A CRITIQUE ON METHODS
OF DETERMINING FREE IRON OXIDES

A CRITIQUE ON METHODS OF DETERMINING FREE IRON OXIDES EMPLOYING PODZOLIC SOILS FROM THOR LAKE, N.W.T.

By

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ABSTRACT

The study of free iron oxides in soils has for many years been an important area of research in the soil science. The development of many standard procedures over the years has led to confusion as to which method is most suitable for extracting free iron oxides. This study presents a systematic review of (a) the development of chemical processes and iron deposits in the podzolic group of soils, a major Canadian soil group in which free iron oxides deposits are found; (b) a review of the theory and experimental data behind some of the most widely accepted procedures of iron extraction; (c) a systematic review of four of the major methods of free iron extraction through experimental and statistical analysis employing soil samples from Thor Lake, N.W.T. The results of this study show that the most useful method for free iron oxide extraction is one that is independent of complexing variables such as pH, C.E.C., temperature and time.

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CHAPTER I

INTRODUCTION: THE SCOPE AND PHYSICAL BACKGROUND OF THE RESEARCH AREA

1:1 Purpose: Introductory Remarks

The methodology for determining free iron oxides has, for many years, been an important field of research in the soil sciences. This has resulted in many varied and complex processes being developed by soil researchers to more easily determine this important soil property. However, what this continued research tended to do, was to develop more complicated and confusing procedures for free iron removal, when the researchers' goals should have been to simplify and improve existing procedures. This trend tended to force the individual researchers to employ several of the better techniques in order to determine which technique was most useful in extracting the information he required for his particular area of research. This process was a time-consuming one, and must have been neglected in order to allow the researcher more time to investigate his particular research problem. Therefore, for several years the problem has been which method of free iron extraction, based on universally recognized pre-defined ideals of what a suitable extraction technique should entail, is most suitable for the removal of free iron oxides from soils found in regions climatically similar to Canada.

This thesis is undertaken to investigate this problem of finding a suitable method, from the various methods available, of determining amounts of free iron oxides in soils of low to moderate oxide content, typical of the Canadian Podzol. These techniques will be tested on podzol soils from the Thor Lake Region of the North West Territories, and the established technique will be useful on any similar soil with satisfactory results. The recommended method, however, should not be employed on soils from distinctly different physiographic zones, nor on soils very high in free iron oxide content, for the procedure will not have been tested on such soils and, therefore, might prove to be inadequate in such a circumstance.

1:2 Scope

A wide variety of free iron oxide extraction methods are available for the soil researcher's use; however, it has been determined from research carried on by others in the field that some of these procedures are more applicable for use on certain soils than are others. Therefore, this thesis need only look at procedures useful for extracting free iron oxides from soils physiographically similar to the soils found in most regions of Canada and other northern countries. These soils typically will be of a podzolic type, found in cold to cool damp climates and will contain small to moderate amounts of free iron oxides.

Chapter II defines, from a chemical point of view, the podzolic group of soils and the specific chemical reaction at work on the various mineral and organic constituents of this soil group. This will define the chemical properties of the podzol, showing its uniqueness from other soils and, therefore, defining the need for employing a particular extraction -- in this case, free iron oxide -- with a particular type of soil in order to achieve the most useful results.

Chapter III will present the reader with a critical summary of the various procedures available by a review of the literature concerning the particular field of interest. This will enable the selecting of specific procedures, based on data presented in this chapter to be tested on the group of soil samples in order to determine the most practical method of free iron oxide extraction. In Chapter IV, the various procedures are tested against pre-defined standards of what a good system should and should not entail, and the results of the study are presented herein.

Chapter V draws specific conclusions from the study and attempts to make recommendations concerning the establishment of a particular procedure for free iron oxide extraction from podzolic soils.

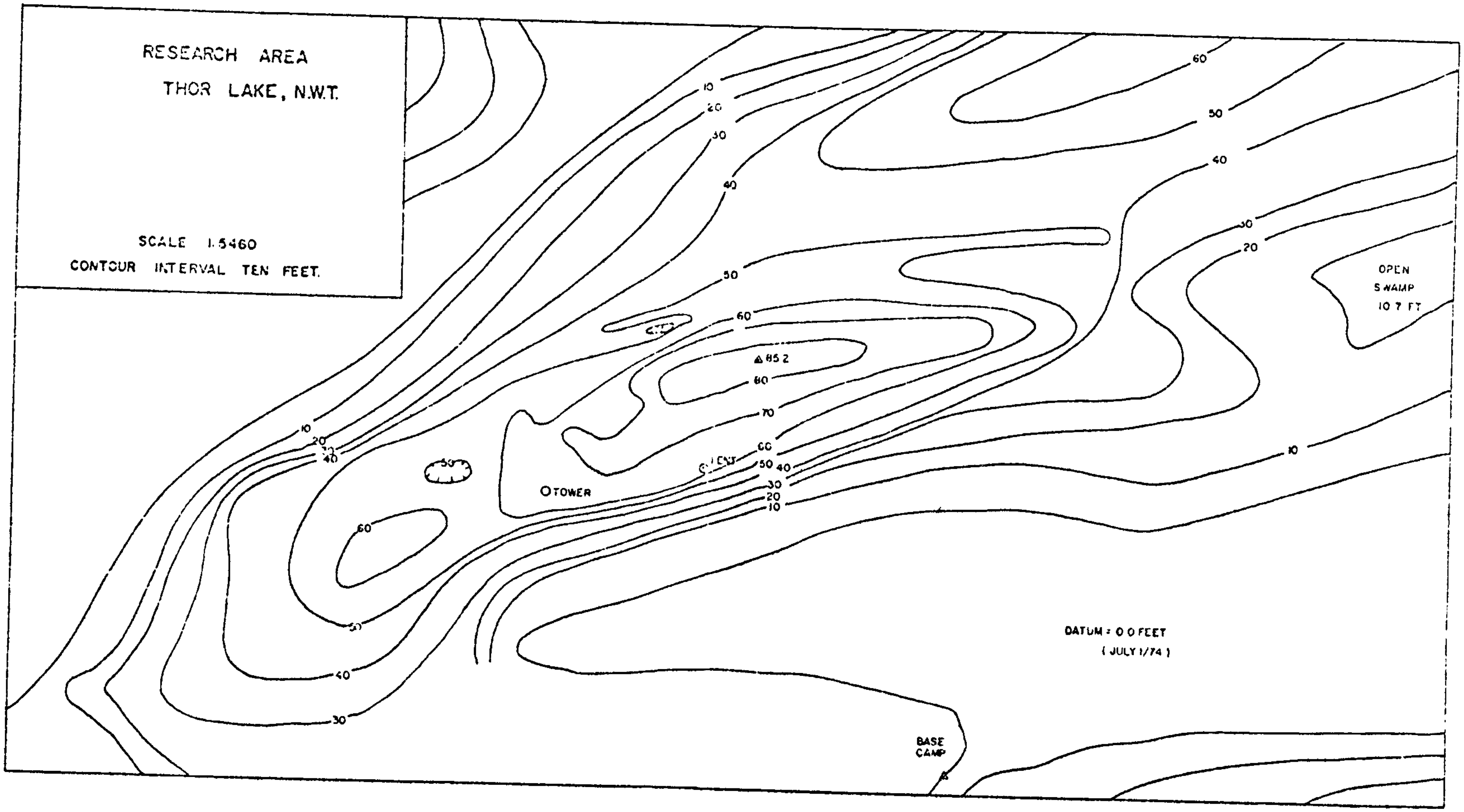

RESEARCH AREA
THOR LAKE, N.W.T.
SCALE 1:5460
CONTOUR INTERVAL TEN FEET.
10
20
30
40
50
60
OPEN SWAMP 10.7 FT
85.2
80
70
TOWER
TENT
DATUM = 0.0 FEET
(JULY 1/74)
BASE CAMP

