A METHOD

for

THE ESTIMATION OF COPPER IN SOILS

and

ITS APPLICATION IN BRITISH COLUMBIA

by

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ABSTRACT

The dithizone titration technique devised by Grubitsch and Sinigoj was adapted for the determination of total and available copper in soils. The proposed procedure was short and simple and its accuracy when tested by recovering copper added to soils and solutions was found to be satisfactory.

The proposed procedure was used to determine total copper in the surface soils and parent materials of 38 uncultivated soil profiles from the Peace River Area, Fraser Valley, Vancouver Island and the central and southern Interior of British Columbia. The total copper content of the soils ranged from 12 to 98 p.p.m. Considerable variation was noted in soils from the same geographic area and no overall trends could be noted between the four areas. The total copper content of the soils compares favorably with those reported for other countries. Copper extracted with 0.1N hydrochloric acid from a number of soils from the Fraser Valley was determined by the dithizone method. The acid extractable copper ranged from 0.65 to 2.72 p.p.m.

Total copper was determined in the horizons of two soil profiles from the Fraser Valley, three from Vancouver Island and four from the Peace River Area. It was noted that soil development had a marked influence on the distribution of copper in the profiles. In the brown podsolic coastal soils podsolization resulted in a significant and consistent removal of copper from the A and B horizons. In the northern podsols the element was strongly leached from the A_2 and slightly from the B_1 horizons while it was accumulated in the A_{0-1} and retained in the B_2 horizons. Copper was accumulated in the A_1 and B_2 horizons of the degraded black profiles and removal

was restricted to the A_2 horizons. Poorer drainage position
in the coastal soils favoured a greater retention of copper
in the solum. The reverse was true in the Peace River profiles.

ACKNOWLEDGMENTS

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1. INTRODUCTION

The essentiality of copper as a plant nutrient was established about a quarter of a century ago. Since then a great many investigations concerning the role of copper in plant metabolism have been undertaken. Numerous experiments have also been performed on the use of copper fertilizers under field conditions.

The copper content of soils and the factors affecting its availability to plants have not been studied to the same extent as has been the case with certain other minor elements, particularly manganese and boron. In recent years, increasing attention has been given to the fraction of soil copper available to plants, but even this work must be considered as introductory.

One factor contributing to the limited study of copper has been the lack of suitable methods for quickly and accurately estimating the element in the soil. Apparently the dithizone titration technique first described by Grabitsch and Sinigoj in 1938 (24) has been overlooked in this connection. Since the volumetric method has been successfully applied to the detection of copper in plant material (67, 68) it was decided to investigate its use with soils. A portion of this thesis deals with these investigations.

No published report of the copper content of a British Columbia or other Canadian soil has been observed. Therefore, after studying the dithizone method, it was used to estimate the total copper present in a number of soil samples collected from various areas of British Columbia. The available copper in a number of samples from the Fraser Valley was also estimated. These studies are reported in the thesis.

2. REVIEW OF LITERATURE

Historical

The earliest agricultural use of copper was as a fungicide. Sprays containing copper were found valuable as a means of controlling certain fungal diseases, such as phytophthora infestans on potatoes and pronospora infestans on vines (14). It was only natural, therefore, that much of the early work was concerned with toxic effects resulting from the use of copper compounds in sprays.

At the beginning of this century, reports concerning the stimulating effect of copper on plants were quite prevalent (14). It does not appear, however, that the element was considered necessary for plant growth at that time. Not long afterwards there appeared numerous instances of the use of copper compounds to prevent or cure "dieback" in citrus fruits, pears, peaches, plums, apricots, and a host of other fruits. Copper fertilization was found to ameliorate "reclamation disease" of cereals grown on the peat soils of Europe (51). This disease is also known by a variety of other names whose origins appear to depend upon the manifestations of the deficiency, or the country or soil type in which it occurs. Thus "wither tip", "yellow tip", Heidemoorkrankeit, Gulspids, Ontginngszeitke, signify the same disorder (8). Allison Bryan and Hunter (1) state that, of all the minor elements added in plot tests, copper gave the most striking improvement on the saw grass soils of Florida. It was these workers who first began to suspect that copper was essential for plants.

The essentiality of copper was not fully proven until relatively recently. The amount of copper needed for plants in culture solutions

is very small and there is only a narrow range in which copper may
be used before toxic effects are produced. As with all minor elements,
extreme care must be taken to prevent contamination of the solution in
which the plants are grown. Thus Brenchley (7) reports that only toxic
effects resulted from the addition of copper to solution cultures. Not
until the advent of more sensitive methods for the direction of copper
was it realized that nutrient solutions previously used contained, from
a nutrient point of view, relatively large amounts of copper as an
impurity. It was found that special precautions were necessary to purify
salts (63). Water had to be distilled in an all pyrex apparatus, as the
copper stills commonly employed contributed impurities (10). Sommer
(63) in 1930 first proved copper to be essential for plants. She showed
the effect of copper deficiency on tomato, sunflower, and flax. The
symptoms were visible in the early stages of growth. Later, Arnon and
Stout (4) produced copper deficiency symptoms in tomatoes and showed
that the disease could be cured either by the addition of copper to the
culture solution or by spraying the plants. These and other experiments
proved the direct use of copper by plants.

With these improved culture techniques, it was possible to show
the similarity between reclamation disease and copper deficiency (51).
In Australia, Piper (59) showed that the symptoms of plants grown on a
sandy soil were identical to those produced in a copper deficient
solution. Both could be remedied by the application of copper salts.

Copper deficiency symptoms have now been established and
described for a large number of plants. Deficiency symptoms manifest
themselves in different ways, growth is poor, and the plants die back

without reaching maturity (Brenchley); chlorosis of leaf tips is common, as in white tip disease of barley and oats (59). Reproductive processes may be inhibited (73). Reed (52) reports that in tomatoes copper deficiency causes dwarfing, curling of leaflets, colour changes and necrosis resulting from shrinkage of the palisade cells of the leaves.

The function of copper in plant metabolism is not known; however, it is suggested that it plays an important part in the production of oxidative enzymes and the formation of chlorophyll (22).

Copper deficiency diseases in livestock have been known for some time. Investigations in Europe established that wasting disease in cattle was due to copper deficiency (22). In other countries "enzootic ataxia" or "swayback" has been attributed to copper deficiencies (17). In Australia, "coasty disease", "stringy" or "steely" wool, and "falling disease" are caused by a lack of copper (6). In animals, although copper is not a constituent of haemoglobin, it functions in the utilization of iron for the formation of haemoglobin (45).

Soil Copper

Copper Minerals

Copper is a widely distributed element and may occur in native form or combined with oxygen, selenium arsenic, antimony and chlorine. Also, it is often found as the arsenate, nitrate sulphate vanadate and silicate (16).

The most important copper mineral is chalcopyrite ($CuFeS_2$), which in most cases is the only primary copper mineral present in a copper

deposit. The other important sulphrelles - bornite (Cu_5FeS_4) and chalcocite (Cu_2S) - are of secondary enrichment. Native copper occurs in some deposits, although this is rather uncommon (16).

Other important Cu minerals:-

Tetrahedrite ($Cu_8Sb_2S_7$)

Cuprite (Cu_2O)

Malachite ($Cu(OH)_2.CuCO_3$)

Azurite ($Cu(OH)_2.2CuCu_3$)

Chrysocolla ($CuS_1O_2. 2H_2O$)

Copper is known to be a widely diffused trace element in igneous rocks (13); however, little appears to be known of the mineral forms in which it generally occurs. It would be expected then that the majority of secondary geologic formations, especially those more immediately derived from igneous material, would contain copper to a greater or lesser extent.

Although copper is a common and widespread trace constituent of soil, there is no information on the mineralogic forms in which it occurs.

Total Copper

Total soil copper includes all the various fractions of copper present in the soil. For the estimation of total soil copper, the sodium carbonate fusion method is most satisfactory (59); however, perchloric and hydrofluoric are also frequently employed. These chemicals are known to convert virtually all of the metal present into a soluble form (30).

Since the essential nature of copper for plant and animal life

has been established, we may infer that the element is contained in nearly all soils. The few exceptions in which soils are reported to contain little or no copper probably signify development under peculiar conditions.

Amounts of copper, ranging from 5 to 5,000 p.p.m., have been reported for soils (44), but 20 to 40 p.p.m. seems to be a usual upper limit for the soils of the United States (29). In Russia, Sedletsky and Ivanov (58) found that the average copper content of chernozems and red earths was 60 p.p.m. Peaty podsolized soils contained 30 p.p.m., while highly podsolized sands possessed only 3 p.p.m. of copper. The copper content of a virgin soil will depend to a large extent on the parent material and the soil-forming processes. Holmes (29) reports that the copper content of the surface horizons is generally slightly higher than those below. The Russian worker, Maliuga, states that the A_1 horizon contained more copper than the A_2, but that the ratios remained approximately the same for all the great soil groups studied (43). Krasnozems and serozems proved an exception. It appeared that the copper content was roughly proportional to the organic matter content of the particular horizon. The author felt, however, that the nature of the organic matter and the type of soil development should have been taken into account before such a generalization was made.

Available Copper

Due to the limited amount of work done, very little is known concerning the various fractions of copper present within the soil. Available copper exists (as would be expected from its ionic behaviour) as an ion on the exchange complex (49). It is apparently very strongly

held, and, in some cases, adsorption appears almost irreversible (46).

There is no accepted extractant for the detection of this so-called available fraction. Peech (49) raises objections to the use of ammonium acetate on theoretical grounds. He believes that the formation of a copper complex with ammonia would make the method undesirable. In place of ammonium acetate, Peech employs normal sodium chloride. King (38) has employed ammonium acetate buffered at pH 4.8. Other extracting solutions that have been employed are 0.5 N potassium chloride (27) and ammonium acetate, and at pH 7.0 (75).

Wood (75) suggests that copper may be further subdivided on the basis of extraction with acids of different concentrations. He considered ammonium acetate extractable copper easily available to plants. Copper extracted with boiling N and 5N nitric acid was termed "difficulty" and "very difficulty available", respectively. Results obtained by these methods proved to be very consistent, but Wood does not show any relation between these fractions.

