	.069	.050	.062
2	.056	.068	.045	.062
3	.046	.068	.052	.062
4	.053	.064	.056	.061
5	.054	.063	.046	.061
6	.046	.063	.055	.065
7	.051	.060	.059	.062
8	.056	.063	.057	.059
9	.050	.065	.058	.056
10	.050	.058	.062	.059
11	.060	.060	.061	.060
12	.057	.060	.065	.061
13	.050	.059	.051	.070
14	.050	.056	.050	.070
15	.053	.058	.075	.069
16	.052	.061	.071	.072
Total	.834	.995	.913	1.020
Mean	.052	.062	.057	.064

Sum of squares of differences within blocks of 16 plots $= (.052 - .050)^2 + (.052 - .056)^2 +$

$= .001841$

Sum of squares of differenees between blocks of 16 plots $= \frac{(\text{Mean of Block totals} - .834)^2 + \cdots + (\text{M.B.T.} - 1.020)^2}{16}$

$= \underline{0.001265}$

TABLE XVI

(C) 16 Blocks of 4 plots each

Plots	Blocks															
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI
1	.050	.050	.069	.065	.046	.060	.068	.060	.050	.058	.062	.056	.052	.061	.062	.060
2	.056	.050	.068	.058	.053	.057	.064	.060	.045	.062	.062	.059	.056	.065	.061	.061
3	.054	.050	.063	.059	.051	.053	.060	.058	.046	.051	.061	.070	.059	.075	.062	.069
4	.046	.050	.063	.056	.056	.052	.063	.061	.055	.050	.065	.070	.057	.071	.059	.072
Total	.206	.200	.263	.238	.206	.222	.255	.239	.196	.221	.250	.255	.224	.272	.244	.262
Mean	.051	.050	.066	.059	.051	.055	.064	.060	.049	.055	.062	.064	.056	.068	.061	.065

Sum of squares of differences within blocks of 4 plots) $= (.051-.050)^2+(.051-.056)^2+\ldots+(.065-.069)^2+(.065-.072)^2$

$= .0008570$

Sum of squares of differences between blocks of 4 plots) $= \frac{(\text{Mean of Block totals} -.206)^2+\ldots..+(\text{M.B.T}-.262)^2}{4}$

$= 0.002225$

ANALYSIS OF VARIANCE

TABLE XVII

Component	Degrees of Freedom	Sum of Squares	Mean Square	Standard error/ sample	Standard error/ composite.	%Standard Error
Within blocks of 64 plots	63	.005500	.0000873	.009343	.009343	16.1
16 "	60	.001841	.0000307	.005541	.002770	4.8
4 "	48	.000857	.0000178	.004219	.001055	1.8

Where

Mean square = sum of squares / Degrees of freedom

Stand. error/sample = $\sqrt{\text{Mean Square}}$

Stand. error/composite = $\sqrt{\text{Mean square}} / \sqrt{\text{No.of blocks.}}$

$$\% \text{ Stand. error} = \frac{\text{Stand. error} \times 100}{\text{General mean.}}$$

II GRAHAMSTOWN

TABLE XVIII
(a)

Plots	1	2	3	4	5	6	7	8	Total	
1	.135	.132	.148	.134	.130	.138	.150	.137	1.104	
2	.133	.133	.137	.138	.137	.136	.155	.147	1.116	
3	.139	.131	.131	.122	.130	.139	.150	.137	1.079	
4	.126	.130	.124	.134	.127	.128	.144	.142	1.055	
5	.122	.132	.139	.129	.132	.136	.142	.137	1.069	
6	.129	.140	.133	.126	.125	.148	.129	.131	1.061	
7	.123	.133	.136	.133	.129	.135	.139	.140	1.068	
8	.119	.131	.133	.125	.117	.124	.128	.133	1.010	
Total	1.026	1.062	1.081	1.041	1.027	1.084	1.137	1.104	8.562	Grand total
Mean	.128	.133	.135	.130	.128	.135	.142	.138	.134	General Mean.

