SCIENTIFIC APPARATUS AND LABORATORY METHODS

METHODS FOR THE DETERMINATION OF REPLACEABLE BASES IN SOILS

IT is not the purpose of this preliminary paper to discuss the general subject of base replacement in soils or to suggest its importance in soil economy. These phases of the subject have already received extensive attention by Van Bemmelen, Gedroiz, Hissink, Kelley and others. Our object is rather to advance a method whereby such replaceable bases may be readily determined quantitatively and with a minimum expenditure of time and effort. Writers on this subject from its inception record attempts to perfect such methods, but even the most recent contributions deplore the fact that to-day no procedure is at hand which gives accurate results alike with either acid or alkaline soils and with soils carrying organic matter in any considerable amounts.

The displacing solutions most commonly employed have been those of NH_4Cl, KCl and NaCl, but, as it is often desirable to determine replaced K and Na, the latter two salts are not always applicable. We thus have NH_4Cl left as the salt almost universally used for this purpose. It is unsatisfactory for three major reasons. First, where sufficiently large samples of soils are extracted to give proper amounts of Ca, Mg, Na and K for accurate gravimetric determination, and where tenth-normal (or stronger) solutions of NH_4Cl are employed, there remains upon evaporation an enormous amount of NH_4Cl which must be gotten rid of before these determinations can be made. This is often accomplished by volatilization, and, as is well known, where the amounts of NH_4Cl are large (many grams) and the amounts of Ca, Mg, Na and K small (often but a few milligrams) the possibilities of error due to mechanical loss are great. Furthermore, such a procedure is time-consuming and requires constant attention. Repeated evaporization with HNO_3, as used in some laboratories for this purpose, is also wasteful of time and disagreeable. The second, and, to us in the arid southwest, a very important reason for condemning NH_4Cl is that $CaCO_3$ is appreciably soluble in its solutions (280 ppm in tenth-normal NH_4Cl). The soils of this section are, almost without exception, calcareous, varying from 1 to over 50 per cent. $CaCO_3$; hence any solution which appreciably dissolves this salt is of questionable value where replaceable Ca is to be determined. Magnesium carbonate (finely ground magnesite) is also soluble in solutions of NH_4Cl, but to a lesser degree. The third reason for censuring NH_4Cl as a replacing agent is that it dissolves and removes from the soil large amounts of organic matter (especially from alkaline soils) which, as a soil colloid, may have a bearing on the replacement reaction.

The method which we propose for the determination of replaceable Ca, Mg, Na and K in mineral soils follows. A tenth-normal solution of $BaCl_2$, as suggested by C. S. Scofield, was finally adopted as the replacing agent, and for the following reasons: $CaCO_3$ or $MgCO_3$ are less soluble in it than in 10th-normal NH_4Cl; it does not appreciably dissolve soil organic matter; it is exceedingly active as a replacing agent. Five hundred grams of air-dry soil are placed in a glass percolation tube and leached with tenth-normal $BaCl_2$ solution until free from replaceable Ca (1,000 to 1,500 cc). The percolate is then made up to a definite volume with distilled water, and if at all turbid (which is not usual) filtered through a porcelain pressure filter. Two hundred cc are placed in a 250 cc graduated flask, 4 or 5 drops of con. acetic acid and 20 cc of sodium chromate solution (175 g. $Na_2CrO_4\,10H_2O$ per liter) are added in the cold to precipitate the Ba. The whole is made up to 250 cc, thoroughly agitated, and allowed to stand over night to clear. Careful examination has shown no absorption of either Ca or Mg by the $BaCrO_4$ precipitate. Two methods of procedure are here possible. The Ca and Mg may be determined by the soap titration method, or by the standard methods, after separating them from the chromate solution. Both are often used in this laboratory as checks. A full description of the soap method as modified by us will be given in the detailed report of this work soon to appear. Where the standard methods are to be followed, 150 cc of the clear, supernatant liquid are pipetted into a beaker and the Ca and Mg precipitated completely as insoluble phosphates by adding an excess of 2 per cent. ammonium acid phosphate solution in the cold and making alkaline with NH_4OH, as in the ordinary precipitation of Mg. Let stand over night, filter, wash with 2 per cent. NH_4OH, dissolve the precipitate in a small amount of hot dil. HCl, make up to a volume of about 100 cc with distilled water and bring to a boil. Add *just enough* NH_4OH to make *slightly* alkaline and throw out the phosphates, then with stirring add 10 cc of a 5 per cent. solution of oxalic acid and boil. The solution should now be distinctly acid, while the Ca will be precipitated completely as the oxalate. Filter and determine the Ca by titrating with a standard solution of $KMnO_4$. Evaporate the filtrate to a bulk of about 50 cc, cool, add 2 or 3 cc of the ammonium acid phosphate solution and precipitate the Mg as $MgNH_4PO_4$ by making alkaline with NH_4OH in the usual way, finally weighing as $Mg_2P_2O_7$.