Using N sodium acetate, Peech (48) found an average of 0.28 p.p.m. of available copper in sandy soils from Florida citrus groves. He reports that the soils responded to fertilizers containing magnesium magnanese, zinc and copper. Wood (75), using N ammonium acetate buffered at pH 7.0, extracted quantities of copper ranging from 0.16 to 0.6 p.p.m. from some Oregon soils. No copper deficiency symptoms were reported. Working with potato soils, King (38) found available copper present in amounts up to 60 p.p.m. His extractant was N ammonium acetate buffered at pH 4.8. The crops growing on some of the plots had previously been treated with Bordeaux mixture, which would explain the high results.

Most authors do not present sufficient data on the correlation of analyses with the incidence of copper deficiency symptoms. In the final analysis, the adoption of a general method of extraction should be based upon such a correlation. This will have to await further investigation.

Factors Affecting Availability of Copper

Soils high in organic matter, particularly the newly cultivated peats of Europe and the so-called muck soils of the Eastern United States, most frequently exhibit copper deficiency. Copper deficiency, however, has been reported on many soil types. Bryan (11) points out that a lack of copper may occur on any soil type, but that "a deficiency is more prevalent on acid soils with clean cultural practices than on neutral soils with plenty of cover crop". Australian workers have reported copper deficiencies in many areas, but particularly on sandy and gravelly soils (70).

Copper deficiency in soil is difficult to detect, as plant symptoms may vary from slightly stunted growth to the extreme cases previously described.

Very little is known about the actual mechanism of adsorption and fixation of copper in soils. As previously stated, it appears to be tenaciously held, both by organic and inorganic colloids. Peech (46) reports that it is strongly fixed, even at low pH. He found that on a light, sandy soil, as much as 90 per cent of the copper was rendered unavailable, and that as the pH was increased, fixation increased proportionately. Steenbjerg (64) has shown copper availability to be at a maximum between pH 5.5 and 6.5. Jamison (34) found that phosphates

have little effect on the utilization of copper by plants as a result of work with Florida soils. Harris (25) reports that there was no evidence of any interaction between the minor elements cobalt, copper, manganese and boron.

A point, perhaps largely of academic interest, is that raised by Sullivan (56). While experimenting with adsorption of copper by clays, Sullivan found a remarkable interchange of bases. Copper apparently, instead of being adsorbed by the clay, entered into the silicates, releasing an equivalent amount of base, K_2O, Na_2O, CaO, MgO or MnO, which went into solution. Of the clays used, feldspar proved more efficient than kaolin and removed from 60 to 100 per cent of the copper from the liquid. Such behaviour may explain in part the strong, almost irreversible fixation of copper in soils.

Where the organic matter content of soils is high, it has been found that much more copper is required to ameliorate a deficiency than on light textured soils, where similar quantities might be toxic. In Europe it was found that 2 to 3 milligrams of copper per kilogram was was sufficient to produce reasonably high yields on peats, but that amounts up to 1280 milligrams brought about even further increases without toxic effects (51). This would indicate that organic matter has a strong affinity for copper. Peech (47) reports that the adsorption of copper is roughly proportional to the organic matter content of the soil. Organic residues applied to the soil are capable of rendering much copper unavailable (38). Hoffman (28) has produced copper deficiency by the addition of a purified humus preparation to culture solutions. It seems very likely that on peat and muck soils the problem of copper

deficiency is one of availability rather than a total absence of the element.

From the extensive work on reclamation disease, there developed a rather interesting theory respecting its cause. It had been suggested that some specific agent produced the disorder. Following this suggestion, Smith (61) succeeded in isolating from a black moor (gliede) soil two organic fractions extracted by hot alcohol. One fraction remained in solution on cooling, and from this he prepared a crystalline substance which was fairly volatile up to 100° C. Very small quantities of this substance, which he called "gliedene", when applied to the soil were capable of producing typical symptoms of reclamation disease. Rademacher (51), elaborating on Smith's theory, states that "gliedene", if it exists at all, probably acts by adsorption of copper. Smith had postulated that "gliedene" was toxic to plants and that copper added to sick soils served to inactivate the toxin.

The relation between the occurrence of copper deficiency and an unfavorable soil water relationship has been noted by Rademacher (51), who regards the effect as one of solubility, suggesting that insufficient copper went into solution in the absence of much "free" water. Piper (50) observed a marked reduction in reclamation disease symptoms on a calcareous soil as a result of a rise in soil temperature. He attributes the effect to an increased solubility of the "unavailable" copper. Arnd and Segeberg (2) state that copper added t o the soil alters the physical condition of the colloids in such a way as to increase the amount of "free" water. These workers further postulate that copper sulphate flocculates the organic soil colloids which serves to keep the

capillaries open when the humus dries out, thus allowing the upward

movement of moisture. However, since copper deficiency has been estab-

lished to be the cause of reclamation disease, these effects, if they

do influence the amelioration of the disease, are probably of secondary

importance.

There is some additional evidence which indicates that the

action of copper may be an indirect one. Lazarev (40) states that, in

some cases, plants suffering from what appeared to be reclamation

disease contained large amounts of iron and manganese. The plants

responded to applications of copper. However, he found that hydrogen

peroxide also remedied the condition, as did other oxidizing substances,

and suggested that reclamation disease, in many cases, may be due to

reducing conditions leading to the formation of ferrous iron. Arnon

(3) found that copper improved barley plants grown in solutions with and

without aeration. Willis and Piland (71) noted that the soil potential

was quite markedly increased by the addition of copper when air was

present, but that the reverse was true when air was excluded. These

investigators concluded that the action of this element in the soil was

largely catalytic. They state that copper is a general oxidation

reduction catalyst and the direction in which it acts is determined by

the oxidation conditions existing in the soil. These authors also present

evidence for the antagonism of copper and iron - in field work, appli-

cations of copper appeared to reduce the availability of iron and iron

chlorosis developed quite rapidly. Copper also served to decrease the

uptake of manganese by the plants. In culture solutions, the presence

of copper has been found to reduce the availability of the iron present

(12). Sommer (60), who noted the same effects, attributed it merely to

the precipitation of iron and the rapid growth of the plants when copper was present. The evidence seems to suggest that copper plays a part in the oxidation reduction system of the soil. Whether such action may be attributed to a direct function of copper, or whether it is brought about by the stimulation of bacterial growth, as it could very likely be, is still somewhat in doubt.

Copper Fertilizers

The use of copper as a fertilizer is increasing rapidly in limited areas. However, as the majority of soils seem adequately supplied at present, there is little justification for its universal use. Further, in regions where copper is employed as a fungicide, it seems likely that these sprays would supply the needs of plants as absorption can take place through the leaves as well as the roots (65).

No generalization can be made as to the rate of application. The severity of the deficiency and the nature of the soil should always be taken into consideration. In the Florida Everglades, applications of 30 to 50 pounds per acre have improved yields greatly (65). In New York, applications up to 300 pounds of copper sulphate per acre have served to prevent the production of poorly coloured scales and premature dying hack of onions (39). These are both organic soils. On lighter textured soils the amount of copper that could safely be applied would be expected to be roughly proportional to the adsorptive capacity of the soil. Thus in Australia about 10 pounds of copper sulphate are recommended for use on light soils, while up to 42 pounds per acre have increased yields on finer textured soil (70).

In British Columbia, fertilizers containing copper are at

present being sold. However, their use is not recommended by official agricultural agencies (9).

Methods of Analysis

A great deal of work has been done on the determination of copper when present in small quantities. The methods described in the main seem satisfactory insofar as accuracy is concerned. However, the majority of the procedures are somewhat tedious and not well adapted to routine occasional analysis, where, besides a reasonable degree of precision, simplicity and rapidity are often important factors.

Dithizone

The reagent most commonly used for both the separation and determination of copper, and many other heavy metals, is diphenylthiocarbazone or dithizone:-

$$S = \begin{array}{l} NH.\ NH.\ C_6H_5 \\ N = N - C_6H_5 \end{array}$$
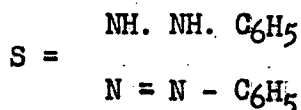
This compound was first prepared by Emil Fischer, who noted its action with the heavy metals. It was not used analytically until 1925, when Hellmut Fischer (19) showed that the coloured dithizonates could be used for the determination of certain heavy metals. Since that time a great deal of work has appeared in the literature on its use as an analytical reagent.

Dithizone itself is a violet black solid, which dissolves in a great many organic solvents, forming an intense green solution. The most commonly employed solvents are chloroform and carbon tetrachloride. The latter is generally preferable, as there are less hazards in its use. When dithizone dissolved in carbon tetrachloride is shaken with a

solution of some heavy metal, an internal complex salt is formed (20). This dithizonate is generally soluble in the organic layer, to which it imparts a violet, red, orange, or yellow colour, depending on the metal present.

When dithizone is used for the colorimetric determination of metals, two general methods are available - the mono- and mixed-colour methods. In the mono-colour method, the solution containing the metal is shaken with an excess of dithizone so that the organic layer remains green, indicating complete extraction of the metal. The excess dithizone is then removed by shaking with a dilute solution of a base, such as ammonium-hydroxide. The absorption of light by the undecomposed metallic complex may then be measured. Sandell (57) points out that such a removal of excess dithizone may possibly introduce error. There may be decomposition of a portion of the dithizonate if the alkalinity is too high, or incomplete removal of the dithizone if it is too low. Another objection to the mono-colour method is the possibility of converting the keto complexes of certain metals to the enol tautomers on washing with an aqueous solution of a base. The enol form is often of quite different colour and so may markedly affect the visual and colorimetric determination of the metal.

The so-called mixed colour method permits a higher degree of accuracy (57). In this case, the excess of dithizone is allowed to remain in the organic solvent with the dithizonate. In visual work, the colour of the solution is compared to a series of standards, each containing the same volume of dithizone as the sample. If an electrophotomer, or some similar device, is to be used, a choice of two wave-

lengths is available. Either the absorption of light by the metal complex (625 mu for copper) or by the excess dithizone (510 mu) may be measured (41). Copper, lead, zinc, and some other dithizonates appear to obey Beers' law when monochromatic light is used. When filters are employed, deviations can be expected, and the extent of the deviations will depend upon how truly monochromatic the transmitted light is, and how nearly this light approaches the wave-length of maximum absorption.

The mechanism of extraction of a metal by the formation of an internal dithizonate is now the established basis for the analytic separation of certain elements. Although dithizone reacts with a large group of metals, the reaction may be made relatively specific in one of two ways: first, the pH of the solution from which extraction is made may be adjusted so that only a small number of metals will react; secondly, a complex-forming agent may be employed to prevent the reaction of certain ions.