Sum of squares of all plot yields = 1.1570

8.562 x .134 = 1.1480

Sum of squared deviations = 0.0090

TABLE XIX

Plots	Blocks			
	I	II	III	IV
1	.135	.122	.130	.132
2	.132	.132	.138	.136
3	.148	.139	.150	.142
4	.134	.129	.137	.137
5	.133	.129	.137	.125
6	.133	.140	.136	.148
7	.137	.133	.155	.129
8	.138	.126	.146	.131
9	.139	.123	.130	.129
10	.131	.133	.139	.135
11	.131	.136	.150	.139
12	.122	.133	.137	.140
13	.126	.119	.127	.117
14	.130	.131	.128	.124
15	.124	.133	.144	.128
16	.134	.125	.142	.133
Total	2.127	2.083	2.226	2.125
Mean	.133	.130	.139	.133

Sum of squares of differences within blocks of 16 plots = 0.003025

Sum of squares of differences between blocks of 16 plots = 0.000704

TABLE XX
(c)

Plots	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI
1.	.135	.139	.122	.123	.148	.131	.139	.136	.130	.130	.132	.129	.150	.150	.142	.139
2	.132	.131	.132	.133	.134	.122	.129	.133	.138	.139	.136	.135	.137	.137	.137	.140
3	.133	.126	.129	.119	.137	.124	.133	.133	.137	.127	.125	.117	.155	.144	.129	.128
4	.133	.130	.140	.131	.138	.134	.126	.125	.136	.128	.148	.124	.147	.142	.131	.133
Total	.533	.526	.523	.506	.557	.511	.527	.527	.541	.524	.541	.505	.589	.573	.539	.540
Mean	.133	.131	.131	.126	.139	.128	.132	.132	.135	.131	.135	.126	.147	.143	.135	.135

Sum of squares of differences within blocks of 4 plots = 0.001806

Sum of squares of differences between blocks of 4 plots 0.002145

ANALYSIS OF VARIANCE
TABLE XXI

Component	Degrees of freedom	Sum of Squares	Mean Square	Stand.error sample.	Stand. error composite	% Stand. error
Within Bl.of 64 plots.	63	.009000	.00014290	.011960	.011960	8.93
16 plots	60	.003025	.00005041	.007100	.003550	2.65
4 plots	48	.001806	.00003762	.006134	.001533	1.14

III PROEDERSBANK

TABLE XXII
(a)

Plots	1.	2.	3.	4.	5.	6.	7.	8.	Total
1	.387	.382	.379	.379	.371	.397	.429	.417	3.141
2	.486	.456	.388	.399	.365	.376	.395	.421	3.286
3	.423	.390	.410	.408	.429	.449	.461	.459	3.429
4	.460	.452	.448	.448	.432	.448	.406	.409	3.503
5	.444	.426	.397	.393	.384	.395	.403	.400	3.242
6	.401	.411	.412	.405	.408	.429	.417	.437	3.320
7	.381	.347	.409	.408	.423	.399	.466	.447	3.280
8	.451	.441	.445	.440	.383	.379	.379	.385	3.303
Total	3.433	3.305	3.289	3.280	3.195	3.272	3.356	3.375	26.505
Mean	.429	.413	.411	.410	.399	.409	.419	.422	.414

Sum of squares of all plot yields = 11.02860

26.505 x .414 = 10.97

Sum of squared deviations = 0.05860

TABLE XXIII

(b)

Plots	Blocks I	II	III	IV
1	.387	.444	.371	.384
2	.382	.426	.397	.395
3	.379	.397	.429	.403
4	.379	.393	.417	.400
5	.486	.401	.365	.408
6	.456	.411	.376	.429
7	.388	.412	.395	.417
8	.399	.405	.421	.437
9	.423	.381	.429	.423
10	.390	.347	.449	.399
11	.410	.409	.461	.466
12	.408	.408	.459	.447
13	.460	.451	.432	.383
14	.452	.441	.448	.379
15	.448	.445	.406	.379
16	.448	.440	.409	.385
Total	6.696	6.616	6.666	6.540
Mean	.418	.413	.416	.408

Sum of squares of differences within blocks of 16 plots = .05395

Sum of squares of differences between blocks of 16 plots = 0.000878

TABLE XXIV
(c)