Sodium and potassium are determined in the original $BaCl_2$ percolate as follows: an aliquot (100 cc or more) is placed in a porcelain evaporating dish, slightly acidified with HCl and 5 cc or more of a 14

per cent. solution of $(NH_4)_2SO_4$ added. Evaporate to dryness on the water bath, dry in the oven and drive off slight excess of ammonium salts in the electric muffle at low heat, finally heating to dull redness. Take up in dil. HCl, digest on the water bath for an hour or more, filter and determine Na and K by Hilgard's methods. The $BaSO_4$, *after heating,* has little or no tendency to absorb Na and K. This, however, is not true in the cases of Ca and Mg.

Where the soils carry soluble salts ("white alkali" soils),[1] the soil in the percolator must first be leached free from these salts with pure water before being subjected to the $BaCl_2$ treatment, or, where percolation with water is slow as is the case with heavy soils, a separate analysis may be made for water soluble bases and these subsequently subtracted from those found in the $BaCl_2$ solutions.

In the case of acid soils (unsaturated with respect to bases), the amounts of replaceable H-ion may be determined in the $BaCl_2$ percolate by means of titrations as recommended by Gedroiz and recently modified by Joffe and McLean.[2]

Representative data, solubility determinations and certain other work leading up to the adoption of these methods is in press in the technical series of bulletins of the Arizona Agricultural Experiment Station.

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SPECIAL ARTICLES

ANALYSIS OF THE COLOR OF THE SKIN AND ITS SIGNIFICANCE

OUR complexions and the colors of the skin are dependent on a variety of causes. Recent experimentation by methods to be briefly described here indicates that these causes include (1) pigmentation, or melanin and (2) the character, amount, distribution and velocity of flow of the blood in the capillary bed in the skin. Normal blondes and brunettes differ in the amount of pigmentation only. It is said: "That the pigmentation of the skin bears some relation to health is well recognized. Tanned individuals are generally healthy. But whether the action is a direct or indirect one is unknown."[1] I have found, however, that the condition of tan per se, due to pigmentation, is not such an indicator because of the fact that the blood, by reason of the reflection of light from the capillaries in the surface of the skin, contributes its quota to the composite color of the skin as seen by the eye. The eye is a poor instrument for analyzing or resolving the constituents of color.

Tintometer methods for estimating and recording the color of the skin may be of value to the medical profession in the course of the treatment of diseases in which appreciable color changes occur in the skin, but they do not in any manner analyze the light reflected by the skin and therefore can not record skin color in terms of the three attributes of color, that is, brilliance, hue and saturation. Spectrophotometric analyses of the light reflected by the skin and the subsequent analysis of these data into the components of red, green and violet excitation values and relative luminosity on the basis of the noonday sun as a standard furnish the only scientific method for obtaining information on the rôle played by pigment and blood in the color of the skin. So far as I know, no work has previously been done on this subject. This paper is a preliminary report of my recent investigations.

Accurate determinations of the color of the skin in terms of spectral wavelengths and amounts, with the subsequent analysis of such data, are doubtless of decided value in cases of jaundice, cyanosis, polycythemia vera (in which capillary dilatation and increased cell volume play a part), Addison's disease, hemochromatosis and anemia.

The instrument employed in these investigations, which will be reported in detail elsewhere in medical literature, is the Keuffel and Esser color analyzer. Reflection curves from various portions of the fingers or hands may be obtained in terms of the reflection of light from a block of magnesium carbonate by placing the hand or fingers in the position ordinarily occupied by the second magnesium block. I have also built and adapted to this spectrophotometer an attachment whereby the face or arm may be used and reflection curves obtained.

Figure 1, curve 1, shows the spectral distribution of light reflected from the fingers of a normal blond; curve 2 gives similar data in a case of Addison's disease; curves 3 and 4 are from two cases of polycythemia vera. In each instance corresponding fingers and areas were used. The ordinates give the percentages of reflection, while the abscissae give the wavelengths as read on the drum of the spectrometer.

These data as plotted in Figure 1 (and other similar data) have been analyzed into percentages of red, green and violet color excitation values and relative luminosity with noonday sunlight as the standard, in the manner described in detail in the report of the

[1] Soils carrying "black alkali" must be treated differently. A discussion of this case will appear in the bulletin referred to later.

[2] "Colloidal Behavior of Soils and Soil Fertility: II. The Soil Complex Capable of Base Exchange and Soil Acidity." In *Soil Science,* vol. 21, no. 3, pp. 181–195 (1926).

[1] Matthews, "Physiological Chemistry," 4th ed., p. 711, 1925.