Generally, if the amount of reacting metals is small, it may be desirable to perform the extraction under such conditions that certain other metals are also removed from the aqueous solution. Such a preliminary extraction, involving an excess of dithizone, is very often used, and is of great advantage as a means of avoiding interference, especially by oxidizing substances (57). The organic layer can then be separated and shaken with suitable acids and complex-forming agents so that the metal under investigation passes into the aqueous layer or remains in the organic solvent, thus effecting a separation from other metals. Dithizone is also used to separate certain elements prior to spectrographic analysis (55).

Carbamate

Another reagent quite commonly used for the detection of copper in trace amounts is diethyldithiocarbamate $(N(C_2H_5)_2CS_2Na)$, or carbamate. This compound, however, is not as sensitive nor as specific for the detection of copper as is dithizone (57).

In acid or ammoniacal solutions of cupric salts, a brown colloidal suspension is produced with carbamate. This copper carbamate is soluble in amyl alcohol, amyl acetate, carbon tetrachloride, and other solvents. In practice, the suspension is generally extracted into carbon tetrachloride and the light absorption of the resulting yellow-brown solution measured.

Other metals besides copper give coloured precipitates with carbamate, the majority of which are soluble in carbon tetrachloride. Zinc, cadmium, mercury silver, lead, and tin yield white precipitates. Iron produces a dark brown suspension, but the interference of this metal can be reduced, if it is not present in large amounts, by carrying out the precipitation at pH 9 or above (57). Pyrophosphate is reported to reduce the interference of much iron, but in the presence of calcium difficulties due to precipitation are encountered (15). The principall interfering metals are bismuth, cobalt , and nickel (59). If these elements are present in unduly large amounts, special precautions must be observed. Manganese imparts a pink colour to the organic solvent, but fortunately this oxidation product is not stable and decomposes rapidly (57).

A blue filter or light at 440 mu is generally employed, as it permits a more sensitive determination of copper, especially when much

iron or manganese is present (57). The relation between copper concentration and light absorption is unfortunately not logarithmically linear with a blue filter.

To reduce the possibility of interference, copper is usually extracted with dithizone before this reagent is employed.

Procedures Employed for the Determination of Copper in Soils

The procedures employed at present for the colorimetric analysis of copper in soils are generally adaptations of methods previously developed for foods, silicate, rock, metals, and other materials. Special precautions are required with soils, as the concentration of interfering substances is higher than in many other materials; for example, plants.

Holmes (30) describes a procedure in which the preliminary extraction with dithizone is made at pH 2.5, so that besides copper, lead, zinc, and bismuth are also extracted. The carbon tetrachloride layer is then shaken with 0.02 N HCl to remove lead and zinc; bismuth is extracted with an acidic solution of potassium iodide. Copper remains in the organic solvent and is determined colorimetrically with carbamate after the destruction of dithizone. This procedure was designed by Holmes for the subsequent determination of lead, zinc, and cobalt. If only copper is to be determined, a shorter overall procedure could be used.

Sandell (57) outlines a procedure for the determination of copper in silicate rocks, and points out that if only copper is to be determined it could be isolated directly from a dilute acid solution. He states, however, that no data is available on the reliability of this modification. A procedure employing carbamate directly has been developed by Sherman and McHargue (59). The interference of iron is reduced by

carrying out the precipitation in the presence of citrate and at pH 9.0 or above. One serious objection to this method is the possibility of interference by bismuth, cobalt and nickel. If these metals are present to any extent, it would certainly be necessary to introduce additional precautions.

Other workers have used spectrographic methods for the detection of copper (60, 54). These methods involve rather expensive equipment, and therefore unlikely to be employed in the ordinary laboratory.

As part of this study, it was decided to try to develop a more direct method for estimating copper in soil. To accomplish this, as many as possible of the numerous manipulations required in the presently used methods would have to be eliminated. It was realized that if this could be accomplished it would be highly beneficial for copper fertility studies, which are handicapped by the lack of a short, direct method for estimating soil copper.

The volumetric technique first devised by Grubitsch and Sinigoj (24) appeared to be the simplest and most direct method available for the detection of copper. A study of the possibility of adopting this technique to soils was considered to be worthwhile. The method involves simply a titration of copper in a dilute acid solution with dithizone. When a carbon tetrachloride solution of dithizone is shaken with an aqueous solution of copper, a red violet complex is formed. When there is just a slight excess of dithizone the c olour becomes reddish-purple. If a further excess is added, the mixing of colours will produce a neutral gray tint with approximately equal quantities of dithizone and dithizonate. Thus two end points are available for the titration, although the gray one is preferable, being much easier to detect and

permitting greater speed. Also a less critical colour appreciation is required (67).

The author consulted Dr. Delavault, of the Geology Department at this University, and no serious objections could be raised against the use of this technique. Dr. Delavault and Miss Irish have employed the method with considerable success for the analysis of plant material (67,68). These workers concluded that an accuracy of five per cent could be expected for a person with normal colour vision.

3. EXPERIMENTAL

Preliminary Study of Method of Analysis

Soil, after it had been ignited, was decomposed with hydrofluoric and perchloric acids. Excess perchloric acid was driven off by heating. The residue was taken up in sufficient hydrochloric acid to make the final concentration 0.1 N. In a solution of this acid concentration it was thought that the copper present would be dissolved. Adsorption of copper by any residue, would be negligible as the amounts of the ions adhering, would be proportional to their concentration in the solution. Hydroxylamine hydrochloride was added to reduce the interference of iron (57).

In a hydrochloric acid solution of the strength used, the metals palladium, gold, silver, mercury and copper will react with dithizone (21). Bismuth also reacts, but only incompletely when a slight excess of dithizone is present. Manganese, nickel, cobalt, lead, and moderate amounts of zinc, do not react under these conditions. Ferric iron interferes with dithizone extractions chiefly by oxidation, since it does not form a dithizonate (57).

During ignition, mercury which might be present in small amounts would be volatilized to a large extent, and so would not interfere. In a hydrochloric acid solution, silver would be expected to react only with difficulty. Bismuth, as stated previously, reacts only incompletely, especially so in the titration technique employed where but a slight excess of dithizone would be present. Some workers, too, have failed to detect bismuth in soils (54, 66). Fiegl (18) states that gold dithizonate flocculates in carbon tetrachloride, and so would be detected easily if present in comparatively large amounts. Palladium in all likelihood would not be present to any great extent in soils. Thus it may be expected, under normal conditions, that dithizone in a dilute mineral acid solution would be relatively specific for copper in soils.

The first problem encountered with the method of analysis was that there appeared to be an extensive oxidation of dithizone. An increased amount of hydroxylamine hydrochloride did not serve to eliminate the oxidation. It was then thought that bismuth might have interfered by producing its characteristic orange colour. Shaking the carbon tetrachloride layer with an acidic 2 per cent potassium iodide solution did not remove the brown discoloration. The extent and rapidity of the reaction also indicated that bismuth was not the cause of the discoloration, as one would expect this element to react at an even slower rate than copper.

The possibility that the oxidation was a catalytic reaction activated by the presence of colloidal material was then considered. The nature of the reaction strongly suggested some such action. To

test this, the soil extract was filtered, using both filter paper and sintered glass funnels. Filtering, although it did reduce the frequency of oxidation from about 50 to 20 per cent, did not eliminate it. Previously, filtering had been avoided, as it was reported that a slight residue did not interfere (67). Filtering the solution eliminated one disturbing form of behaviour. Occasionally, without filtering, the carbon tetrachloride layer formed a suspension, apparently by adhering to the finely divided residue. In such cases, oxidation had proceeded even more rapidly, and the two layers took considerable time to separate. With the absence of any residue in the filtered solutions, this no longer occurred.

Although the use of a stronger reducing agent was considered, it was deemed inadvisable to employ one, since it might have a marked influence upon the valence states of the ions present. Changes in valence could possibly alter the specificity of the dithizone reaction.

No serious errors could be attributed to the procedure itself, and the difficulties encountered thus far appeared to be more a matter of degree than due to inherent fault in the method. The perchloric acid had previously been driven off at a temperature of about 120° C. Such a temperature was considered adequate, as perchloric acid decomposes under atmospheric pressure at 92° C. That the oxidation of dithizone could have been achieved by perchlorates which, although stable at lower temperatures, could be decomposed by further heating, was considered possible. Consequently, the residue from the hydrofluoric and perchloric acid digestion was heated on a sand bath where a temperature up to 300° was attained. The heating was continued for varying lengths of time.

It was found that heating until the whiteness of the residue was replaced with a moderate amount of iron staining proved most satisfactory. The stained residue was then evaporated with 6 N hydrochloric acid. This would be expected to reduce adsorption and to increase solubility by converting the metallic ions present to the generally more soluble chlorides. Only three cases of oxidation were noted after the introduction of this modification, and replicates showed much closer agreement. The colloidal and siliceous residue remaining no longer gave any evidence of interfering with the determination, and filtering could be eliminated.

Two further refinements were considered: firstly, Lundell, Hoffman and Bright (42) found that iron did not interfere with the extraction of copper by dithizone when sulfuric acid was used. The method, however, did not appear to offer any advantages, and the possibility of precipitating calcium would make the use of this acid unsatisfactory with soils. Further, the behaviour of the various metal dithizonates in the presence of sulphuric acid is not well enough known to justify the use of this method. In steels, where the procedure is used, many of the interfering elements are known to be absent. When tried with soil in the present study, the method appeared to have no advantage; secondly, the use of potassium iodide in the solution was attempted as a means of reducing even further the interference of bismuth. The iodine produced discoloured the solution and made the detection of the end point impossible. For reasons previously stated, it was felt that it would be unwise to add a further excess of a fairly strong reducing agent to remove the colour. The presence of potassium

iodide appeared to reduce the interfacial tension between the aqueous and carbon tetrachloride layers. A brownish suspension formed at the interface and the layers did not separate rapidly. This refinement was therefore abandoned.

Procedure Proposed for Total Copper

Reagents

1. Water - redistilled in an all-pyrex apparatus.

2. Hydrochloric acid - redistilled acid is preferable.

3. Perchloric acid - 60 per cent.

4. Hydrofluoric acid.

5. Dithizone solution - 60 milligrams per litre of carbon tetrachloride. Store in a black bottle in a cool place. If the dithizone used is of good quality, no purification is necessary.

6. Carbon tetrachloride - C.P. or reagent quality. The used carbon tetrachloride may be recovered by first washing with dilute HCl, then with dilute ammonium hydroxide. After drying with calcium chloride, distil.

