

# A Note on a Method for the Estimation of Exchangeable Bases in Black Soils Containing Free Calcium Carbonate and Soluble Salts Including Gypsum

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**Introduction:** There are several methods for the estimation of exchangeable bases in soils. All of them are satisfactory for normal non-calcareous soils. When the soil contains free calcium carbonate none of the methods is quite good. But fairly accurate values can be obtained by Hissink's Sodium Chloride method and Kelly's alcoholic potassium chloride method provided the soil contains a fair amount of free calcium carbonate (i. e., more than a sufficient amount of calcium carbonate in 25 grms. of the soil to saturate 2 litres of the leaching solution). These methods also fail, however, when the soil contains soluble salts such as chlorides and sulphates. In the case of soils containing free calcium carbonate and soluble salts no satisfactory method is available for the estimation of exchangeable bases. The idea that would strike one immediately would be to wash out the soluble salts and then to estimate the exchangeable bases by Hissink's or Kelly's method. There are, however, many practical and theoretical considerations which prevent this idea being adopted. First of all during the removal of the soluble salts by washing with water, changes are brought about in the exchange complex of the soil which would vitiate the procedure. On the practical side it is found that even before the major portion of the soluble salts are washed out the soil becomes dispersed and passes through the filter.

A. N. Puri (Soil Science 40, 1935, pp. 239—241) had suggested leaching the soil with ammonium carbonate and estimating the exchangeable magnesium and the degree of alkalisation in the leachate after evaporation. The leached soil after treatment is to be used for the determination of the base exchange capacity. The method is simple in that the exchangeable bases are estimated by simple titrations. But it fails altogether for saline and alkaline soils and for soils containing gypsum. The soluble salts present in these soils would be converted into carbonates (law of mass action) and would be taken as exchangeable bases. Another defect of the method is that the extracting agents employed are not quite satisfactory. In Puri's method 50% alcohol is used for dissolving out the alkali carbonates and normal ammonium carbonate solution for extracting magnesium carbonate. It has been found that even with synthetic mixtures of carbonates of sodium, potassium, magnesium and calcium 50% alcohol does not extract more than 75% of sodium and potassium carbonates while normal ammonium



carbonate solution extracts only about 50% of magnesium under the best of conditions. So Puri's method is not suitable for estimating the degrees of alkalisation in soils; nor is it satisfactory for the determination of exchangeable magnesium.

In our work on "Cholam Effect" we have had to study the physico-chemical properties of Koilpatti soils. In Koilpatti it has been found over the last 25 years that cotton following Irungu cholam in crop rotation is stunted in growth and the yield of cotton is on the average about 16% lower than when it succeeds cumbu. This harmful effect of Irungu cholam on the succeeding cotton crop is termed "Cholam Effect". The chemical investigation of the phenomenon has been undertaken and the Koilpatti soils are being studied in detail. These are heavy clay soils which crack deeply in summer. They have been formed under semi-arid conditions. There is an abundance of free calcium carbonate (Kankar) in the soil and appreciable amounts of gypsum are also found.

As one of the hypothesis put forward to account for the harmful effect of cholam on the cotton following it, was a rise of sodium in the soil it became necessary for us to estimate the exchangeable sodium by a direct method. There were no satisfactory methods for the estimation of exchangeable bases in a soil containing free calcium carbonate, gypsum and soluble salts. As a result of a large amount of preliminary work the following method was adopted.

**Procedure for Calcareous Soils and Alakaline Soils not Containing Gypsum:** Ten grammes of the air-dry soil are weighed out into a beaker and stirred with 50 cc. of 40% alcohol adjusted to pH 7.05 with ammonia. It is allowed to stand and the clear supernatant liquid is transferred to a filter. The soil is washed by decantation three times for calcareous soils not containing much of soluble salts especially sulphate in the form of gypsum. The washed soil is leached in the cold with 500 cc. of N/2 ammonium acetate solution adjusted to pH 8.4 with ammonia. The leachate is evaporated to about 100 cc. and calcium is estimated in it as calcium oxalate by the volumetric method.

