THE ESTIMATION OF POTASSIUM AVAILABILITY IN MACKAY SOILS
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Introduction

Potassium exists naturally in the soil in several primary mineral forms usually associated with the clay complex. In the partially-weathered state, these forms enter into cation exchange reactions in which a certain proportion of the total potassium found in these minerals is exchanged for other cations. The more weathered the primary minerals, the more potassium is available to enter into exchange reactions. By devising a method for determining exchangeable potassium in the laboratory, Kerr and von Stieglitz (1938) were able to deduce the critical levels of soil potassium for the sugar cane growing areas in Queensland. This test, with some modification, forms part of the fertilizer advisory service which has been offered to the Queensland cane grower for over 30 years by the Bureau of Sugar Experiment Stations.

However, one of the most recurring aspects encountered in the field work relating to sugar cane nutrition is that, for a given level of exchangeable potassium, some soils exhibit a greater crop response to potassium fertilizer than do others, even under similar climatic conditions. It is apparent, therefore, that the level of exchangeable potassium, as a single value, does not form a sound basis for forecasting fertilizer requirements.

The object of this paper is to outline the development of a method which measures part of the non-exchangeable soil potassium together with the exchangeable form of the soil potassium to the extent that the total level so measured leads to a better correlation, on the single value basis, with crop response. It is expected that this method will be adopted on a routine basis for the fertilizer advisory service operating in the Mackay district in future years.

Soils in the Mackay District

Of the four major soil types currently under cultivation, the alluvials are the most widespread in this district. The remaining three are the prairie soils on undulating land areas, the black earths on the lowest lying section and the recent alluvials on flood plains. Profile descriptions have been given by Chapman (1968) for each soil type. Leverington (1955) investigated the nature of the clay fractions found in the soil types throughout the sugar cane growing area in Queensland. X-ray diffraction and associated techniques indicated the presence of illite as well as the occurrence of mixed layer minerals composed of illite and montmorillonoid layers for the forest loam soils in this district. While nontronite and kaolinite were the major constituents of the black earths, illite was also detected. This investigation was restricted to soil samples representative of the forest loam and black earth soil types under cultivation in this area.
Selection of Method

Wood and de Turk (1941) proposed the use of boiling 1N nitric acid on soil samples in the ratio of ten to one as a means of extracting the non-exchangeable forms of potassium. A ten-minute boiling period was selected on the basis that the value so determined gave the best correlation with crop yield. This method was also used by Reitemeyer and co-workers (1947) who found that a similar acid-to-soil ratio for a similar boiling time correlated well with yields of clover on surface soils. In both studies, an estimation of exchangeable potassium was made and deducted from the nitric acid value to obtain the release value. Rouse and Betramson (1949) investigated the nitric acid extraction technique more thoroughly, and included X-ray analysis of the clay fractions. They concluded that illite was the controlling factor in characterizing the potassium-supplying power of the soil while other primary minerals, such as muscovite and microcline, made significant contributions as their particle size diminished.

Metson and co-workers (1956) proposed a method of determining the potassium-supplying power in New Zealand soils, using the nitric acid technique. This method involved repeated extractions with boiling 1N nitric acid on the same soil sample until a constant rate of release of potassium was obtained. The exchangeable form is extracted on a separate sample. They concluded that the potassium being released at a constant rate is derived from the primary minerals, especially from the more inaccessible surfaces of hydrous mica and, as such, has a very low order of availability. The following formula was given as a means of measuring the more accessible interlayer potassium, $\Delta K$, and probably includes some potassium from the partly weathered primary mineral of fine size fractions.

$$\Delta K = \Sigma K - nK_c$$

Where $\Sigma K$ is the difference between the total amount of potassium extracted and the level of exchangeable potassium, $n$ is the number of extractions carried out on the sample before the constant rate of release, $K_c$, is obtained. This method is extremely useful in characterizing the potassium reserves and in establishing the rate of release from the non-exchangeable primary forms. Vallance and co-workers (1962) used this method to investigate the potassium reserves of the coastal soils in Queensland cane growing areas. From the seven sites examined, the constant rate of release, $K_c$, ranged from 0.195 m.e.K per cent in the alluvial soils of the Lower Burdekin to 0.01 m.e.K per cent in the red sandy loams of Bundaberg. A sample from Mackay, a grey podsolic, gave a rate of 0.07 m.e.K per cent.