7. Hydroxylamine hydrochloride - should normally be free from copper without further purification.

8. Standard copper solution - dissolve electrolytic copper in nitric acid. Expel oxides of nitrogen and make up to volume with 1.0 N hydrochloric acid.

Determination

1. Soil which has been passed through a 2 mm. iron sieve is ground in an agate mortar to pass 100 mesh bolting cloth. Copper or brass screens should be avoided.

2. 0.5 gms. of soil is weighed into a platinum crucible and placed in a muffle furnace. The temperature is slowly raised to 500° C. and heated until organic matter is destroyed, approximately 2 hours.

3. 1 ml. of perchloric acid and 8-10 ml. hydrofluoric acid are

added and, after stirring, evaporated on a water bath. The residue should normally be white or greenish-white.

4. Place the crucibles on a hot-plate or sand-bath and heat at 250-300° C. until the residue is distinctly stained with iron. It is essential that none of the white crust obtained from the previous evaporation remains.

5. Add 4-5 ml. 6 N hydrochloric acid, washing down the sides of the crucible. Evaporate to dryness.

6. Take up the residue in enough hydrochloric acid to make the acid concentration of the final solution 0.1 N. (The final volume of the solution in the following titration may be any constant, exact volume between 20 and 30 mls. The analyst must select the most convenient volume for his determinations and calculate the amount of acid needed to produce the desired concentration).

7. Transfer to a stoppered 50 ml. graduate and wash with hot water to the previously selected volume. The water and crucible should be kept as hot as possible to reduce adsorption.

8. The solution is then titrated with standardized dithizone. Shake for 20 to 30 seconds after each addition of dithizone. When the neutral grey end-point has been reached, shake for 1 minute, to ensure complete extraction of the copper.

Standardization of Dithizone

In practice it will probably be most convenient to employ a standard solution containing 20 γ of copper in 0.1 N hydrochloric acid. The titration is performed in the usual manner. If the unknown sample requires a large amount of dithizone, it may be advisable to employ a

standard containing a greater amount of copper, so that the volume of dithizone is approximately the same for the unknown and the standard. The dithizone solution should be standardized at least every second day.

Notes

1. Precautions should be exercised throughout the procedure to guard against contamination with copper, especially since the metal is often a constituent of laboratory equipment. Blanks should be run through the procedure and the necessary corrections made.

2. All glassware used should be chemically clean. The method of cleaning will largely be governed by the analyst's preference. The author found that allowing the equipment to stand over-night after the addition of hot 10 to 15 per cent nitric acid was most efficient and convenient. The vessels were then washed several times with tap water, followed by three rinsings with redistilled water.

3. The concentration of dithizone should not be varied from the concentration given. It was thought during this study that perhaps greater sensitivity could be achieved by employing a more dilute solution. However, the quantity of 60 milligrams per litre employed by Grubitsch and Sinigoj afforded the most sensitive colour appreciation.

Study of Ion Interference

Several tests were made in order to attempt to assess the effect of various ions on the accuracy of the procedure. Since ferric iron is known to oxidize dithizone, an estimation was made of how effectively hydroxylamine hydrochloride, as employed, would reduce this interference. Ferric chloride, which had been purified by shaking with dithizone, was used. In the first series of studies, the ferric iron was added to solutions containing known concentrations of copper. Some

of these solutions were left untreated, while hydroxylamine hydro-
chloride was added to others. The results are compared in Table I.
It was found that the presence of iron in the solutions to which no
hydroxylamine hydrochloride had been added served to increase the amounts
of copper found. This apparently was due to the formation of the brown
oxidation product which would lead to a high apparent end point. After
treatment with hydroxylamine hydrochloride, the interference of iron
was virtually eliminated.

TABLE I -

Effect of Iron and Zinc on the Determination of Copper
(Dithizone Titration Technique)

Copper Present γ	Ions Added	Copper Found γ
20	40 mg. ferric iron	24.7
20	80 mg. ferric iron	27.2
20	40 mg. ferric iron - reduced with hydroxylamine hydrochloride	20.6
20	80 mg. ferric iron - reduced with hydroxylamine hydrochloride	20.8
20	80 γ zinc	20.0
20	240 γ zinc	20.4

Soil to which additional quantities of iron had been added were analyzed and these results compared to those obtained with the untreated samples. The results in Table II show that the increased quantities of iron had but a negligible effect on the estimation of the copper present. The samples in all cases were treated with hydroxyl-amine hydrochloride.

TABLE II –

Effect of Iron and Zinc on the
Determination of Copper in Soils

Soil	Copper present-- p.p.m.	Ions Added	Copper found-- p.p.m.
Whatcom Silt (A horizon)	27.1	10 mg. iron 20 mg. iron 40 ppm. zinc 80 ppm. zinc	26.8 27.8 27.1 27.6
Cowichan Clay Loam (C. horizon)	62.3	10 mg. iron 20 mg. iron 80 ppm. zinc 120 ppm. zinc	62.8 62.3 62.6 63.0
Fort St. John Clay (C. horizon)	41.0	10 mg. iron 20 mg. iron 40 ppm. zinc 120 ppm.zinc	41.2 41.8 41.2 41.0

Zinc was added to both solutions containing copper and to soils. As shown in Tables I and II, these additions did not produce any marked effect on the determination of copper in either case. Metallic zinc used was dissolved in dilute nitric acid, evaporated nearly to dryness and taken up with hydrochloric acid. Copper impurities

were removed by shaking the 0.1 N hydrochloric acid solution with dithizone.

The soils used in the above and subsequent tests were ground to 100 mesh. The powder was then placed in bottles containing a few glass beads and shaken for four hours to ensure maximum uniformity of the sample. All additions of elements to soils were made just before treatment of the soil with hydrofluoric and perchloric acids.

An attempt was made to compare the titration technique to an alternate procedure for the determination of copper in soils. The method of Holmes (30) was employed with the exception that perchloric and hydrofluoric acids were used for the decomposition of the sample. As outlined previously, Holmes' procedure involves a preliminary separation of copper followed by its colorimetric determination with carbamate. One serious obstacle was encountered when this procedure was followed. The transmission range for the normal soil content of from 20 to 80 p.p.m. of copper was only about 25 per cent with the electrophotometer in the laboratory. Variations in the size of the aliquot taken for analysis and the volume of carbon tetrachloride used to extract the copper carbamate were tried without success. Since the light intensity could not be varied, a modification of the procedure would have to be made to avail oneself of the maximum possible sensitivity of the instrument. As insufficient time was available, this was not attempted. The results obtained did show agreement of from 8 to 20 per cent between the two methods. It was felt that an estimation of accuracy based upon such a comparison was not warranted.

A more satisfactory estimate of the accuracy of the method was

made by adding known amounts of copper to soils. In Table III are
shown results obtained by this method. That the recovery can be achieved
with a reasonable degree of success is apparent. One peculiarity noted
was that the error is positive in the majority of cases; that is, a
greater quantity of copper than added was usually recovered. Such results
would indicate that the adsorption of copper by any residue remaining was
negligible. This positive error is due in part at least to the addi-
tional shaking required during titration with increased amounts of copper.
This source of variation was minimized by attempting to keep the amount
of shaking as uniform as possible for all samples. Also the increased
volume of the dithizone would affect colour appreciation through intensity
effect.

In determinations of such small quantities of metal, accuracies
of the order of those obtained appear quite satisfactory. One criticism
which may be made of the method of testing the procedure is that such
adding of additional copper to soil does not take into account the initial
interference by ions present which may react with dithizone.

The standard error was calculated for the recovery of copper at
the different levels. This statistic, it should be noted, does not
represent an estimation of the absolute accuracy of the procedure, but
serves as an indication of concomitant errors affecting the determinations.
These errors may be brought about by contamination from glassware and
other equipment, the possibility of variation in the individual samples,
slight differences in acidity, and personal inconsistencies in the
estimation of the end-point and the manner of shaking. The sensitivity
of dithizone and the small amounts of copper present could make these

TABLE III -

Recovery of Copper Added to Soils

Soil	Copper Present - p.p.m.	Copper Added - p.p.m.	Copper Present - p.p.m.	Copper Found - p.p.m.	Recovery of Copper - Per cent	Standard Error	No. of Samples
Monroe Clay loam (C horizon)	56.0	8 16 40	64.0 72.0 96.0	64.4 72.4 97.7	+5 +2.5 +4.3	±0.58 ±0.76 ±1.35	8 8 8
Alderwood Sandy loam (A horizon)	62.3	8 16 40	70.3 78.3 102.3	69.7 79.4 103.1	-7.5 +6.9 +2.0	±0.42 ±0.385 ±0.19	4 4 4
Whatcom Silt (A horizon)	27.1	8 16 40	35.1 43.1 67.1	34.3 44.0 70.7	-10 + 5.6 + 9.0	±0.21 ±0.28 ±3.25	4 4 4
Fort St. John Clay (C horizon)	41.0	8 16 40	49.0 57.0 84.0	49.2 55.0 84.4	+ 2.5 -12.5 ± 8.5	±0.49 ±0.92 ±0.32	4 4 4
Montney Clay (C horizon)	38.2	8 16 40	46.2 54.2 78.2	45.7 55.0 82.4	- 6.3 + 5.0 +10.5	+0.69 ±0.82 ±1.68	4 4 4

factors important.

The standard error may then be looked upon as a measure of the variation which could be expected between individual samples containing the same amount of copper. This calculated error indicates that the technique is capable of reproducible results. In soil work, where the sampling error may be very large, absolute accuracy is not as essential as reproducible results which can be used for purposes of comparison.

Sherman and McHargue (59) estimated the accuracy of their proposed procedure by a similar method without application of the standard error. These workers' results are shown in Table IV. The accuracy obtained by the author with the titration technique compares very favorably with that obtained by these investigators.

TABLE IV -

Recovery of Copper Added to a Soil -
From Data by Sherman and McHargue (59)

Copper Added	Copper Present	Copper Found	Error of Added Copper
p.p.m.	p.p.m.	p.p.m.	Per cent
0	8.1	8.2	--
4	12.1	12.3	5
8	16.1	17.0	11
14	22.1	23.2	8
32	40.1	41.8	4
56	64.1	60.2	-7

Study of an Alternate Method for Decomposition of Soil Samples

Since platinum-ware is expensive and therefore frequently not available, it was felt that an investigation of a method which did not require it would prove useful. Holmes (30) suggested the use of

perchloric acid alone for the digestion of the sample, but he states that any excessive quantity of siliceous residue be treated with hydrofluoric acid. It was thought that this subsequent treatment would be necessary for coarse textured soils where the amount of unweathered material is high, while with well weathered soils and those containing large amounts of organic matter, perchloric acid probably would be satisfactory. A series of analyses were made to test the validity of this reasoning and the results are shown in Table V.