FIGURE: 1

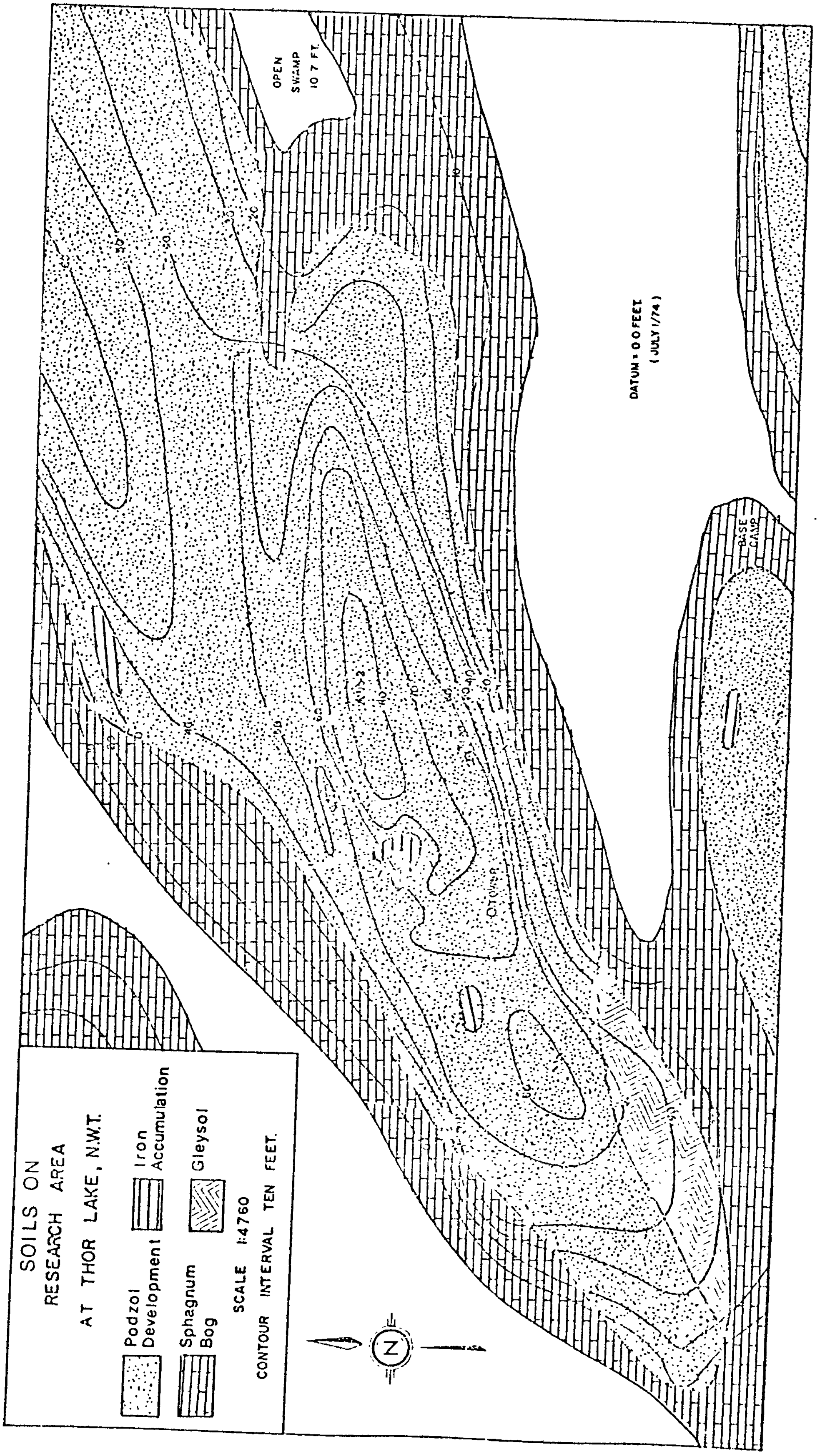

SOILS ON
RESEARCH AREA
AT THOR LAKE, N.W.T.
Podzol Development
Iron Accumulation
Sphagnum Bog
Gleysol
SCALE 1:4760
CONTOUR INTERVAL TEN FEET.
N
OPEN SWAMP 10.7 FT.
DATUM = 0.0 FEET (JULY 1/74)
BASE CAMP
TOWER

FIGURE: 2

1:3 The Geomorphological Setting of Thor Lake, N.W.T.

Location and Physiography

The study area, consisting of a zone surrounding Thor Lake, N.W.T., is located northeast of Uranium City, Saskatchewan between latitudes 60°22'N and longitudes 106°50'W (G.S.C. map 55-10).

The topography, except in the extreme northwestern and southwestern parts of the mapped area, is generally flat in marked contrast to the rugged, rocky terrain to the south and west of the study area. Elevations in the area can range from 1,400 feet to 1,800 feet above sea level, with the local relief varying from 25 to 200 feet, but over most of the specific study area the elevation does not exceed 50 feet. The divide between Hudson Bay and Mackenzie watersheds crosses the area from the southeast to the northwest; however, drainage is generally poor throughout the area due to the geology, perma frost, and glacial features.

The entire area is well wooded. The predominant trees tend to be spruce with an average diameter of 6 to 9 inches. There are also sparse stands of pine and tamarack, which contribute to the very acid nature of the soils. These trees are predominantly found on the higher, better-drained drumlins, while scrub birch is sparsely scattered along the creeks and lakeshore. The area is generally covered by dense growths of various species of lichens (eg. cladonia mitis), vaccinium myrtilis, and other low-growing, hardy plants which tend to hold large amounts of water which gradually percolates down into the soil over time.

Glacial drift covers at least 90 percent of the area. Glaciation has produced the characteristic grooving, rounding, and polishing of the bedrock with most glacial striae trending west-southwesterly. The drumlins and drumlinoid forms, which vary in length from a few hundred feet to more than a mile, tend to parallel the glacial striae in most places. They form an almost unbroken inter-locking network over more than 75 percent of the area. Many have rock cores that occasionally outcrop on the stoss (north-eastern) ends. This is particularly true where the stoss end occurs on a lakeshore. Numerous eskers up to 200 feet high traverse the area more or less continuously from northeast to southwest, roughly paralleling the regional movement of ice. They tend to mark the loci of pleistocene drainage channels. These are marked, particularly in the southeastern corner of the mapped region, by angular boulders up to 30 feet in diameter. These boulders were derived from nearby underlying bedrock and completely mantle the terrain, testifying to the predominantly glacial physiography of the region.

1:4 Geology

The study area is located in the Churchill Province, which is a subdivision of the Canadian Shield defined on the basis of its geological evolution and characterized by distinctive structures. Its boundaries are defined by zones in which these structures truncate those of older provinces or are truncated by those of younger provinces. Raidometric dating has confirmed the relative ages deduced from these cross-cutting relationships, and indicate that the orogenic development of the province had ceased by about 1,700 m.y. ago. The structural evolution of the Churchill province has been ascribed to the Hudsonian Orogeny, but the present level of knowledge does not satisfactorily demonstrate that the various structural styles are related to a single orogenic system. On the contrary, it seems likely that the Hudsonian Orogeny was not a single widespread event, and that the Churchill Province evolved during a series of orogenic events that culminated at different times in different places.

There seems to be a fundamental difference between the rocks of the northwestern zone of the Churchill Province and those lying to the southeast of an ill-defined line extending northeastwards from northwest Saskatchewan to the southern Boothia Peninsula. Northwest of this line is a deep crustal zone in which granulite facies are common and supracrustal rocks are essentially absent; main structural trends are essentially between northeast and north, and supracrustal rocks on the whole tend to be very rare. Southeast of this line, metamorphic grade varies widely; main structural trends are generally northeast and east, and supracrustal rocks both of Archean and Aphebian ages are readily recognizable in many places. Thus, not only in this region of the province but also in the region on the west side of Hudson Bay, there appears to be a crude alternation of fold belts and greenstone terrain. The significance of the alternation is not completely understood, but it is conjectured that it could have come through the breakdown in stability during the Aphebian of a previously continuous Archean crust, with the result that Aphebian sedimentary troughs or basins formed in the unstable zones, now represented by fold belts, between more stable blocks now represented by greenstone areas.