Plots	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI
1.	.387	.423	.444	.381	.379	.410	.397	.409	.371	.429	.384	.423	.429	.461	.403	.466
2.	.382	.390	.426	.347	.379	.408	.393	.408	.397	.449	.395	.399	.417	.459	.400	.447
3.	.486	.460	.401	.451	.388	.448	.412	.445	.365	.432	.408	.383	.395	.406	.417	.379
4.	.456	.452	.411	.441	.399	.448	.405	.440	.376	.448	.429	.379	.421	.409	.437	.385
Total	1.712	1.725	1.684	1.621	1.545	1.714	1.608	1.702	1.510	1.758	1.618	1.584	1.662	1.736	1.659	1.678
Mean	.428	.431	.421	.405	.386	.428	.402	.425	.377	.439	.404	.396	.415	.434	.414	.419

Sum of squares of differences within blocks of 4 plots = 0.03598

Sum of squares of differences between blocks of 4 plots = 0.01885

ANALYSIS OF VARIANCE
TABLE XXV

Component	Degrees of Freedom	Sum of Squares	Mean Square	Stand. error sample	Stand. error composite	% Stand. error.
Within Bl. of 64 plots	63	.05860	.0009303	.03050	.03050	7.37
16 plots	60	.05395	.0008992	.02998	.01499	3.62
4 plots	48	.03598	.0007498	.02738	.00684	1.65

In Table XXVI a comparison of the variance of the three different areas is given.

TABLE XXVI

	Degrees of Freedom	Robbe Koek	Graham-stown.	Broeders-bank.
Mean Percentage K_2O		.058	.134	.414
Sum of Squares,				
a) Within block of 64 plots	63	.005500	.009000	.05860
b) Within blocks of 16 plots	60	.001841	.003025	.05395
c) Within blocks of 4 plots	48	.000857	.001806	.03598
Mean Squares,				
a) Within 64 plots		.0000873	.0001429	.0009303
b) Within 16 plots		.0000307	.0000504	.0008992
c) Within 4 plots		.0000178	.0000376	.0007498
Standard Errors,				
a) Single sample from 64 plots/block		.009343	.011960	.03050
b) Composite of 4, one from each block		.002770	.003550	.01499
c) Composite of 16, one from each block		.001055	.001533	.00684
Stand. Errors, % ages of Mean:				
a) Single sample.		16.10	8.93	7.37
b) Composite of 4 samples.		4.80	2.65	3.62
c) Composite of 16 samples.		1.80	1.14	1.65

L. DISCUSSION

Table XXVI provides the basis for a good estimate of the size of the errors likely to be involved in sampling. If only one sample (i.e. a composite of 4 borings as taken by the author) is taken at random to represent the area of 1/40th acre, its potash content may differ by 7-16% from the mean. A composite of 4 samples (16 borings), one taken at random in each quarter of the area, will give much better results (2.5 - 5% difference) and for most purposes such sampling will be sufficient. It is interesting to note that for a sampling accuracy of 1 - 2 % a composite of 16 samples (64 borings) is necessary.

It is obvious that for an increase in sampling efficiency, a large increase of sample numbers is necessary. To illustrate this fact more clearly, the statistical approximation, $n = \frac{2t^2 S^2}{D^2}$ (see page 7) may be applied to the data given in Table XXVI.

Here n = number of samples.
t = "t value" of Student, obtained from tables (40)

S = Standard error per sample, given in Table XXVI.

D = Maximum sampling error permissible.

Calculation of D. To simplify the calculation, potash is given as g. per 100 kg. soil rather than as a true percentage.

(I) Broedersbank : From Table XXVI, n=1 for 7.4% ie ±10%

S = 30.5. t = 6.314 for n=1 and probability =.1

from tables. (P = .1 is equivalent to 10%)

Now $D = \sqrt{\frac{2t^2 s^2}{n}}$

$= \sqrt{\frac{2 \times 39.82 \times 930}{1}}$

$= 272.$ g.

This figure was obtained by taking n = 1 for 10%. Actually n = 1 for 7.4% and a correction has therefore to be introduced giving

D = 201 g. for 10% accuracy.