Table V shows that the results obtained with perchloric acid alone approach those using both hydrofluoric and perchloric acids most nearly in the samples from the surface horizons. In the case of the Langley Clay Loam Sample, which was very high in organic matter, the amounts of copper found are but slightly different for the two methods. Although perchloric acid alone gave higher results for this soil, it is felt that this was not due to the greater efficiency of the method. The parent material samples show consistently lower results when hydrofluoric acid was not used. Both the lower results obtained and the inconvenience of the method make the use of a combination of perchloric and hydrofluoric acids preferable. Therefore it seems that the method requires that platinum-ware be available.

TABLE V –

Comparison of Methods of Decomposition of

Soil Samples for Analysis

Soil	Horizon	Copper Found – p.p.m.			
		Treatment			
		1 ml. HClO$_4$ 8-10 ml. H$_2$F$_2$	5 ml. HClO$_4$	10 ml. HClO$_4$	Residue from 5 ml. HClO$_4$ treated with H$_2$F$_2$
		1.	2.	3.	4.
Lynden Silt	A C	19 33	16 24	16 25	17 31
Langley Clay Loam	A C	74 67	75 49	75 49	74 62
Montney Clay Loam	A C	45 40	39 34	40 33	45 40

Treatments:

1. 0.5 gm. sample, ignited at 500° C., treated directly with 1 ml. HClO$_4$ and 8-10 ml. H$_2$F$_2$, Evaporated with 5 ml. 6 N HCl taken up in 0.1 N HCl.

2. 2.0 gm. sample digested under reflux with 5 ml. HClO$_4$ for 1 hr. Evaporated to dryness and HClO$_4$ driven off. Heated with N HCl made up to 100 ml.; 25 cc. aliquot taken for analysis.

3. As in 2 above, but using 10 ml. HClO$_4$.

4. As in 2 above, but any siliceous residue treated with H$_2$F$_2$ and added to first extract.

After it was satisfactorily demonstrated that the dithizone titration technique could be used for the determination of total soil copper, it was decided to try to extend the application of the method to the estimation of available copper. It was thought that in the availability test the concentration of interfering substances would be less and that therefore the method could be readily adopted. When tried experimentally, this was found to be correct, as no difficulty was encountered with oxidation or excessive residues such as was troublesome in the total copper determination.

As pointed out previously, a number of different extractants have been employed for the estimation of available copper, and no agreement has been reached as to the most satisfactory. The selection of the extractant to use for this study therefore presents a problem.

Using the dithizone titration procedure, it would be undesirable to employ an extractant such as sodium acetate, since the concentration of sodium ions in the final solution would be very high and might even reach saturation. Wear and Sommer (69) found that 0.1 N hydrochloric acid as an extractant permitted good correlation between analytical results and the incidence of zinc deficiency. Since the soils of the Fraser Valley possessed similar reactions to those investigated by these workers, and since the retention of copper would be expected to be similar to zinc, the use of this extractant seemed justified. Another reason for choosing 0.1 N hydrochloric acid arose from the fact that the main purpose of the study was the application of the dithizone titration technique rather than the correlation of the

copper extracted to plant deficiency. Hydrochloric acid was therefore used as it was most suitable for this main purpose, and on the basis of present knowledge it may be expected to give as close correlation to plant availability as any other extractant.

Procedure

1. Weigh 20 gms. of 2 mm. soil. This may be adjusted so that the final solution contains approximately 20 ɣ copper.

2. Place a pad of absorbent cotton in a leaching funnel and wash with dilute HCl, then with water.

3. Add soil and leach with 200 ml. 0.1 N HCl, adjusting the rate of leaching so that extraction requires 2 hours.

4. Evaporate leachate to dryness. Destroy organic matter with 6 per cent H_2O_2 containing a few ml. $HClO_4$. Add 5 ml. 6 N HCl and evaporate to dryness.

5. Add sufficient HCl to make final acid conc. 0.1 N and transfer to a 50 ml. stoppered graduate (See procedure for total copper). Add 0.25 gm. hydroxylamine hydrochloride.

6. Titrate with standardized dithizone solution.

> Note: Observe the same precautions for water, reagents and equipment required in the total copper procedure.

To estimate the accuracy of the procedure, 40 gms. of soil were leached with 400 ml. 0.1 N HCl and the leachate was made up to an exact volume. Four equal aliquots were taken and treated as in the outlined procedure, with the exception that to two aliquots from each sample copper representing 1 p.p.m. in the soil was added. This test was repeated on four soils and an average of 0.92 p.p.m. was recovered. The method also gave close agreement between duplicates.

The Copper Content of Some British Columbia Soils

Having been satisfied respecting the proposed dithizone titration method for estimating soil copper it was used to study the copper content of some British Columbia soils. This section of the thesis has been divided into three parts. The first part deals with the estimation of the total copper content of a number of surface soils and parent materials, the second with the estimation of available copper and the third with the distribution of total copper in some important soil profiles.

Copper content of surface soils and their parent materials

The soil samples used in this study were selected with the aid of soil survey reports (35), (36), (37). The samples were chosen to be as representative as possible of the surface soils and parent materials of the more important agricultural areas of British Columbia. In each case the complete soil profile was sampled. However, to cover as large an area as possible, only surface or A horizons and parent material or C horizons were analyzed. In order to obtain samples representative of the soils to plow depth, the Al and A2 horizons were composited. The results will be discussed by geographical regions.

Peace River Block

The data in Table VI indicates that the soils of this region are generally well supplied with copper when compared to those of other countries (30), (54).

No consistent trends are observable with respect to

TABLE VI

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Copper Content of Some Virgin Soils of the Peace River Area of British Columbia

GREAT SOIL GROUP	PARENT MATERIAL	SOIL ASSOCIATION	HORIZON	TOTAL COPPER p.p.m.
Degraded Black	Lacustrine	Arras	A	26
			C	33
Slightly Degraded Black	Lacustrine	Rolla	A	37
			C	42
Slightly Degraded Black	Lacustrine	Sunset	A	29
			C	37
Slightly Degraded Black (Solonetsic)	Modified Till	Farmington	A	37
			C	36
Grey Wooded	Modified Till	Bessborough	A	18
			C	20
Slightly Degraded Black	Modified Till	Montney	A	45
			C	39
Grey Wooded	Modified Till	Montney	A	40
			C	38
Degraded Black	Lacustrine	Ft. St. John	A	42
			C	39
Grey Wooded	Lacustrine	Ft. St. John	A	59
			C	41
Slightly Degraded Black	Alluvial	Davis	A	14
			C	18
Shallow Black	Lacustrine	Black Mesa	A	29
			C	20
Grey Wooded	Acid Till	Alcan	A	15
			C	20

the distribution of copper between the A and C horizons. One
might expect that in the degraded soils copper would accumulate
at the surface under the influence of grass vegetation. The
fact that this trend was not evident may be due to the method
of compositing the A1 and A2 horizons. In some cases, con-
siderable amounts of the A2 horizons were included with A1
horizons in order to represent the soil to approximately plow
depth.

Of particular interest is the comparative uniformity
of the copper content of the parent materials. On the basis
of copper content two groups emerge -- those materials low in
copper (Bessborough, Davis, Black, Mesa and Alcan) exhibiting
a range of 18 to 20 p.p.m. copper and those with a copper con-
tent close to an average of 38 p.p.m. Although insufficient
information is available to fully explain this observation, it
may be possible to do so after further geological and soil
study.

Fraser Valley

The total copper content of the Fraser Valley soils
is shown in Table VII. There is a wide range in the copper
content of these soils, the range found being from 19 to 91
p.p.m. in the A horizons and from 20 to 67 p.p.m. in the C.
No consistent trends are again observable, although the
lacustrine materials are on the whole slightly higher than the
glacial or alluvial materials. Such a generalization does not
seem warranted since the copper content of the parent materials
within the same association showed marked variations. When

TABLE VII

Copper Content of Some Virgin Soils From the Fraser Valley Area of British Columbia

GREAT SOIL GROUP	PARENT MATERIAL	SOIL ASSOCIATION	HORIZON	TOTAL COPPER p.p.m.
Brown Podsolic	Coarse Alluvial	Everett Loamy Sand	A C	21 25
Brown Podsolic	Fine Alluvial	Lynden Silt Loam	A C	19 33
Ground water podsol	Alluvial	Custer Loam	A C	48 45
Alluvial	Alluvial	Monroe Clay Loam	A C	42 56
Brown Podsolic	Glacial Till	Alderwood Sandy Loam	A C	62 22
Brown Podsolic	Glacial Till (old)	Whatcom Silt Loam	A C	27 59
Brown Podsolic	Glacial Till	Whatcom Silt Loam	A C	44 20
Gleizolic	Lacustrine	Milner Clay Loam	A C	32 60
Brown Podsolic	Lacustrine	Haney Clay	A C	91 55
Gleizolic	Lacustrine	Langley Clay Loam	A C	74 67

compared to results reported elsewhere (30,54) the soils appear to be adequately supplied with copper.

Vancouver Island

It will be observed in Table VIII that the copper content of the Vancouver Island soils, like those of the Fraser Valley, show considerable variation in copper content. The parent materials of these soils are on the whole higher in total copper than the samples previously reported. Even the peat soil from Saanich contains comparatively large amounts of copper.

Interior of British Columbia

A number of samples chiefly from the southern and central interior were also analyzed and the results shown in Table IX. The samples were too few and scattered to show any significant trends. In two cases, the parent materials were found to be relatively low in total copper. These were the C horizon of the Penticton silt loam with 12 p.p.m. and the Mapes loamy sand with 14 p.p.m. It should be noted that even these results compare favorably to those reported for many soils not associated with copper deficiency symptoms (30).

Available copper in some Fraser Valley soils

Available copper was estimated in a number of samples from the Fraser Valley by extracting with 0.1 N hydrochloric acid and the results given in Table X. Since the main purpose of this section was to study the application of the dithizone titration technique for the estimation of available copper, only ten samples were analyzed.