This is the general geological picture that evolves from the general trends of geological structures in the province. The study area itself has been superficially mapped, and the following is a summary from the Geological Survey's report on the area.

The Abitau Lake district, of which Thor Lake is a member, has been found to be composed of very old rocks consisting of quartzite and greywacke-type meta-sedimentary rocks exposed over very limited areas; these rocks are found to be the oldest known rocks of the area.

The study area itself is composed primarily of migmatized quartz-feldspar gneiss which is so named for the two dominant minerals. Most of these rocks tend to be garnetiferous, and are thought to have derived from pre-existing sedimentary and volcanic rocks by processes of granitization. Migmatization appears to have occurred, as a late phase in the process, and is identified with the introduction of fairly small amounts of pigmatic granite.

The youngest rocks in the area are fresh-looking mafic dykes and small unmapped stokes of dioritic to gabbroic composition. Many of the faults detected as lineaments on aerial photos are difficult to map in any detail because of infilling of many faults by glacial debris which is very characteristic of the area.

The Churchill Province is an enigmatic tectonic entity. There is a lack of basic data to use as a foundation for a synthesis of the tectonic evolution. Detailed work within the province has been, to a large extent, governed by economic considerations, accessibility, and suitability of the rocks for study. Huge areas, including the study area, which do not satisfy these requirements, have been examined only at a reconnaissance scale. Thus, the lack of information in many instances does not provide a basis for anything more than speculation, particularly at a scale needed in this study. Therefore, although it may be tempting to find order in the Churchill Province as an entity, to subdivide it, to recognize distinct orogenies and ancient geosynelines, the data base upon which such attempts must be made is still too incomplete and too uneven in distribution and detail, particularly at the scale needed in this study, to be of any use to the investigation.

1:5 Climate

TEMPERATURE & PRECIPITATION DATA

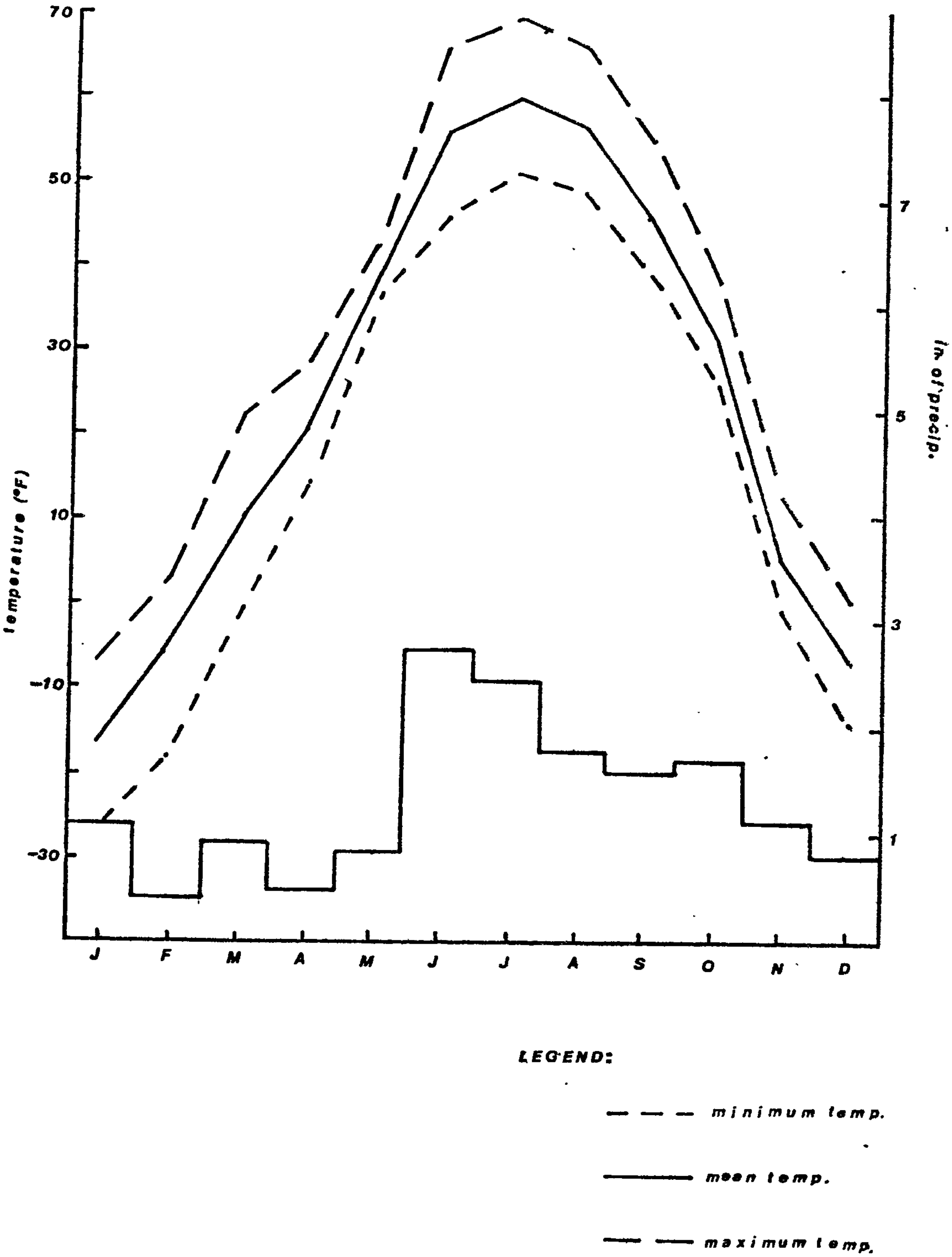


Figure: 3

The climate of the Thor Lake region is very typical of many areas of the world in which podzolic soils are found. Basically, it is a climate dominated by long cold winters, short cool summers, with a summer precipitation maximum. This type of climate allows the physical and chemical processes to interact to their maximum potential in the development and maturity of the podzolic soil.

In detail, the climate of the study area is characterized by minimum winter temperatures of -20° F., with winter maximums of only -7.8° F. The annual precipitation during the winter season on the whole is small (6.83 inches), with all of this falling in the form of snow (82.6 inches of snow annually). This snow cover allows for maximum protection of the vegetation during the cold season, which in turn acts as an insulation layer to plant life, which is important in the development of the podzolic soil. The snow cover also acts as storage reservoir for water which is supplied to the soil as spring thaw begins, which aids in the further development of the soil profile.

The summer season is typically short and cool, with maximum-minimum temperatures ranging between 69.2°F. to 39.6° F. The summer season in this area receives the maximum annual precipitation of 9.51 inches; this, in combination with the precipitation stored in the form of snow (6.83 inches) leads to a maximum amount of water being available at the surface of the soil. The region's climate makes it possible to store precipitation until the correct season, when it can be used by the soil-forming processes; however, the very cold winter and short summer also makes the development of the mature podzol a very slow process due to the short period of time when the soil is truly an active layer.

1:6 Soils

The dominant soils found in the study area are podzolic soils which are developing from pale yellow grey glacial till which overlies much of the bedrock in the area.

The soils themselves are composed of various horizons, the uppermost of which is a layer of litter varying between 5 and 6 cm. in depth. This horizon is primarily composed of moss and lichen growth. Beneath the litter is a layer of humus composed of roots and decaying organic matter. This horizon can vary anywhere between 1 to 5 cm. in depth, the depth being directly dependent upon the amount of organic matter available for decomposition.

Directly below the humus layer is the A horizon, composed of Ah and Ae layers. The Ah layer generally exhibits the properties of the overlying organic matter. Thus, this horizon is usually found to be dark brown to black in colour with a much heavier texture than the overlying horizon. Upon reaching a 5 cm. depth (approximate), an abrupt change is noted; the soil changes to a light powdery grey colour with a very light texture. This 5 cm. depth marks the beginning of the Ae layer, and the texture and colour make it a very distinctive and easily recognized horizon in the podzolic group of soils.