In view of the relatively high $K_c$ value for this area, and in conjunction with the fact that illite is generally found throughout the clay fractions, it was anticipated that the 1N nitric acid method could provide a means of measuring a level of potassium which related more closely with crop response than exchangeable K alone. Such a value would consist of the level of exchangeable potassium together with the more accessible inter-layer potassium not extracted by reagents used to measure the exchangeable form. A soil-to-acid ratio of one to forty was selected as suitable for this area on the basis that the amount of potassium so extracted can be estimated on a flame photometer without loss of sensitivity following a single dilution to a constant volume. Having fixed the soil-to-acid ratio, it was necessary to investigate the rate of extraction of potassium so as to establish a suitable boiling time. For different soil...
types, this time of boiling may be variable, since Haylock and co-workers (1956) found that the amount of potassium extracted by this technique was influenced by the concentration of other cations, especially ammonium, calcium and the amount of potassium itself. The following method was adopted.

Method

A sample weighing 2.5 g of air-dried soil, crushed to pass a two (2) mm screen is placed into a 500 ml erlenmeyer flask and 100 ml of 1N HNO₃ is introduced. Two glass beads are introduced to reduce bumping, a reflux condenser inserted in the neck of the flask and the flask transferred to an electric hot plate which has been previously brought to operating temperature. The contents are timed to boil for a selected period as soon as boiling commences. Immediately at the conclusion of this period, the condenser is removed and 100 ml of cold water introduced. The contents are rapidly cooled in a water bath and a portion centrifuged at 1,500 rpm for five minutes. The potassium in the extract is determined by flame photometry. Potassium standards are prepared in 0.5N nitric acid for the calibration of the instrument.

Result

Figure 1 indicates the milliequivalents of potassium per 100 g of soil extracted over periods of up to five hours when using the above procedure. Each point represents the mean of four determinations for that
particular time. This tends to reduce errors in the values obtained by
reducing the errors due to sampling. The extractions were done on
individual samples for each time period and were not carried out on a
single sample over the whole time period.

Both soil types exhibit a similar trend in the potassium extraction
rate. The rapid rate of extraction during the first ten minutes is attri-
buted to the acid uptake of the readily soluble and exchangeable forms
of potassium which occur on the exterior surfaces of the clay complex.
From 10 to 50 minutes, the rate of extraction diminishes, after which a
constant rate is obtained. This former period is attributed to the fixed
forms of potassium being brought into solution, after which the more
inaccessible lattice potassium is subject to acid attack. The latter period
occurs at a constant rate and the values obtained depend entirely upon
the primary potassium minerals present in the soil. The fixed potassium
is held between the basal planes of micaceous minerals and is either fixed
or released in the soil according to prevailing conditions. Illite is one
mineral which can fix potassium in the soil in such a manner. The lattice
form is held tightly between the hexagonal oxygen cavities in primary
minerals thus giving it a low order of availability. Figure 2 shows the
rate of release of potassium in increments per unit time for both of the
soil types examined.

![Fig. 2—Release of potassium in m.e. percent at five minute intervals under reflux conditions.](image-url)

The proximity of the values obtained for both samples indicates that
a similar mode of extraction operates. Again, the time intervals of zero
to 10 minutes, 10 to 50 minutes and 50 minutes plus indicate that
different forms of potassium are being brought into solution from their
various positions within the mineral structures.

For further laboratory studies, an extraction time of 30 minutes was
selected. This is the mid-point of the second extraction period, and any
errors due to timing will not significantly affect the value so obtained on
analysis.
Application of the Method

Two distinct applications arise from the method. Firstly, the nitric acid value obtained after a 30-minute boiling period may be used as a soil test criterion or, secondly, when used in conjunction with the exchangeable potassium value estimated in the usual manner, the difference between the two values may be a measure of the fixed or non-exchangeable available (N.E.A.K.) fraction.