TABLE VIII

Copper Content of Some Virgin Soils From
The South Eastern Portion of
Vancouver Island, British Columbia

GREAT SOIL GROUP	PARENT MATERIAL	SOIL ASSOCIATION	HORIZON	TOTAL COPPER p.p.m.
Brown Podsolic	Glacial Till	Cowichan Clay Loam D-2	A C	50 64
Brown Podsolic	Glacial Till	Cowichan Clay Loam D-3	A C	23 65
Brown Podsolic	Glacial Till	Cowichan Clay Loam D-5	A C	53 51
Brown Podsolic	Lacustrine	Cowichan Clay	A C	62 58
Brown Podsolic	Glacial Till	Bainbridge Loam	A C	61 84
Alluvial	Alluvial	Chemainus Loamy Sand	A C	89 96
Brown Podsolic	Residual Shale	Cedar	A C	54 68
Organic	-----	Saanich Peat	A C	18 47

TABLE IX

Copper Content of some Virgin Soils of the Interior of British Columbia

GREAT SOIL GROUP	PARENT MATERIAL	SOIL ASSOCIATION	HORIZON	TOTAL COPPER p.p.m.
Southeastern Portion:				
Brown Podsolic	Glacial Till	Big Bend	A C	57 58
Alluvial	Alluvial	Creston	A C	79 98
Okanagan Valley:				
Brown	Alluvial	Penticton Silt Loam	A C	19 12
Shallow Black	Glacial Till	Armstrong Gravelly Sandy Loam	A C	25 20
Deep Black	Glacial Till	Kamloops	A C	44 39
Prince George Area:				
Degraded Black	Lacustrine	Nulki Clay	A C	35 47
Grey Wooded	Lacustrine	Vanderhoof Clay	A C	27 37
Degraded Black	Glacial Till	Mapes Loamy Sand	A C	12 14

TABLE X

Available Copper in Some Virgin Soils From
The Fraser Valley, British Columbia

SOIL ASSOCIATION	AVAILABLE COPPER p.p.m.	pH
Everett Loamy Sand	0.85	5.8
Lynden Silt Loam	1.61	5.8
Custer Loam	1.20	5.0
Monroe Clay Loam	2.72	5.6
Alderwood Sandy Loam	1.02	5.6
Whatcom Silt Loam	0.65	5.4
Milner Clay Loam	1.24	5.0
Haney Clay	0.95	5.3
Langley Clay Loam	1.35	5.3

The range in acid extractable copper found was from
0.65 p.p.m. in Whatcom silt loam to 2.72 p.p.m. in Monroe clay
loam. When considering these results it should be recalled
that the soils were well supplied with total copper; also no
evidence of copper deficiency in plants growing on the soils
have been found. Consequently, one would expect the soils to
be well supplied with acid extractable copper. In similar
vein Harris (25) reports that, although some soils in the
Fraser Valley responded to copper fertilization, there was no
evidence of deficiency. The results of the available copper
determinations are in accord with these observations.

Apparently in the soils studied there is no relation-
ship between total copper and that extracted with 0.1 N hydro-
chloric acid. Neither does there appear to be any correlation
between the copper extracted and the pH of the soil samples.
Similar observations have been made by other investigators (73).

From the study it was concluded that the dithizone
titration method was admirably suited for the rapid estimation
of available copper. The selection of the most suitable ex-
tractant and the correlation of results to plant deficiency
should receive further study.

Distribution of Copper in some British Columbia Soil Profiles.

Copper distribution in the soil profile has been found by Russian pedologists (58, 43) to be governed largely by soil forming processes. However relatively little is known of the actual way the different processes affect the movement of copper. With a view to finding out something further in this regard profiles developed under contrasting conditions were analyzed. Two profiles were chosen from the Fraser Valley, three from Vancouver Island and four from the Peace River area. Detailed descriptions of all the profiles are included in the appendix.

Whatcom Silt Loam and Milner Clay Loam profiles were selected from the Fraser Valley (36). These soils are developed under a heavy forest vegetation in a region where the annual rainfall is approximately sixty inches. The profiles are highly leached and strongly acid throughout. Both are derived from fine textured parent materials. The Whatcom series is believed to be the older and now occupies an upland position with undulating topography. The whole series possesses slightly restricted subdrainage. Milner Clay Loam occurs at lower elevations and is also somewhat impervious to water due to the rather dense clay from which it is derived.

The analytical results of the two profiles are given in Table XI and Figure I. The distribution is similar although in the Whatcom soil there has been a greater removal of copper from the A and B horizons in both profiles. The highest amount of copper was

found in the parent material and therefore has been a significant
and consistent loss of copper from the horizons above. In both the
profiles the A₁ horizon does not retain copper to any great extent.
This is somewhat surprising since this horizon contains considerable
organic matter. Apparently the organic materials added to the soil
were low in copper or during the leaching process the element has
been removed. Despite the fact that approximately 44 per cent of
copper from the surface and 39 per cent from the subsurface has been
removed the profiles are well supplied when compared to total copper
values reported for other regions. (30, 54).

The three soils from Vancouver Island all are developed
on the same fine textured, rather impervious glacial till, similar
to those from the Fraser Valley; the Vancouver Island soils are
developed under heavy forest vegetation but the rainfall is consider-
ably lower as the annual precipitation seldom exceeds 30 inches.

The profile sites represent three different drainage con-
ditions. The well drained profile occurs at the top of a long slope
while the poorly drained profile occurs in a depression. The other
profile is found about midway between. The drainage of the first
soil would compare favourably with that of the Whatcom profile from
the Fraser Valley.

The distribution of total copper in the three Vancouver
Island soils is given in Table XII and Figure 2. The three soils
were thought to be developed from the same parent material and the
total copper content of the C₁ horizons of the well and moderately

TABLE XI

DISTRIBUTION OF COPPER IN TWO
PROFILES FROM THE FRASER VALLEY, BRITISH COLUMBIA.

Milner Clay Loam

Horizon	Depth	Total Copper P.P.M.
A_0	$1\frac{1}{2}$ - 0"	28
A_1	0 - 6"	34
A_3	6 - 10"	35
B_1	10 - 16"	35
B_2	16 - 28"	37
C	28" ↓	53

Whatcom Silt

Horizon	Depth	Total copper p.p.m.
A_0	$1\frac{1}{2}$ - 0"	30
A_1	0 - $4\frac{1}{2}$"	27
B_1	$4\frac{1}{2}$ - 12"	28
B_2	12 - 17"	34
B_3	17 - 22"	35
C	22" -	59

FIGURE I

MILNER CLAY LOAM
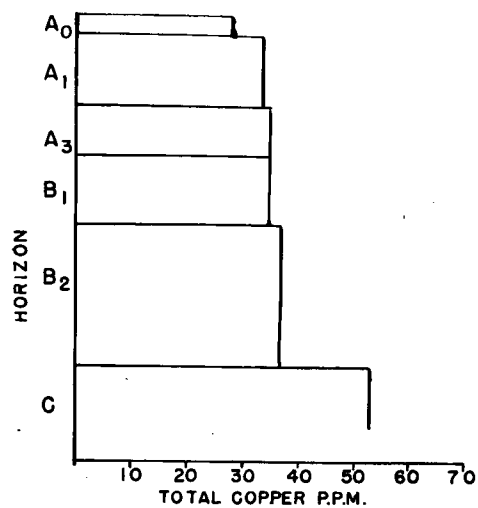
WHATCOM SILT
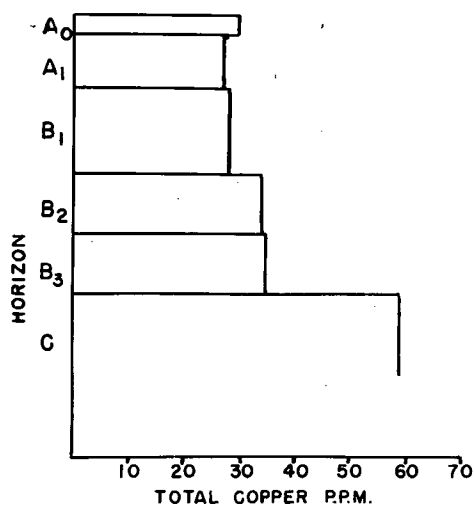
FIG I. DISTRIBUTION OF TOTAL COPPER

TABLE XII

DISTRIBUTION OF COPPER IN SOIL PROFILES

OF THREE DRAINAGE MEMBERS OF THE COWICHAN ASSOCIATION,

SAANICH, BRITISH COLUMBIA.

Well drained member			Moderately Drained Member			Poorly Drained Member		
Horizon	Depth	Total Copper p.p.m.	Horizon	Depth	Total Copper p.p.m.	Horizon	Depth	Total Copper p.p.m.
A_o	1-0"	22	A_o	2-0"	12	A_o	2-0"	28
A_1	0-2"	23	A_1	0-9"	50	A_1	0-8"	53
B_1	2-6"	32	A_2	9-14"	32	A_2	8-14"	26
B_2	6-11"	26	B_g	14-26"	46	B_g	14-23"	45
B_3	11-19"	28	C_1	26" $\neq$	64	C_1	23-28"	-
C_1	19" $+$	65				C_2	28"	51