The B horizon lies directly beneath the A horizon, and is composed of much darker (dark red brown), heavier, and coarser soils than are found in the A horizon. The B horizon is usually composed of B, Bfe, B2, and B3 sub-horizons. The colour tends to decrease, while the texture increases, with depth. Thus, the Bfe tends to be a much darker red-brown colour with a finer texture than the B2 sub-horizon. Therefore, the B horizon in podzolic soils, can be defined in terms of colour, texture, grain size, and organic (roots, pieces of twigs, etc.) matter.

The C horizon, at a depth of 20 to 50 cm., is really just unweathered parent material, which in this case is a yellow grey glacial till. For a more complete description of the soil samples from Thor Lake, the reader is referred to Table B-4.

CHAPTER II

CHEMICAL PROPERTIES OF PODZOLIC SOILS

2:1 Introduction

In the forest or taiga zone, the most widespread soils are of the podzolic type. For this reason, the zone is known as that of podzolic soils. The term originated in a land where over 32 percent of the total area is occupied by this soil group; the land is Russia. From this land comes the term zola, meaning ash. This term seems to describe most distinctly one of the features which characterizes the podzolic group, that being the ash grey colour of the A2 horizon.

Podzolic soils are named according to the degree of podzolization. The names range from strongly to weakly podzolic, and the degree of podzolization is determined by the intensity of the ash grey colour of the A2 horizon.

2:2 Morphology of Podzolic Soils

I shall now briefly discuss the morphology of the podzolic group in order to allow the reader to obtain a greater understanding of the processes active in the various horizons. This is done so that the reader may better understand the chemical processes of the podzolic soil, which is the subject of this chapter.

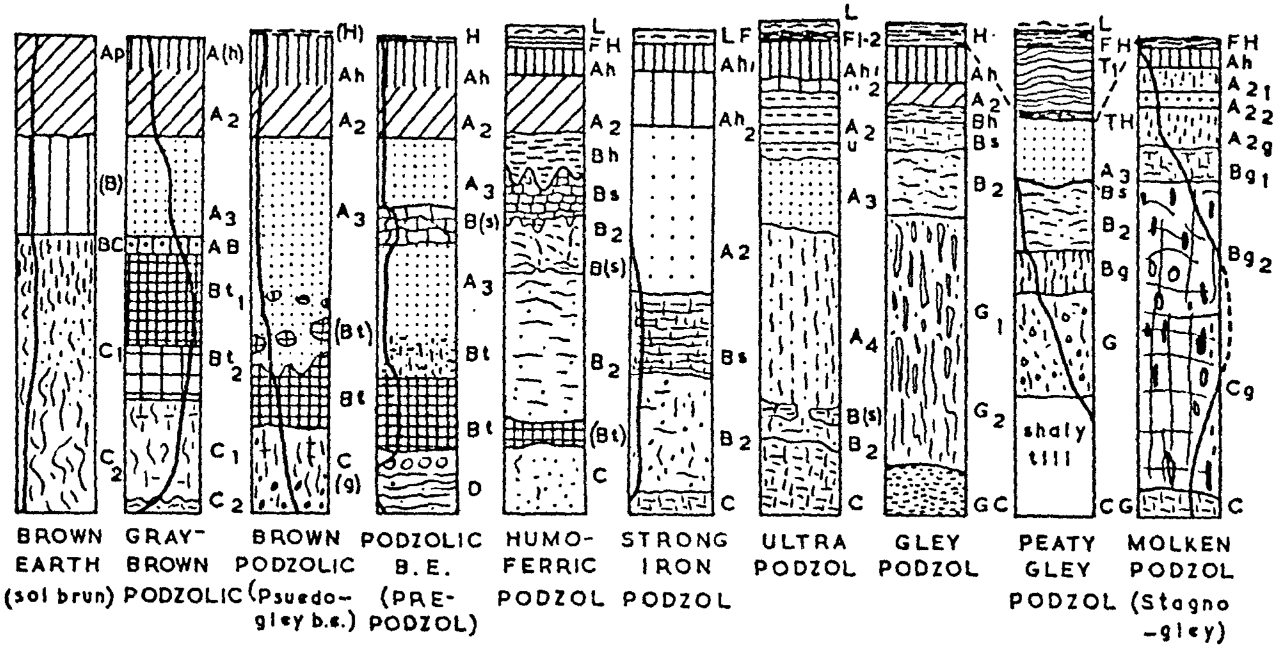


FIGURE: 4 Comparative profile morphology of brown earths, podzolic and podzol soils, including gleyed and peaty podzol forms. Column depth is 125 cm.; width equivalent to 25% clay (as shown by curves of clay content in profiles). The last three profiles are formed on finer parent materials, the gley podzol with less than 25% clay. The ultra-podzol is devoid of clay.

after: B. T. Bunting (1965)

The podzol, like most soils, is composed of a number of horizons, the uppermost of these being the organic layer. In the forest, this layer usually consists of forest litter, which is generally 2 to 3 centimeters thick and is usually referred to as a humus layer. Generally, this horizon may be divided into several sub-horizons: (a) the undecomposed litter from the latest fall of leaves, (b) the litter left from last season that is undergoing decomposition processes, and (c) the oldest layer, undergoing the most severe reduction processes. These, then, are the three sub-horizons of the A0 horizon from the surface of the soil to the greatest depth of the A0 horizon in a forested environment.

The meadow podzol consists primarily of an A0 layer of dead grass. Meanwhile, in the peat podzol or in places where conditions are favourable for flooding, the A0 horizon may reach up to 65 centimeters in depth. However, in the light sandy soil that is well aerated, the A0 horizon may not even exist. Through this brief discussion, I hope that the reader is able to understand two important concepts concerning A0 horizons: (a) that they can form under different types of vegetation, and (b) the environment plays an important role in determining the depth and chemical characteristics of this horizon.

The A1 horizon lies directly below the A0 horizon in most podzolic soils. Usually, the upper 3 to 5 centimeters of this horizon exhibit the properties of the overlying humus layer or organic matter. Thus, this area of the horizon usually is black to dark brown in colour with a much heavier consistency than the overlying A0 horizon. Upon reaching the 5 centimeters in a podzol, an abrupt change is noted in this horizon. The soil changes colour to a grey powdery substance with a very loose consistency. It loses its crumb-like structure, which is replaced in this zone by a platy structure. Roots generally are able to penetrate this horizon but not to the degree of dense growth that is noted in the chernozem soil.

It is in the horizon underlying the A1 horizon where the podzolic is truly differentiated from any other soil group. The A2 horizon of podzolic soils is easily recognized by its colour. In the strongly podzolized soil, the A2 horizon is bleached an ash grey to an almost white colour. The thickness of this horizon can be anywhere from 10 to 16 centimeters in depth in the loamy soils, and much thicker in sandy soils. Usually, this horizon retains the physical properties of the overlying horizon. Thus, this horizon is characterized by a very powdery consistency when crushed, while in the field a platy structure with few pores and concretions is typical of this horizon.

In the less podzolized soils, the A2 horizon is less pronounced, for the bleached ash grey colour is not as well developed. Thus, it would seem that the colour of the podzolic soils A2 horizon is an excellent indicator of the degree of podzolization in the field case. From this idea, a method of classifying podzolization according to the colour of the A2 horizon has been developed; the more greyish brown the A2 horizon is, the less developed is the podzolization process.

While the A horizon in general seems to be a zone of eluviation, the B horizon is definitely a zone of illuviation in the podzolic soil. The B horizon is typically 20 to 40 centimeters deep, of a brown colour with tonguing of light and brown material at the contact between the A and B horizons. The light coloured material of these tonguing features is usually derived from the bleached material from the overlying A2 horizon. The darker material, which is usually soluble organic material, comes from the A0 and A1 horizons. This material precipitates due to the higher pH, concentrations of electrolytes at this level, and possibly because of the mutual coagulation of the positively charged Al and Fe with the negatively charged organic matter.