Similarly D = 100 for 5% accuracy

and = 40 and 20 g. for 2 and 1% accuracy respectively.

Similarly for

(2) Grahamstown : D = 94 g. for 10%
47 g. for 5%
19 g. for 2%
and 9.5 g. for 1%

(3) Robbe Hoek : D = 39 g. for 10%
19g. for 5%
8 g. for 2%
4 g. for 1%

Calculation of n :

Broedersbank S = 30.5

10% level : D = 201; t = 6.314 for 1 degree of freedom and P = .I

$n = \frac{2t^2 s^2}{D2}$

$$= \frac{2 \times 39182 \times 930}{40400}$$

$$= \underline{1 \text{ sample}}$$

5% level : D = 100; t = 4.303 for 2^{o} of F.and P = .05

$$n = \frac{2 \times 18.51 \times 930}{10{,}000}$$

$$= \underline{3 \text{ samples}}$$

2% level : D = 40; t = 2.821 for 9^{o} of F.and p =.02

$$n = \frac{2 \times 7.958 \times 930}{1600}$$

$$= \underline{10 \text{ samples}}$$

1% level D = 20; t = 2.75 for 30 and more ^{o}F. and P=.01

$$n = \frac{2 \times 7.563 \times 930}{400}$$

$$= \underline{35 \text{ samples}}$$

n is calculated in a similar way for Grahamstown and Robbe Hoek and the results are given in Table XXVII. The figures in brackets represent the number of borings equivalent to the number of samples.

TABLE XXVII

No.	Soil type	n = number of samples for 10% acc.	5%	2%	1%
1	Broedersbank (.414% K_2O)	1 (4 borings)	3 (12)	10 (40)	35 (150)
2	Grahamstown (.134% K_2O)	1 (4)	2 (8)	7 (28)	25 (100)
3	Robbe Hoek (.058% K_2O)	1 (4)	4 (16)	17 (68)	76 (304)