FIGURE II

COWICHAN

WELL DRAINED

MODERATELY DRAINED
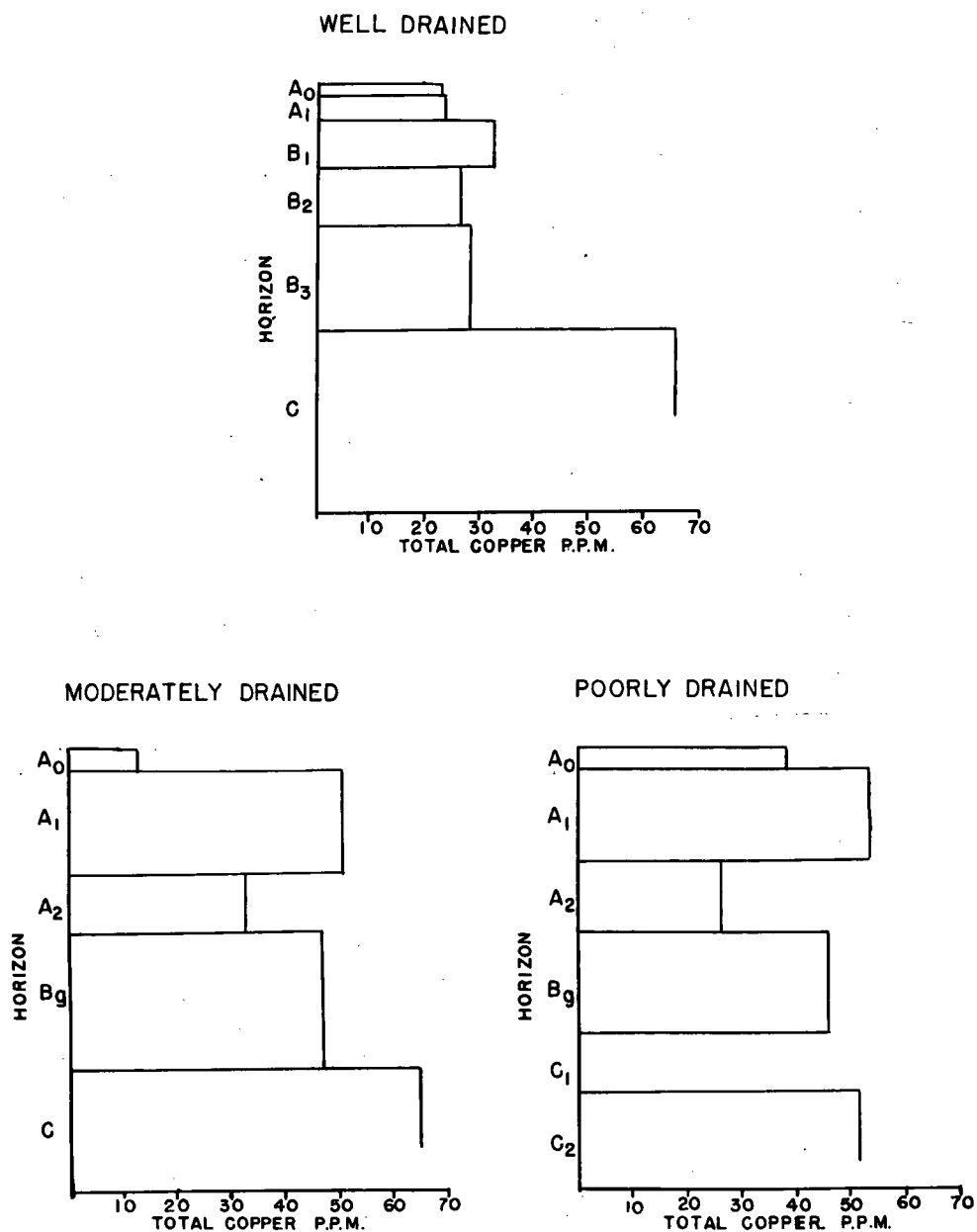
POORLY DRAINED

FIG 2. DISTRIBUTION OF TOTAL COPPER

drained profiles would support this conclusion. However, the copper content of the C_2 horizon of the poorly drained profile is somewhat lower. Field observations indicate that in this case more weathering had occurred and some copper loss may have resulted.

The distribution of copper in the moderately and poorly drained soils follows a different pattern from the well drained member and the Fraser Valley soils. Extensive leaching is confined to the A_2 horizons and the A_1 and B horizons retain a greater proportion of the element. The poorly drained member differs slightly, however, from the moderately drained soil. The former possesses considerably more copper in the A_0, which one would expect from the different nature of these horizons, and the A_2 of this soil is slightly more leached.

Peace River Profiles

The four profiles from the Peace River area represent two profile pairs. The first pair which form part of the Fort St.John association was developed from a varved clay. One member of the pair is a degraded black soil and the other a depression podsol. The degraded black soil is found under mixed grass and deciduous forest vegetation. The depression podsol is in a slight depression at the bottom of the slope and receives considerable runoff water from above. The vegetation is mixed deciduous and coniferous forest.

The total copper content of the profiles is shown in

Table XIII and Fig. 3. Clearly, the soil forming processes active in the development of these soils have had a different effect upon the distribution of copper than in the Fraser Valley and Vancouver Island profiles. Thus in both soils the A_1 and B_2 horizons contain more copper than the parent material. There is also a tendency for the A_{0-1} horizon to accumulate copper which was not evident in the other profiles. Leaching of copper is quite marked only in the A_2 horizon of the Fort St.John soils. When the effect of drainage is studied in the two profiles it appears more copper has been removed from the poorly drained profile which has a much deeper A_2.

The second pair of profiles from the Peace River area forms part of the Montney association. Both profiles have been developed from a fine textured till. One member is a slightly degraded black soil and occurs on a well drained slope under mixed glassland vegetation. The other member is a grey wooded soil and is found on level topography where runoff is slight. The impervious subsoil gives rise to restricted drainage. The soil has developed under a mixed deciduous forest.

The distribution of total copper in these profiles is given in Table XIII and Figure 3. The degraded profile like the Fort St.John soils shows a tendency to accumulate copper in the A_1 and B_2 horizons. In the grey wooded soil the only horizon containing more copper than the parent material is the A_{0-1}. Both soils show a tendency to loose copper in the A_2 and B_1 horizons but this effect is much more pronounced in the grey wooded soil.

TABLE XIII

DISTRIBUTION OF COPPER IN FOUR SOIL PROFILES
FROM THE PEACE RIVER AREA OF BRITISH COLUMBIA

Fort St.John

Degraded Black			Grey Wooded (Depression Podsol)		
Horizon	Depth	Total Copper p.p.m.	Horizon	Depth	Total Copper p.p.m.
A_1	0-8"	41	A_{0-1}	0-2"	59
A_2	8-10"	27	A_{21}	2-7"	30
B_1	10-16"	37	A_{22}	7-10"	35
B_2	16-21"	45	B_1	10-16"	38
B_3	21-28"	47	B_2	16-23"	44
C	32" -	39	C	23" -	41

Montney

Slightly Degraded Black			Grey Wooded		
Horizon	Depth	Total Copper p.p.m.	Horizon	Depth	Total Copper p.p.m.
A_1	0-6"	45	A_{0-1}	0-2"	39
A_3	6-9"	27	A_2	2-6"	17
B_1	9-18"	35	B_1	5-12"	21
B_2	$18-22\frac{1}{2}$"	43	B_2	12-16"	37
C	$22\frac{1}{2}$" -	39	C	20" -	38

FIGURE III

FORT ST. JOHN

DEGRADED BLACK

GREY WOODED

MONTNEY

SLIGHTLY DEGRADED BLACK

GREY WOODED
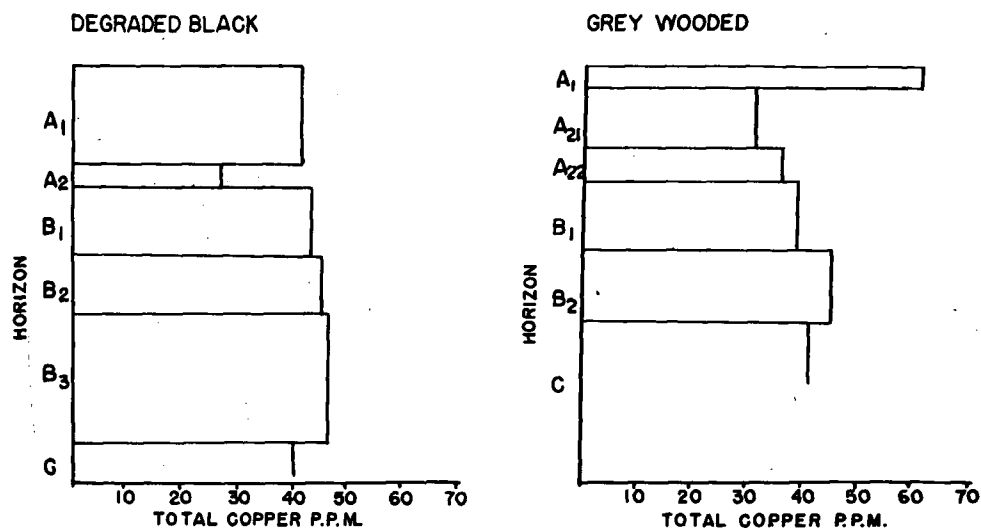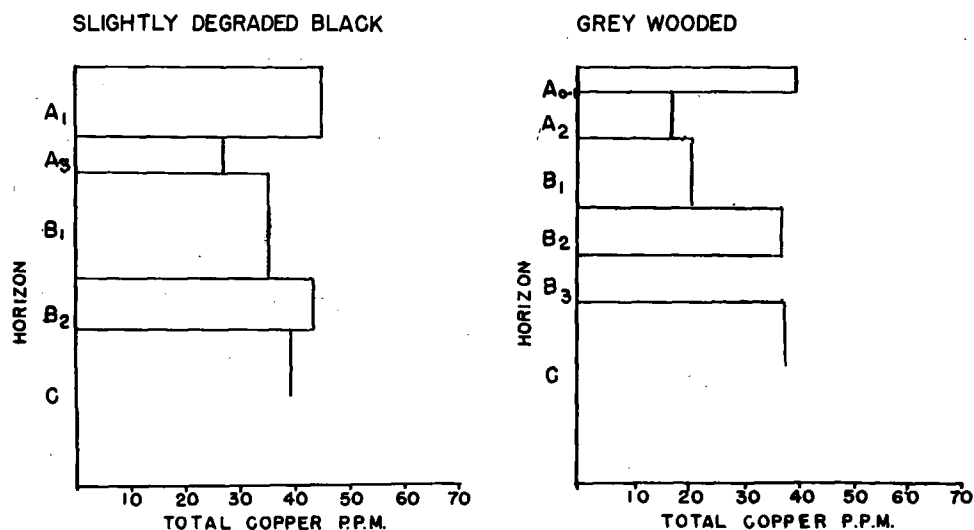
FIG 3. DISTRIBUTION OF TOTAL COPPER

SUMMARY AND CONCLUSIONS

1. The dithizone titration method was adapted for the determination of total and available copper in soils by developing a special procedure to eliminate interference by oxidizing and other substances. When compared to other methods the proposed procedure was both short and simple and its accuracy when tested by recovering copper added to solutions and soils was found to be satisfactory.

2. Using the proposed dithizone procedure total copper was determined in surface and parent material samples of 38 soils from the Peace River area, Fraser Valley, Vancouver Island and the Central and Southern Interior of British Columbia. The range in copper found was from 12 to 98 p.p.m. as much variation was found between results from the same geographic area as was apparent when the results for the different areas were compared. The total copper content of the samples compared favourably with those reported elsewhere.

3. The copper extracted with 0.I N hydrochloric acid from a number of samples of uncultivated soils from the Fraser Valley was determined by the dithizone method. The range of copper found was from 0.65 to 2.72 p.p.m.