As depth increases, the soil becomes much heavier and darker brown in colour due to the movement of clay and hydrated iron oxide. The structure is usually laminar but can be lumpy or even prismatic, depending upon the environment and vegetation cover of the area.

The B2 horizon begins at the point where the texture is heaviest and extends to depths of 40 centimeters. This horizon has none of the bleached material of the A2 horizon nor does it have any organic matter. As depth continues to increase, the colour of the soil becomes a much lighter brown and the soil texture becomes lighter.

At the lower limit of the horizon, the soil's colour and texture become lighter still and seem to blend into the underlying parent material or C horizon.

In many podzolized soils, heavy coatings of manganese are noted. This is particularly the case in the unconsolidated material of the coastal plain in the U.S.A. Other coatings can occur in podzols such as silica, organic and oxides of Fe and Al. These coatings are usually found on the faces of the structural units and along the paths of roots and channels. These coatings can develop into, particularly in lighter soils, hardpans and/or concretions.

2:3 Chemical Processes of Podzols

Now that the reader has obtained a general idea of some of the physical properties of podzolic horizons, I feel that I may proceed with the topic of this chapter -- the chemical properties at work in podzolic soils.

The A0 horizon, as previously stated, is composed of dead leaves, grasses, and other types of vegetation. These substances carry large amounts of alkali and alkaline-earth bases. Upon reaching the surface of the A0 layer during the early fall, when this layer is thickest, they release the bases after the first few rains, causing a pH increase in the soil. The pH is higher than at any other time of the year. The late fall rains tend to leach these bases from the A0 horizon. In their downward movement, some combine with the organic and inorganic exchange complexes of the A and B horizons and others are washed into the ground water systems.

At that time, the humification process sets in, releasing organic and inorganic acids which impart a low pH to the soil. From this point to the next fall, except for a brief period in the spring, the A0 layer is almost always acid (pH lower than 7.0); the acidity depends upon the type of plant species and organic material present (Bloomfield 1953). In the early spring, when the electrolyte content is low, the unsaturated organic and inorganic materials are subjected to depression. They move downwards, carrying the excess acids and acid salts which react with the mineral components. This results in the decomposition of the primary minerals and the formation of secondary minerals. The further decomposition can result in a reaction series being developed. Thus, the A0 is the starting point of many reactions. It is the potential source and storehouse of substances which react with the underlying horizons and impart to the profile the characteristics of the soils known as podzols.

One of the distinctive chemical properties of the AO horizon is its high cation exchange capacity, as compared with other horizons. In no other soil type is the difference in exchange capacity between the AO and the underlying horizons as great as it is in the podzol. Table 2:2 presents rather old data collected by Joffe, which seems to show this point quite well. It illustrates the exchange capacity of several podzolic soils. According to Joffe, the exchange capacity of the C horizon is given merely to serve as a measure of the exchange capacity of the mineral portion of the soil. Joffe says that he found it difficult to assign a cation exchange capacity value to the mineral fraction of the soil that would be applicable to all horizons. This is possibly because of the dynamic nature of the soil-forming process. However, Joffe's data does show the role of the organic and mineral fractions in the exchange reaction of the soils in the AO and C horizons. Table 2:2 demonstrates that the exchange capacity lies primarily in the organic matter for the AO and mineral fraction for the C.

CHEMICAL PROPERTIES OF "AO" HORIZONS

TABLE 2:2

Soil Series	Depth of AO	Reaction		Base Exchange Capacity	Unsaturation		Base Exchange Capacity of "C" Horizon
		H O Extract	Neutral Salt Extract				
	cm	pH	pH	m.e.	me dH	percent	m.e.
Sassafras Loam	3	5.0	3.8	22.3	19.7	88.3	5.2
Penn. Silt Loam	3	5.2	4.3	26.4	18.64	70.6	11.2
Chester Gravelly Loam	3	6.2	5.0	18.5	5.83	31.5	5.3
Washington Loam	5	7.2	6.8	37.2	1.98	5.3	5.03

From Joffe, 1931.

By Oden's method, J. R. Skeen prepared humic acid having an exchange capacity of 306.4 m.e. per 1,000 gms. When he analysed 12 AO samples, four of which were similar physically and chemically to Joffe's samples in Table 2:2, he recorded only one case when the C.E.C. was equal to 37.2 m.e. per 1,000 gms. At best, then, the organic matter could contain only 12 percent of the humic acid. Concerning this point, Joffe says that, "the humic acid is not the only organic constituent capable of cation exchange. The state of decomposition has something to do with the formation of many organic complexes in the AO which influences the exchange complexes" (Joffe 1931). In Table 2:3, data is presented showing the influence of the stage of decomposition on the exchange capacity of organic material.

An important chemical feature or property of the AO horizon and one that was not brought out by many papers, particularly the older ones, is the degree of unsaturation of the AO horizon. This property was discussed by H. O. Buckman in his book, 'The Nature and Properties of Soils' (1969). He cites other examples; however, I will refer to the data in Table 2:2 in order to avoid confusion. In the soil samples, the unsaturation varies from 5.3 to 90.0 percent of the exchange capacity. Buckman speculates that this could be primarily due to two factors: Parent material and vegetation. In the podzolization process, the mineralized bases from the AO horizon move downwards. In the B horizon,

BASE EXCHANGE IN DECOMPOSING ORGANIC MATTER

TABLE 2:3

Time	Base Exchange Capacity per gram dry weight		
	Soybean	Straw	Manure
	m.e.	m.e.	m.e.
Beginning	0.58	0.00	0.73
After 3 weeks	----	0.22	1.03
After 2 months	0.52	0.30	1.08
After 3.5 months	0.48	0.33	1.11
After 6.0 months	1.20	0.38	1.45
After 9.0 months	----	0.59	1.67

After: Muller, 1949.

these bases are retained temporarily before being absorbed, leached, or picked up by plant roots. The same process, supposedly interacts on the bases of the organic material in the intermediate layers between the AO and the B horizons, namely the A horizon. These bases tend to show up in the circulation when the leaves, twigs, and stems of the vegetation die and are redeposited in the AO layers to decompose. The richer the parent material is in the bases, the greater is the circulation of these bases. Therefore, the state of unsaturation depends upon a balance between the outgoing and return of the bases. It must also be remembered that parent materials rich in bases tend to resist podzolization.

Another factor affecting the rate of podzolization of the AO horizon is the specificity and wide variation in the ash content of the plants. From numerous authors, the following conclusions can be drawn regarding how decomposition rates and the various types can affect podzolization: (a) hardwood litter decomposes much faster and more completely than coniferous litter, (b) hardwood forests, due to their base content, tend to slow down the rate of podzolization when compared to coniferous forests. Finally, in studies carried out by Rhodes, he was able to show that the Ca and Mg content of organic horizons (AO) tend to be high in spite of the low pH environment. The Ca, on a percentage basis, tends to approach the quantity of the Mg even in soils having a high (very high) Mg content. Rhodes believed this condition to be due to a larger quantity of Ca returned to the A0 horizon by plants and to the insolubility of Ca humate when dry, while Mg does not become insoluble when dry.

Bloomfield, in one of his many papers on the subject, makes an excellent statement on the effects of vegetation cover and the podzolization process, when he states that pine trees tend to have surface rooting habits which tend to exhaust the bases from the horizon of eluviation more intensely than any other plant series. Therefore, from the above information and the much greater volume of data from the literature which is not cited, I feel that I am correct in concluding that the surface vegetation plays a major role in determining the degree of podzolization.

The A horizon lies directly below the A0 horizon. The outstanding chemical characteristic of this horizon, especially the A2 horizon, is its high degree of acidity. The A1 horizon tends to be more basic than A2; however, the A horizon, even at its least acidic state, has a much more acid pH than the B horizon. This is thought to be due to the higher organic content of the A1 horizon and thus the higher cation absorption. For as the bases are released from the A0 horizon, some are caught and trapped in the A1 horizon. This point is illustrated (rather poorly) by Table 2:4,

TABLE 2:4

Profile Descriptions for Chapter 13

(Colors for moist soil unless otherwise stated)

Profile No. 77

Area: Bardufoss, Norway.