Both techniques have been used by Chapman (1971) in his examination of potassium trials conducted in the Mackay area since 1958, and, as a result, the nitric acid K values are to be used for soil test criteria for the Bureau’s Fertilizer Advisory Service in the Mackay area (Table I). In his study, both the nitric acid extractable K and the N.E.A.K. levels gave better correlations with responses to potassium fertilizer than the exchangeable K values.

| TABLE I—Critical levels of soil potassium using the nitric acid method |
|----------------------|----------------------|----------------------|
| Soil K m.e./100 g    | Category             | Recommended lb/ac K   |
| Below 0.80           | Low                  | 110                  |
| 0.80 - 1.50          | Medium               | 90                   |
| 1.50 - 2.50          | High                 | 50                   |
| Above 2.50           | Very High            | 0                    |

The techniques have now been used to examine soil samples from a series of four long-range potassium trials, planted in 1967 in the Mackay area, to determine long-term trends in potassium requirements on soils considered to be reasonably well supplied with this nutrient.

Treatments on these trials range from 0 to 175 lb K/acre/year. The results of the analyses of samples taken at planting in 1967 and at harvest in 1968 and 1969 are shown in Table II. The results are the mean of 24 determinations at each sampling of each trial and cover the complete range of treatments.

| TABLE II—Summary of potassium soil test data from four trial sites over the period 1967-1969 |
|------------------------------------|------------------------------------|------------------------------------|
| Trial site | Year | Exch. K. | Nitric acid K. | N.E.A.K. |
| SC-67-1    | 1967 | 0.17     | 12.3           | 0.87     | 4.9   | 0.70 | 4.5 |
| SC-67-1    | 1968 | 0.11     | 21.1           | 0.81     | 4.7   | 0.70 | 3.7 |
| SC-67-1    | 1969 | 0.12     | 44.2           | 0.80     | 6.4   | 0.68 | 5.4 |
| SC-67-2    | 1967 | 0.23     | 9.2            | 1.20     | 4.9   | 0.95 | 5.5 |
| SC-67-2    | 1968 | 0.11     | 13.5           | 1.07     | 11.1  | 0.95 | 12.0  |
| SC-67-2    | 1969 | 0.16     | 21.4           | 1.11     | 7.0   | 0.96 | 7.1  |
| SC-67-3    | 1967 | 0.17     | 8.7            | 1.18     | 4.4   | 1.01 | 5.5 |
| SC-67-3    | 1968 | 0.11     | 14.0           | 1.09     | 2.4   | 0.98 | 2.8 |
| SC-67-3    | 1969 | 0.11     | 24.1           | 1.06     | 2.5   | 0.95 | 3.8 |
| SC-67-4    | 1967 | 0.28     | 19.8           | 1.58     | 17.7  | 1.33 | 24.4 |
| SC-67-4    | 1968 | 0.25     | 24.5           | 1.55     | 17.1  | 1.30 | 21.6 |
| SC-67-4    | 1969 | 0.21     | 23.8           | 1.52     | 17.1  | 1.32 | 22.6 |
Treatment and block effects have been removed before the calculation of the standard errors and the co-efficients of variation, so that these values represent the within-site variation of the various types of potassium. It is obvious that the exchangeable K values usually exhibit a much greater co-efficient variation than the corresponding nitric K and N.E.A.K. values. This probably accounts for the comparatively poor correlation obtained with exchangeable K by Chapman (1971) in his study.

It is also noted that there is a proportionally large year to year variation in the exchangeable K levels. This may be due to seasonal effects rather than to any actual decrease in potassium reserves in the soil as, from data not presented here, there does not appear to be any strong relationship between exchangeable K levels and treatments.

It is suggested that the N.E.A.K. value could provide an excellent stable site characteristic for the long-term potassium-supplying ability of the soil, but it is not known at present, whether it will, on its own, be suitable for short-term fertilizer recommendations. The nitric acid K values are also relatively stable, most of the variations being due to the variation in the 10-20 per cent fraction which is exchangeable.

The continuation of these trials until significant and consistent responses to potassium fertilizer are obtained will be of considerable value in deciding which type of potassium test is most suitable for making fertilizer recommendations.

Conclusion

For the generally illitic soils under cultivation in the central district, the application to the nitric acid method should provide a means of accurately assessing the potassium status of the soil. The method has been found to estimate both the exchangeable and non-exchangeable available levels of the potassium reserves giving a value which has been found to be relatively stable. Seasonal variations in these values are also proportionally small, which makes the system of analysis applicable to fallow land also. The system therefore has a wider application than the present leaching technique and could find use in other areas where X-ray analysis has indicated the occurrence of illite or other similar primary potassium minerals.

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REFERENCES