When comparing the results of Table XXVII with those

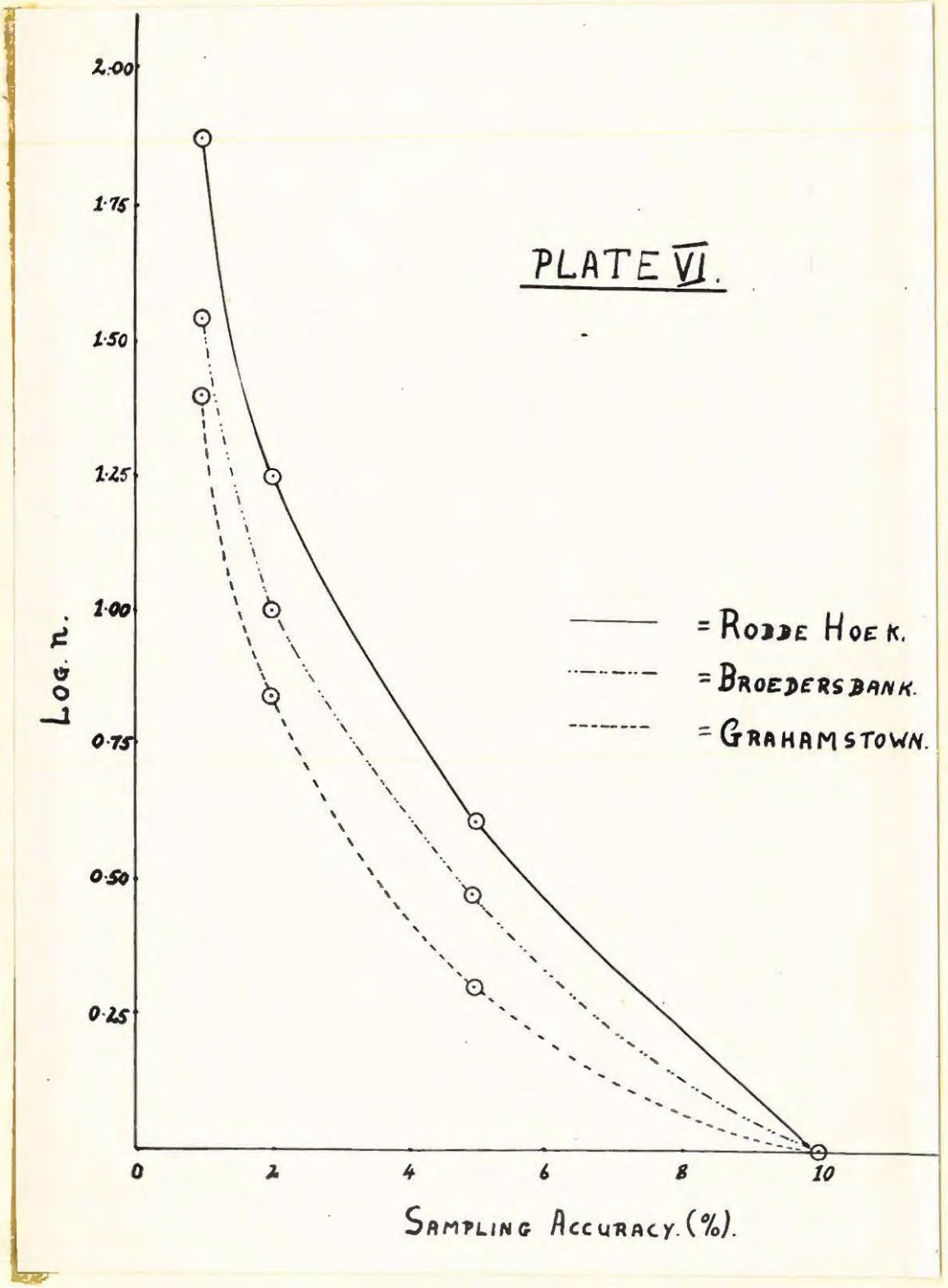


PLATE VI.
2·00
1·75
1·50
1·25
1·00
0·75
0·50
0·25
LOG. n.
0
2
4
6
8
10
SAMPLING ACCURACY. (%).
= RODDE HOEK.
= BROEDERSBANK.
= GRAHAMSTOWN.

based on the experimental figures in Table XXVI, it will be noticed that no big difference is apparent, so that it would seem that this useful approximation may safely be used for determining the number of samples to be taken to represent a particular area. Some preliminary investigation to determine the variance of the constituent to be estimated in the soil is, however, necessary. If the approximate range of the constituent is known, S can be calculated from the approximation, S = Range/C where C is a constant = 3,4,5 and 6 for 10,25,100 and 500 sampling units respectively (42).

Plate VI shows log n plotted against sampling accuracy. The outstanding feature of these curves is that as the accuracy demanded approaches 1%, a relatively large increase of number of samples required, is apparent. It is clear that in the usual practice a composite sample which will represent an area, 1/40th acre in size, within an accuracy of 1% will require ± 50 sampling units (200 borings), a procedure far too laborious and uneconomic for fertility studies, especially when it is considered that much larger areas have usually to be dealt with in such studies. One may therefore safely say that the term "1% accuracy" must be removed from the vocabulary of the modern soil analyst ! Even for 2% accuracy, anything up to 20 sampling units are necessary if a representative composite sample of 1/40th acre is to be obtained. 5% accuracy seems to be the most

that can be aimed at in actual practice.

Another interesting feature of graph VI is that the actual proportion of potash in the soil appears to make little difference in the sampling efficiency of a given procedure, the homogeneity of the soil character playing the greatest role.

An investigation of the potash distribution in South African soils as published in Dr. van der Merwe's book on Soil Classification (2) shows that 55 of the 70 soils analysed over the Union have a total potash content lying between .1-1.5% K_2O. These values were obtained from sodium carbonate extractions of the soil and therefore gives the total potash content. Total potash values of the three areas sampled by the present author are given in this book as lying between .25 - 2% K_2O. These three types of soil therefore sufficiently cover the above range to make the author's results seem applicable to the sampling of any South African soil.