Vegetation: Alpine birch and a ground cover of moss, heather, and some blueberry.

Parent material: Glacial outwash.

Topography: Very gently sloping to nearly level bench above river; surface is hummocky from frost mounds that are from 6 to 8 feet in diameter and about 2 feet high.

O	6 inches to 0 inch, moss and fresh organic matter.
A2	0 to 3 inches, light-gray (N 7/) silt loam; dark reddish-brown (2.5YR 3/4) mottles which may be bits of the B horizon; abrupt, irregular boundary; horizon 2 to 7 inches thick, depending on recency of heaving.
B2irh	3 to 11 inches, strong-brown (7.5YR 5/6) silt loam; a few patches of the light gray (N 7/) A2 horizon; few, small, prominent, olive (5Y 5/6) mottles; firm, brittle when moist; clear, wavy boundary; horizon 5 to 9 inches thick.
B3irh	11 to 14 inches, dark-brown (10YR 3/3) silt loam; few, small, prominent, olive (5Y 5/4) mottles; friable; diffuse, wavy boundary.
C1	14 to 26 inches, olive (5Y 4/3) very fine sandy loam; few, very fine, yellowish and reddish mottles too small for measurement; structureless; loose.
IIC2	26 inches +, coarse to medium, granitic sand.

Climatic data (Bardufoss, Norway)	J	F	M	A	M	J	J	A	S	O	N	D	Ann.
Mean temperatures, 1901-30 (deg. F.)	17	16	22	31	40	50	57	53	44	32	22	17	33
Mean precipitation, 1934-40 (inches)	2.9	2.0	1.5	1.6	1.3	1.7	2.5	2.1	3.1	3.0	2.2	1.7	25.8

Annual precipitation more than 19.2 and less than 32.4 inches during 9 years out of 10.

Depth, inches	Horizon	Particle size distribution (mm.) (%) Pipette and hexametaphosphate										B.D. (gm. per cc.)	Organic matter		F
		Very coarse sand 2-1	Coarse sand 1-0.5	Medium sand 0.5-0.25	Fine sand 0.25-0.10	Very fine sand 0.10-0.05	Silt 0.05-0.002	Clay <0.002	0.2-0.02	0.02-0.002	>2		C % v	C/N m	
6-0	O														
0-3	A2	0.2	0.7	0.5	2.1	27.1	66.9	2.5	71.4	24.0	0		1.38	26	0.
3-11	B2irh	.3	1.0	.8	2.9	28.2	66.0	.8	73.8	22.5	0		1.26	21	2.
11-14	B3irh	.0	.1	.3	2.0	26.9	68.9	1.8	72.6	24.6	0		.62	21	1.
14-26	C1	.0	.1	.2	8.4	44.2	46.1	1.0	85.5	12.2	0		.14		.
26+	IIC2	3.2	24.9	30.0	34.2	5.7	1.9	.1	20.8	.2	0		.10		.

Cation exch. cap. a	Extractable cations, meq./100 gm.					pH 1:5	pH 1:10	Loss on ignition %	Base sat. % a
	Ca	Mg	H*	Na	K				
116.3	17.1	8.4	93.9	0.7	4.1		4.3	84	19
14.5	.6	.4	13.3	.1	.1	4.5			8
16.0	1.0	.4	14.5	.1	<.1	5.5			9
8.8	1.0	.3	7.4	.1	<.1	5.5			16
3.8	.4	.1	3.2	.1	<.1	5.3			16
1.1	.1	.1	.9	<.1	<.1	5.1			18

*Exchange acidity.

after: U.S.D.A. Soil Survey Report

taken from 'The 7th Approximation'.

As a result of the prevalence of acid in the exchange complex of this horizon, the primary and secondary minerals are disrupted, releasing iron and aluminum. In the acid medium, the silicic acid hydrolyzes to give H O and SiO. It is this SiO that gives the ash grey colour to the A2 horizon, so typical of podzols. It has been found by experimentation that when the A2 horizon is not bleached, the SiO content is high anyway, due to the breakdown of the minerals and the release of the silica. This tends to make the texture of the A horizon much lighter than that of the B horizon. It must also be noted that, during mineral disintegration, some of the finer particules move from the A horizon, leaving behind a coarser texture.

The exchange capacity of the A2 horizon is lower than the exchange capacity of the A1 horizon, due to the great quantity of organic matter in the A1 horizon. Also, the organic matter present in the A horizon is usually very soluable and thus mobile throughout the horizon.

An interesting point about the A horizon is its relatively low Ca content, yet high Mg content, particularly in the A2 horizon. Chandler (1943) observed the "violent weathering of certain minerals in the A2 horizon". The bases in general tend to be released from the profile, even though there is a relative accumulation of the alkaline earths in the B horizons. The K, Ca, Mg, and Mn are found to be returned to the A horizon by the vegetation.

Jackson (1958) cites a way of using a tracer ion to establish the movement of the other elements in the profile. He does this by using an article by Pelvsk on podzolic soils formed on granite containing 0.01 percent of SnO_2. He found that SnO_2 went up to 0.05 to 0.1 percent in the A1, indicating the immobility of the Sn in the profile under conditions of podzolization. Therefore, this element is a good element to use as a tracer element in podzolic soils.

The B horizon is chemically distinguished by its relatively low SiO_2 content, high sesquioxide content, relative increase of bases, and exchange capacity and lowering of unsaturation. The B1 horizon frequently contains more organic matter than the A2 horizon. This horizon has a high clay content, which is usually kaolinitic, although montmorillonitic type minerals can form where the parent material is high in bases.

The sesquoioxide content is generally highest in the B horizon, although in some soils the accumulation of Al (aluminum) is not absolute. In the B horizon, some of the R_2O_3 is in combination with organic matter, which results in the organo-mineral gels which are highest in the B horizon. These gels hold the bulk of the R_2O_3, which may be extracted by the oxalate method. The results of this analysis serve as an index to the degree of podzolization, a low content indicating a low degree and vice versa.

2:4 Iron in Podzolic Soils

A very important feature of the podzolic soil usually characterized in the B horizon is the presence of iron. Iron in the soil is characteristically divided into two groups: (a) the iron present in the primary minerals, with the type of iron being dependent upon the type of parent material undergoing weathering, and (b) the secondary minerals. The primary minerals containing iron enclose a very large group of minerals; for example, the ferromagnesium silicate minerals (olivine and amphiboles), biotite, and the iron ores (hematite and magnetite, etc.)

The secondary minerals are less easily defined in terms of a name as compared to the primary minerals, owing to their varied and complex origin, making exact naming of the products difficult. Iron can also be found in the sedimentary rocks, dolmite and calcite; however, unless these rocks were formed in very shallow quiet seas, they will usually contain less than 1 percent iron, making them useless or rather unimportant contributors into the various weathering systems.

In his paper, Oades found Jackson's (1948) thirteen stage weathering system of the primary minerals to deal with the weathering sequence of the iron-rich rocks and/or minerals in the following manner. "At stages 3 and 4 illite and hydrous micas, intermediates at stages 7 and 8 respectively, followed by smecitites and kandites and finally hematite and anatose, at stages 12 and 13" Oades (1963). He went on to discuss the idea that iron could be released and incorporated into montmorillonite. This system that is given by Oades seems to suggest to the reader that there is a definite system whereby iron is weathered, producing various mineral components over time. This idea, however, is incorrect, for it must be made clear that although hematite is the climax stage in the weathering process, it can still occur as coatings on the surface of minerals throughout the weathering sequence. Therefore, although an adequate system for the weathering of iron minerals does exist, as proposed by Jackson et al., the system does not cover all possible combinations of processes and components found in nature.

The primary minerals in the soil are usually found in the larger fractions of the soil. Therefore, by removing the larger fraction (eg. sieving), the clay minerals are left -- primarily illites and nontronite, iron oxides, iron salts, and the iron associated with organic material. These materials are collectively known as the free iron constituents of the soil. Free iron oxides usually constitute the bulk of the free iron and, for the purpose of this paper, are found primarily in the lower B horizon of podzolic soils.