4.   From the distribution of total copper in the profiles
of two Fraser Valley, three Vancouver Island and four Peace River
soils it was evident that copper is markedly affected by soil
development.   In the brown podsolic soils of the coastal region
podsolization has resulted in the consistent removal of a signi-
ficant proportion of the copper from the A and B horizons.   In
the Northern podsols the element has been strongly leached from
the A_2 and slightly from the B_1 while it was accumulated in the
A_{0-1} and retained in the B_2 horizon.   Copper was accumulated in
the A_1 and B_2 horizons of the degraded black soils and leaching
was restricted to the A_2.   Poorer drainage position in the
coastal soils favoured a greater retention of copper in the
solum.   The reverse was true in the Peace River soils.

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APPENDIX

PROFILE DESCRIPTIONS

Whatcom Silt Loam

Drainage   Moderately to fairly well drained.

Location   3 miles south east of Langley, British Columbia.

Vegetation   Second growth forest, predominantly alder, fir and cedar with some birch and maple. Heavy undergrowth of fern and other shrubs.

Horizon	Depth	Description
A_o	$1\frac{1}{2}$-0"	Dark brown forest litter of needles, twigs, etc., well decomposed in lower $\frac{1}{2}$".
A_1	0 - $4\frac{1}{2}$"	Reddish brown silt loam finely granular, loose, open with many iron concretions. Occasional small stone or gravel.
B_1	$4\frac{1}{2}$-12"	Reddish brown silt Loam. Medium nutty structure. Fairly open nature, occasional iron concretion. Few small stones and gravel.
B_2	12-17"	Yellowish and reddish brown clay loam, blocky structure, quite dense. Iron stained.
B_3	17-22"	Yellow brown clay loam, medium blocky structure, dense. Quite plastic, stained with iron.
C	22"-	Parent material, weakly cemented, iron stained, angular structure, dense, hard and tough when wet. Clay to clay loam.

Milner Clay Loam

Drainage   Moderately well drained.

Location   4 miles Northeast of Langley, British Columbia.

Vegetation Second growth poplar, maple, alder with scatter-
            ed fir undergrowth of fern snowberry, rose, etc.
            This sample taken in a fir grove.

Horizon	Depth	Description
A_0	0 - 1"	Dark brown layer of leaves, twigs and woody material.
A_1	0 - 6"	Red brown clay loam with a loose granular structure, numerous soft iron concretions. Heavily rooted.
A_3	6-10"	Gray brown clay loam, with a medium nutty structure. The units are loose and friable, breaking down to smaller granular aggregates.
B_1	10-16"	Yellowish brown clay with medium blocky structure. Dense, compact structure. Firm when moist, iron stained.
B_2	16-28"	Greyish brown clay iron stained. Massive structure, tough when wet. Breaks out in medium blocky structure.
C	28" -	Grey brown clay, dense medium blocky structure.

Cowichan Well drained.

Drainage D_2 – well drained member.

Location   South East corner Saanich Indian Reserve,
              Brentwood, B.C.

Vegetation   Second growth forest of fir, with some arbutus,
              maple, alder and cedar. Undergrowth of snowberry,
              rose, salal, oregon grape and bracken. Thin
              cover of ground moss.

Horizon	Depth	Description
A_o	1-0"	Dark brown layer overlain by $\frac{1}{2}$" living moss. Upper $\frac{1}{2}$" composed of twigs, needles, woody material and leaves. Lower $\frac{1}{2}$" well decomposed.
A_1	0-2"	Dark brown clay loam with strong granular structure. Loose, friable with scattered gravel and grit.
B_1	2-6"	Brown friable clay loam with moderately well developed medium – to large – nutty structure breaking down to medium-granular aggregates. A few scattered hard shot mostly in upper portion.
B_2	6-11"	Dark brown clay loam. Weak, soft large – nutty structure. Many roots, scattered pebbles heavily coated with iron. Porous permeable.
B_3	11-19"	Gray brown clay loam, massive plastic, breaking to small nutty structure. Fragments break out in irregular clods which are quite firm.
C	19" –	Very compact clay loam, gray brown in colour. Fragmental structure breaking with horizontal and vertical cleavage. Aggregates about 1" in diameter. Scattered stones gravel grit. Cleavages speckled with manganese.

<u>Cowichan Moderately Drained</u>.

Drainage D_3 Intermediate drainage member.

Location   Saanich Indian Reserve No.I, near Brentwood, B.C.

Topography   2% slope to West, elevation 150 feet.

Vegetation   Second growth forest consisting of fir, cedar,
                maple, arbutus and a heavy undergrowth of salal
                and bracken.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
A_0	0-2"	Dark brown forest litter composed of twigs, leaves, needles, woody material and bark. Undecomposed at surface but lower portion moderately broken down.
A_1	0-9"	Very dark greyish brown. A porous friable horizon with a medium nutty or large crumb structure. Structure appears well developed and stable, break down from large to small crumbs of same type. Scattered gravel and grit consisting of shale, granite and sandstone.
A_2	9-14"	Greyish brown heavy clay loam possessing a medium - to coarse - nutty structure which breaks down into smaller nutty or granular units. Friable, open, porous structure with no tendency to platiness. Small amounts yellow mottling on greyish background. Scattered grit and gravel.
B_g	14-26"	Gray clay with brown and yellow mottling. Friable when moist but appears to become hard when dry. Coarse, blocky, angular structure consisting of fairly dense aggregates. Slight tendency to prismatic arrangement. Organic coating on surface of macro structure. Few pebbles.
C	26" -	Grayish brown heavy clay loam. Compact, hard, massive in appearance breaking down with vertical and horizontal cleavage into small to large angular fragments. Scattered gravel and grit and occasional boulders.

Cowichan Poorly Drained

Drainage D_5 poorly drained member.

Location   East of airport, Patricia Bay, B.C.

Vegetation Virgin forest of fir, maple and mixed undergrowth
            of shrubs.

Horizon	Depth	Description
A_o	2-0"	$\frac{1}{2}$" living moss overlying loose forest litter of twigs, needles, etc. Lower 1" of horizon is well decomposed and dark brown in colour.
A_1	0-8"	Dark brown medium textured clay loam. Well developed nutty structure of friable which break into fine granular aggregates. Scattered stones and gravel.
A_2	8-14"	Gray clay loam containing some very fine sand. Compact, massive structure no particular cleavage.
B_g	14-23"	Gray clay, highly mottled with yellow brown stains. Massive breaking into small fragmental structure. Quite plastic. Root and organic staining along cleavages.
C_1	23" +	Plastic light clay stained with iron. Slightly weathered but quite dense. Scattered stones and gravel. Few root mats along cleavages. (This horizon not sampled).
C_2	28" +	Grayish clay with irregular, blocky structure breaking to similar smaller units. Speckled with manganese. Texture heavier than usual and appears impervious.

Fort St.John Degraded Black

Drainage   Well drained member

Location   1½ miles Northwest of Fort St.John, B.C.

Vegetation   Grasses with interspersed aspen and poplar.

Horizon	Depth	Description
A_1	0-8"	Very dark brown. Large prismatic breaking to large blocky and then to fine crumb structure. Many small scattered feeding roots.
A_2	8-10"	Very dark brown greyish brown fine sandy loam. Medium to coarse platy structure. Quite compact.
B_1	10-16"	Dark brown clay. Medium prismatic breaking very easily to medium granular structure. Firm when moist.
B_2	16-21"	Very dark greyish brown clay. Small to medium blocky structure. Firm to friable when moist.
B_3	21-28"	Dark greyish brown clay. Small blocky structure; friable when moist. This horizon not sampled.
B_{ca}	28-32"	Pale brown, medium platy structure very loose and crumbly when dry. Strongly calcareous. This horizon not sampled.
C	32" -	Brown clay. Quite massive when wet, fine blocky when dry. Moderately calcareous.

Fort St. John Grey Wooded (Depression Podsol)

Drainage   Poorly drained

Location $1\frac{1}{2}$ miles Northwest of Fort St. John, B.C.

Vegetation Grasses with interspersed aspen and willow.

Horizon	Depth	Description
A_{0-1}	0-2"	Very dark grayish brown loam. Loose fine crumb structure. Numerous undecomposed grass roots.
A_{21}	2-7"	Light gray brown very fine sandy loam. Coarse platy structure; streaks of oxidized iron compounds.
A_{22}	7-10"	Light yellowish brown very fine sandy loam. Coarse platy structure; streaks of oxidized iron compounds.
B_1	10-16"	Brown clay. Medium columnar breaking to firm medium sized blocks; sticky when wet, firm when moist. Reddish brown iron stains.
B_2	16-23"	Brown clay. Massive and sticky when wet, breaking to small blocky structure; slightly hard when dry.
C	23" -	Pale brown clay. Massive and sticky when wet, hard when dry.

Montney   Slightly Degraded Black

Drainage   Well drained.

Location   Indian Reserve   North of Fort St.John, British
           Columbia.

Vegetation   Grassland type consisting of sedge.

Horizon	Depth	Description
A_1	0-6"	Very dark brown loam. Medium prismatic breaking to fine crumb structure. Non sticky when wet, friable when moist.
A_3	6-9"	Light gray clay loam. Fine to medium granular structure; moderately sticky when wet, firm when moist.
B_1	9-18"	Very dark grayish brown clay. Medium columnar breaking readily to medium blocky structure. Sticky when wet and slightly hard when dry. The upper portion of B_1 is coated with a fine gray silica dust.
B_2	18-22½"	Dark grayish brown clay. Medium blocky structure. Sticky when wet, slightly hard when dry.
C	22½" -	Banded black and brown clay. Sticky when wet, slightly hard when dry.

Stones occur throughout the profile, chiefly small angular
pink granite and quartzites.

Montney   Grey Wooded

Drainage   Poor

Location   Indian Reserve, North of Fort St. John, British
              Columbia.

Vegetation   Grassland type with interspersed poplar and willow.

Horizon	Depth	Description
A_{0-1}	0-2"	Dark brown loam. Loose with numerous partially decomposed grass roots.
A_2	2-16"	Light grey brown very fine sandy loam. Medium platy structure. Friable when moist slightly hard when dry. Fine streak iron.
B_1	6-12"	Dark greyish brown clay. Medium prismatic breaking to large firm nutty structure. Sticky when wet, hard when dry. Columns streaked when brown iron stains.
B_2	12-16"	Dark grayish brown clay, somewhat mottled breaking to coarse blocky structure. Very sticky when wet, hard when dry.
C	20" -	Dark brown clay. Massive sticky when wet, hard when dry.