The filtrate and washings from calcium estimation are evaporated to dryness on a water bath after the addition of about 1 cc. of 1:1 sulphuric acid. The residue is ignited to remove ammonium salts and then dissolved in dilute hydrochloric acid and made up to 250 cc. In aliquots of 75 cc. magnesium, sodium and potassium are estimated as magnesium pyrophosphate, triple acetate of sodium uranium and magnesium and potassium platinichloride or cobaltinitrite respectively.

The leached soil is saturated with 10 cc. of N/2 ammonium chloride solution and then washed with 40% alcohol adjusted to pH 7.0



until the washings run free from chloride. The washed ammonium soil is distilled with magnesium oxide and the ammonia liberated is estimated to obtain the base exchange capacity of the soil.

**Procedure for calcareous soils containing gypsum:** In the case of such soils after washing 3 to 6 times with 40% alcohol 10 gms. of the soil is digested with 20 cc. of saturated barium hydroxide solution stirred vigorously and allowed to stand for half-an-hour with frequent stirring. Carbon dioxide is bubbled through the mixture to precipitate the excess of barium as barium carbonate. The mixture is then heated on a water bath at about 80°C for about 15 minutes. 100cc. of N/2 ammonium acetate adjusted to pH 7.0 are added to the soil and the mixture is allowed to stand at about 60° for half-an-hour. The mixture is filtered and washed by decantation three times with 50cc. portions of N/2 ammonium acetate. The soil is transferred completely to the filter and leached with ammonium acetate until 500cc. of the leachate are obtained.

The leachate is concentrated to about 100cc. and calcium is precipitated in it as calcium oxalate. The precipitate is filtered and washed until the washings run free from chloride. The precipitate is rejected. The filtrate and washings are evaporated to dryness with 1cc. of 1.1 sulphuric acid. The residue is ignited to remove ammonium salts and then dissolved in dilute hydrochloric acid. The solution is made up to 250cc. and magnesium, sodium and potassium are estimated each in 75cc. aliquots. These are calculated as milliequivalents per 100 gms. of the soil.

The soil on the filter which has been leached with ammonium acetate is saturated with 10cc. of N/2 ammonium chloride solution. It is then washed with 40% alcohol adjusted to 7.05 with ammonia until the washings run free of chloride. The washed ammonium soil is distilled with magnesium oxide and the ammonia liberated is estimated in the usual method by absorption in standard sulphuric acid. From the volume of standard sulphuric acid used up the base exchange capacity of the soil can be calculated.

In calcareous soils it may be assumed that the soil is completely base saturated and that no exchangeable hydrogen is present. So if the sum of exchangeable magnesium, sodium and potassium is subtracted from the base exchange capacity the amount of exchangeable calcium is obtained.

**Discussion of the method:** The first step should consist in the removal of the free soluble salts present in the soil so that they do not complicate the estimation of the exchangeable bases. Water cannot be used for washing since it brings about changes in the exchange complex of the



soil and since it disperses the soil. However, 40% alcohol adjusted to pH 7.05 serves the purpose. It dissolves out the chlorides, carbonates, bicarbonates and a part of sulphate present in the soil. All the sulphate, however, cannot be removed by washing with 40% alcohol. The alcohol does not disperse the soil except when the free electrolytes are washed out. Three washings with 40% alcohol are sufficient in the case of soils not containing much chloride, carbonate etc.,; with saline and alkaline soils six to eight washings are required.

Sulphates, especially gypsum which are only slightly soluble in 40% alcohol can be removed from the solution by treatment with barium acetate or barium hydroxide. The excess of barium is thrown out of solution by bubbling carbon dioxide through the mixture. Exchangeable bases are estimated in the treated soils by leaching them with ammonium acetate solution. In the leachate exchangeable magnesium, sodium and potassium are estimated and the sum of these is subtracted from the base exchange capacity to obtain exchangeable calcium.

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