In general, it would appear that in the well-drained soils the iron oxide is found in the clay fraction which is usually evenly distributed throughout the lower part of the profile. However, in the poorly-drained soils, the iron is associated with the clay fraction once again, but in this case the distribution of clay minerals is usually restricted to clay pans and illuvial horizons. Therefore, in either the well- or poorly-drained soils, the free iron oxides are always associated with the clay minerals and are distributed on the basis of the distribution of the clay minerals. Oades believed that this association was due primarily to the absorption of oxides by the clay minerals. He demonstrated his point by referring to two papers: (a) Barbier (1937), who showed that an electronegative clay mineral will fix ferric hydrate; (b) D'Hoore (1954), who showed by experimentation that the maximum amount of iron oxides that can be associated with kaolinitic clay, without the formation of a pan, is approximately 12 percent. From these two statements, Oades was able to make an important statement concerning the formation of an iron clay dominated horizon. Oades describes, "a giant podzol where the depth of the kaolinitic clay appears to control the dimensions of the A2 horizon. This evidence suggests that a kaolinitic clay can fix iron oxides descending from surface horizons and when the saturation point of 12 percent has been reached, will provide a suitable surface for the initiation of an iron pan" Oades (1963).

Therefore, if the accumulation of clay is responsible for the fixation of the descending iron oxides, clay movement must proceed the accumulation of iron compounds. However, it has been found by Lamberts (1954) that before clay can be peptized prior to movement in the profile, the removal of iron oxides is necessary. Thus, it seems necessary to believe that iron oxides must be removed prior to the migration of the clay. It has been determined that the weathering iron oxides will continue to pass through the horizons until clay accumulations at a point will form a horizon capable of fixing iron oxides. To put this in simple terms, clay must migrate downwards to form a clay-dominated horizon. Only when this occurs will iron oxides be fixed to form a Bfe horizon of a podzolic soil.

When large amounts of iron are found in the less than 20 micron clay fraction of the soil, the cementing action of the iron can form iron concretions or iron pans. These features have been studied by a number of authors and are generally thought to occur between the summer and winter water tables. There seems to be two types of iron pans, each owing its existence to a different process.

The first group of iron concretions appears to have been formed "by the presence of oxidizing and reducing conditions, suggesting that their precipitate is physio-chemical in nature" Sherman (1954). The second owes its existence to the precipitation of iron oxides by biological activities. A good example is given in Oades' paper by Lavorv (1950), where he notes that "in the rhezosphere of the root system of reeds the grey gleyed soil becomes coloured red with ferric oxide in the form of a tube of iron oxide around the root, and this process is verified by laboratory experiments showing that plants are capable of oxidizing ferric iron". Bloomfield (1952) also noted this association of iron concretions with root channels and pointed out that he generally found these features in poorly-drained soils. Therefore, the most highly developed Bfe horizon is a layer of iron oxides cemented together to form a hardpan. This climax stage is not too common in most podzolic soils and will not be dealt with in any great detail throughout the remainder of this thesis.

2:5 Conclusions

An attempt has been made in this chapter to relate the various physical and chemical processes of the great podzolic group of soils. This task was undertaken because I feel that it is impossible to isolate a part of a horizon and still discuss intelligently so complex a system of chemical processes as free iron oxide development in the B horizon. It is because of this belief that I felt it necessary to discuss the chemical properties of all the horizons above the B horizon, for it is from these horizons and the parent material and the climate that the B horizon is able to develop free iron oxides. Therefore, I hope that the reader was able to gain some greater measure of understanding of the chemical genesis of a podzol, so that he may better comprehend the complex chemical processes discussed in later chapters. If so, then this chapter was necessary and worthwhile.

CHAPTER III

LITERARY REVIEW OF THE METHODS OF DETERMINING FREE IRON OXIDES

3:1 Introduction

The removal of coatings and crystals of iron oxides such as hematite and geothite is important in many types of studies of soils and mineral colloids, including procedures of mineral segregation, as well as with procedures for powder and oriented specimens x-ray deffraction, electron and polar zing microscope examination and infrared differential and integral thermal analysis.

Early investigators such as Bemmelen (1877) tried to separate weathering products from unweathered by digestion of the soil with mineral acids and alkalies. Tamm (1922) attempted to dissolve out the amorphous minerals by the use of oxalic acid, half neutralized with ammonium or sodium, of pH 3.3. These very old methods are now obsolete and are never used for the determination of iron oxides in soils due to their poor extracting ability in many types of soils.

3:2 Truog's Method

In 1937, Truog et al. had improved or added to the above methods to such a point that his work can be thought to be most representative of the sodium sulphide-oxalic acid method. In this method, a 4 gm. soil sample is placed in 650 ml. of distilled water, 5 ml. of 20 percent $Na_2S \cdot 9H$ 0 solution is added, and the sample is boiled for five minutes; 10 gm. of N H Cl is added, and the solution is kept at 80 to 90 C during the treatment. Oxalic acid is added to bring the pH to 6.0 with vigorous stirring. Then, 10 ml. more of 20 percent $Na_2S \cdot 9H$ 0 solution is added. Oxalic acid is once more rapidly added until pH 7.0 is reached and then slowly to pH 6.0 and again rapidly to pH 3.5. The mixture is stirred and allowed to stand for a few minutes, as the black FeS is dissolving, then is brought back to pH 7.0 by adding 2N NH_4OH; the pH is slowly brought down to 6.0 and then rapidly to 3.5 with 2N HCl. After digestion for a few minutes, the sample is centrifuged and washed twice with a 0.001N HCl. The final extract is used for Fe, Si, and Al analysis.

Although this method proposed by Truog et al. was a better method, it still had very serious drawbacks. Simonson (1938) discovered that when this method was employed, a severe drop in the cation exchange capacity of several different types of soil was experienced. In general, this decrease was proportional to the severity of the treatment and the amount of iron oxide removed. This method, as documented by Jefferies (1941), was found to cause a 19 to 43 percent loss in the exchange capacity of both montmorillonite and kaolin clays, as well as difficulties in effecting complete and adequately rapid removal of iron oxides. It is for these reasons that the sodium sulphide-oxalic acid method has been rejected by researchers in favour of other procedures, which are far more efficient than this very early method.

3:3 Sodium Dithionite Procedure - Deb's Method

Deb proposed three methods for the removal of free iron oxides: ammonium oxalate and oxalic acid in sunlight (pH 3.8); sodium dithionite in sodium acetate and sodium tarate systems at pH 5.0 to 6.0; and sodium dithionite in water at pH 3.5. The latter was considered by Deb to be faster and less destructive than the first two, and is taken to be representative of sodium dithionite methods prior to Aguilera and Jackson (1953).

Deb's investigation was carried out in an attempt to find a suitable method or modification of existing methods for estimating and removing free iron oxides from soils and clays without affecting the other minerals. With this end in view, preliminary experiments were carried out to find the effect of:

"(1) Soil-solution ratio
(2) Time of digestion or shaking
(3) Effects of repeated treatments

> on the removal of free iron
> oxides by different methods"
> Deb (1950)

In preparing his analysis, Deb employed the clay fraction (0.002 mm.) of four soils which were separated after destroying the organic matter and analysed by methods described in "Wright's Soil Analysis". In his report, he gave a very brief description of his soils:

> "(1) Knottwood -- a light yellowish-red clayey subsoil (9-18") from Knottwood Rothamsted
> (2) Africa -- a subsoil (9-18") from a black cotton soil Nyasaland, Africa
> (3) Nagpur -- a grey decomposed mass at a depth of 13-16 feet developed at Nagpur, India
> (4) Nilgiri -- a deep red subsoil (1-3') from Nilgiri hills, India"
> Deb (1950)

The chemical composition of these soils was given by Deb and may be found in Table 3:1.