It is now necessary to discuss analytical procedures, and in particular potash determinations, in the light of what has been established about sampling efficiency. It is obvious that if an error of 5% and at the least of 2% is involved in the actual sampling of such a small and homogeneous area as 1/40th of an acre, much greater errors may be involved in the sampling of larger areas, especially when these are cultivated and fertilized. The

usual "accurate" analytical data for soils supplied in so many texts seem to be entirely unjustifiable if considered in the light of the possible error of sampling. Moreover, too much attention is probably given to detail in soil analytical procedures, resulting in much waste of time and effort.

It appears that analysts working in soil laboratories will be justified in using Rapid Soil Tests when analysing samples sent in by farmers and other persons, the usual tedious procedures being so much waste of time and money. Accurate analytical procedures are only justified in soil research where the sampling procedure has been adapted to the degree of accuracy required.

Another method of determining chemical elements in soil and which suggests itself as being preferable to the longer gravimetric and volumetric procedures so often used, is that of colorimetric analysis. In the last decade much work on colorimetric procedures for use in soil analysis has been done, and in most cases an accuracy of 1 - 2% is claimed. It need hardly be said that once these methods are standardised for a particular constituent, a great amount of time may be saved by their use, and in addition, far less materials are consumed than in gravimetric or volumetric analysis. Furthermore, the types of photo-electric colorimeters available today, are so easy and convenient to use, that their application to soil determinations is likely to

develop rapidly in the near future.

A review, in the light of the errors involved in the sampling of a given soil area, of the volumetric method for the determination of potash in soils as described by the author, indicated that no justifiable alteration could reasonably be suggested with the object of shortening the procedure appreciably. It seems as if this method is mainly suitable for special research or where sufficient sampling justifies the accuracy obtainable by its use. Where the soil analyst decides to use it for routine work, he should pay attention rather to the time factor than to extreme niceties of practical skill. It is to be borne in mind, however, that although the use of this method does not seem to be always justified for ordinary soil studies, it can be applied to numerous other branches of industrial and chemical analysis as an excellent substitute for the more lengthy and costly platinic chloride or perchlorate procedures.

It is felt that this investigation has served a useful purpose, if only because of the evidence it has provided dhowing how necessary it is to consider sampling procedure most carefully in relation to the aims of the analysis when a natural material of variable composition, such as the soil, is being studied.

It is realised that the data now given could,

with advantage, be considerably extended and it is hoped to pursue in due course the study of sampling efficiency in relation to soil constituents other than potash. When it is realised, however, that the work now being reported, has required the full attention of the author for the period February to November, 1945, the reason why a more extensive treatment of the problem at this stage is not possible, will perhaps be understood.

LITERATURE CITED.

The references are to the figures in the text.

(1) G.W. Robinson and W.E. Lloyd : Probable error of sampling in soil surveys. Journ. Agric. Sci., 7, 144-153 (1915)

(2) C.R. van der Merwe : Soil groups and Sub-groups of South Africa. Published in Science Bulletin 231 of Dept. of Agric. and Forestry (1941).

(3) Methods of Analysis of Soils - Compiled by the Pretoria Chemical laboratories.

(4) C.S. Piper : Soil and Plant Analysis - A monograph from the Waite Agricultural Research Institute, Australia. Hassell Press, Adelaide, Australia (1942)

(5) M.G. Cline : Principles of Soil Sampling. Soil Science, 59, 3 - 6 (1945)

(6) L.A. Bushell ; The sampling of Coal. Journ. Chem., Metall. & Mining Soc. of S.A., 37, No. 8 (1937)

(7) A.R. Clapham : The estimation of yield in cereals by sampling methods. Jour. Agric. Sci., 19, 214-235 (1929)

(8) A.R. Clapham : Studies in sampling technique. Jour. Agric. Sci., 21, 366-371. 376-390 (1931)

(9) Yates and Zacopanay : Estimation of the efficiency of sampling. Jour. Agric. Sci., 25, 545 - 577 (1935)

(10) Frear and Erb ; A study in soil sampling. Jour. Assoc. Off. Agr. Chem., 4, 98 - 103 (1920)

(11) McCall and McKibbin : Memorandum on sampling of soils Jour. Assoc. Off Agr. Chem., 10, 93-96 (1927)

(12) Blaney and Smith : Sampling market garden-soils for nitrates. Soil Science 31, 281 - 290 (1931)

(13) Anonymous : Importance of depth of soil sampling in studies relating to the mineral content of pastures. New Zealand J.Sci. Tech., 13, 284-294 (1932).

(14) Youden and Mehlich ; Selection of efficient methods of soil sampling. Contrib. Boyce Thompson Inst., 9, 59-70 (1937)

(15) Iyengar and Tamhane : Sampling error in irrigated soils. Soil Research, 6, 49-53 (1938).

(16) Kerr and Stieglitz; Some studies in soil sampling technique. Bur. Sugar Expt. Stas., Queensland, Tech. Commun., 9. 179-203 (1938)

(17) Collins and Hodgen : Field variations as a factor in sampling for rapid soil analyses. Assoc. Southern Agr. Workers, Proc. Ann. Meetings, 41, 77-78 (1940)

(18) Hans Riehm; The most suitable type of sampling for chemical soil tests. Bodenkunde u. Pflanzenernahr, 29, 275-290 (1943)

(19) The preparation of soil samples for mechanical analyses. Z. Pflangenernahr Dungung Bodenk, 31A, 113-154 (1933).

(20) Soil sampling and examination of sub-soils. Deut. Landw. Presse, 60, 661 (1933)

(21) Taylor : A procedure for sampling cane juice and soil as used at Pioneer Mill Co. Ltd. Hawaiian Planters' Record, 39, 109-112 (1935)

(22) Itano: A method for collecting soil samples to be studied in the laboratory. Ber. Ohara Inst. Landw. Forsch., 7, 289-291 (1936)

(23) Schlumberger : Taking samples of subsoil, U.S. Re-issue 20, 120 (Sept. 29, 1936)

(24) Felinger : Sampling orchard soils for nitrate determinations. Proc. Am. Soc. Hort. Sci., 28, 515-518 (1931)

(25) Eddins and Scoville : Soil sampling for the pH determination. Soil Science, 43, 219-220 (1937)

(26) Importance of collecting representative soil samples. Reports Assoc. Hawaiian Sugar Tech., Agr. Sect., 15, 55-60 (1936)

(27) Schmitt : Soil sampling in pastures and meadows. Landw. Jahrb., 83, 435 - 455 (1936).

(28) Methods of soil investigation, sampling and mapping, and aims of the Royal Hungarian Geological Survey. Magyar Mernök Epiteszegylet.

(29) Joly and Robaux : Curious influences of the drilling technique on the study of test samples. Bull. Mens. Soc. Sci. Nancy, No. 7-8, 153-160 (1936)

(30) Brown : Technique in pasture research. J. Am. Soc. Agron., 29, 468-476 (1937)

(31) Anon : Method to be used in taking samples of soil for analysis. J. Dept. of Agr. S. Australia, 26 , 875 (1923).

(32) Mitchell and Ford : Factors affecting determination of potash in fertilizers. Ind. & Eng. Chem., Anal. Ed., 17, 115 (Febr. 1945).

(33) C.S. Piper : The volumetric determination of potash by sodium cobaltinitrite. Jour. Soc. Chem. Ind., 53, 392T-396T (1934).

(34) L. Wilcox : Determination of potassium. Ind. & Eng. Chem., Anal. Ed.,9, 136 (1937).

(35) A.Vogel : Quantitative Inorganic Analysis, 475. First edition, Longmans, London.(1939)

(36) Bambach and Rider : Volumetric determination of Halides. Ind. and Eng. Chem., Anal. Ed., 7, 165 and 178 (1935).

(37) Kolthoff and Furman : Potentiometric titrations, 172. Second edition, John Wiley & Sons, New York (1931).

(38) Scully : Jour. C. Soc., 366, May 1942.

(39) Piper : Soil and Plant Analysis, 149. (see ref.(4))

(40) Fisher : Statistical methods for Research Workers. Ninth edition, Oliver and Boyd, Edinburgh (1944)

(41) Saunders : Statistical methods in Field Experiments. Second edition, Cape Times, South Africa (1939).

(42) Patterson : Statistical Technique in Agricultural Research. McGraw Hill, New York (1939).