TABLE 3:1

CHEMICAL COMPOSITION OF CLAY FRACTION

Clay Fraction	SiO_2%	Al_2O_3%	Fe_2O_3%
Knottwood	40.6	24.0	11.7
Africa	35.6	26.9	14.1
Nagpur	50.5	9.76	12.2
Nilgiri	17.8	36.4	27.3

Deb (1950)

Deb's first method was the acid ammonia oxalate sunlight method. The acid ammonia oxalate has a very low pH, which has been found to be very destructive upon the clay minerals present; therefore, the highest pH of oxalate solution at which photo chemical reduction can take place was investigated by Deb. Solutions of 0.2 M. ammonium oxalate and 0.2 M. oxalic acid were mixed in proportions of 2:1, 4:1, and 8:1, to give pH values of 3.4, 3.8, and 4.2 respectively.

Deb observed that the reduction of iron took place more rapidly at the lower pH values. The reaction, he states, was slow at pH 4.2. It was found, for example, for the Knottwood clays, that although the amount of iron in solution was almost the same for the three pH values, the time it took for the reaction to take place was almost 10 times as long at pH 4.2 as at pH 3.8. Although the reaction at 3.2 was faster, the destructive effect on the clay minerals was such that the small time difference between 3.8 and 3.2 (pH) was not significant enough to warrant the more acid solution. Therefore, from these studies Deb was able to conclude that a pH of 3.8 was a standard for the removal of iron oxides.

Deb's preliminary experiments with hydrosulphite showed that the reaction between ferric oxide and hydro sulphite was very slow at room temperature, but became fairly rapid at 40 C, and that the concentration of hydrosulphite over the range of 2.5 percent did not affect the solution of iron to any great extent, although less time was required for a 5 percent solution. He adopted the use of a 4 percent solution.

As the sodium hydrosulphite decomposed to hydrogen sulphite, the reaction of the solution becomes acid. Deb found that with a 4 percent hydrosulphite solution, the final pH varies from 2.9 to 3.5. Deb wanted to carry the extraction as near as possible to neutrality and, therefore, he used a normal acetate containing

0.2N tartrate. Tartrate was used by Deb to "prevent the precipitation or absorption of ferrous ions at high pH" Deb (1950).

In Table 3:2, Deb presents his results, showing the effect of pH on the removal of iron oxides.

TABLE 3:2

Clay	Low pH	High pH
Knottwood	7.6	7.6
Africa	9.6	9.4
Nagpur	2.2	2.4
Nilgiri	26.5	26.8

Deb's results show that the amount of iron dissolved is independent of the pH of the solution.

The effects of temperatures affects (40-2 C and 60-2 C) on the removal of iron oxides was next studied by Deb. At the lower temperature, Deb observed bleaching of the clay after 8 to 10 minutes, with complete bleaching after 30 to 40 minutes. At higher temperatures, however, bleaching started after 2 to 3 minutes and after 5 minutes the clay turned to a black mass, due to the formation of iron sulphide. Deb estimated iron both in the solution and in the residue, with acid ammonia oxalate to dissolve the iron sulphide formed. His results are shown in Table 3:3.

TABLE 3:3

EFFECTS OF TEMPERATURE ON THE REMOVAL OF Fe O

Temperature	Duplicates	Fe_2O_3 in Solution	Fe_2O_3 in Oxalate	Total Fe_2O_3
40 C	a	26.4	0.05	26.4
	b	26.6	0.07	26.7
60 C	a	11.8	15.5	27.3
	b	10.9	16.5	27.4

Deb (1950)

Deb's results show that there is very little difference in the total amount of iron brought into solution at the two temperatures.

Deb then performed two subsequent extractions on the same sample, with the following results (Table 3:4):

TABLE 3:4

THE AMOUNT OF IRON AS PERCENTAGE OF CLAY DISSOLVED
BY TWO EXTRACTIONS WITH HYDROSULPHITE

Clay	First Extraction	Second Extraction	Fe_2O_3 in Second as Percent of First
Knottwood	7.77	0.33	4.0
Africa	9.63	0.31	3.2
Nagpur	2.40	1.00	41.6
Nilgiri	26.6	0.42	1.5

Deb (1950)

The results tend to show that the second extraction brings very little, if any, iron oxide into solution. This shows, Deb states, that the hydrosulphite dissolves almost all the free iron oxide present in the first treatment. Montmorillonite clay minerals containing iron may be partially decomposed by such treatments. Also, iron which comes into solution in the second and subsequent extractions may be derived from partially-decomposed clay minerals and not from free iron oxides.

3:4 Solution of Geothite and Hematite

It was found by Deb that both the geothite and hematite were completely dissolved by the action of sunlight in the presence of an oxalate solution, and also by hydrosulphite. The reaction was found to be very slow in comparison with that of iron oxides in clays. The solubility of these minerals by Tamm's method, Deb points out, is negligible, as shown in Table 3:5.

TABLE 3:5

AMOUNT OF IRON OXIDE REMOVED AS PERCENT
CLAY REMOVED BY DIFFERENT METHODS

Clay	Tamm's Method	Oxalate Sunlight	Sodium Dithionite Method
Knottwood	.56	8.1	7.6
Africa	.19	9.5	9.4
Nagpur	.46	2.4	7.1
Nilgiri	.73	26.8	26.8

Deb (1950)

3:5 Effects of Various Treatments on Base Exchange Capacity of Clays

It is generally accepted that free iron oxides possess little or no exchange capacity, so the removal of any of these constituents from clay should not alter the base exchange capacity of the material.

In Deb's study, the base exchange capacity was estimated both for untreated clays and the same clays after various treatments for removing free iron oxides. His results indicate that, with Tamm's method, the exchange capacity is suggested by Deb to be due mainly "to the removal of ferric oxide which has physically blocked the exchange spots" Deb (1950). However, this explanation does not seem applicable in these clays. The three clays which showed an increase in exchange capacity after Tamm's treatment contain a large amount of free iron oxide as shown by other methods, but Tamm's method brought only a small portion of the free oxides. This small portion cannot possibly alter the physical blocking. The suggestion has been made by other authors that the increase in exchange capacity is due to one or both of the following reasons: (a) removal of the fixed exchange iron, and/or (b) removal of aluminum hydroxide from the outer edges of the crystal lattice.

TABLE 3:6

BASE EXCHANGE CAPACITY OF CLAY FRACTION
BEFORE AND AFTER VARIOUS EXTRACTIONS

Clay	Untreated	Tamm	Oxalate Sunlight	$Na_2S_2O_4$ pH 2.9-3.4	$Na_2S_2O_4$ pH 5.4-6.0
Knottwood	47	48	44.3	49	46.6
Africa	30	32	29.0	32.6	30.6
Nagpur	80	78	68.5	77	78.0
Nilgiri	6.4	8.5	8.3	8.4	8.1

Deb (1950)

3:6 Conclusions

The results of Deb's study show that no method up to that point in time was quite satisfactory for removing free iron oxides without affecting the crystal structure, but hydrosulphite did prove superior to other methods available at the time of the study. Deb summarized the merits of his procedure in the following way:

"(1) Efficient removal of free iron oxides,

(2) Less destructive effect on clay minerals,

(3) Easy and quick manipulation".

Deb (1950)

For years, Deb's method has been thought by many to be the procedure to use when doing free iron oxide determination. This method does have very serious drawbacks, which have been pointed out in papers by Aguilera and Jackson (1953), and by Mehra and Jackson (1960). Their earlier paper also defines a method used by them to extract free iron, which they felt was a definite step forward in determining free iron oxides in soils.

3:7 Mehra and Jackson's Method

A prerequisite to a good method for determining free iron oxide removal, according to Mehra and Jackson, is a high oxidation potential. In all dithionite systems compared up to this point, the hydroxyl source and other variables were applied to 40 ml. of sodium citrate, with 1 gm. of sodium dithionite. The oxidation potential of their system, according to Mehra and Jackson, increases with the increase in pH, owing to the use of four OH groups in the oxidation of each dithionite molecule. The earlier methods, however, used a low pH, which did not give effective removal of iron oxides because of low oxidation potentials.

The required hydroxide may be obtained according to Mehra and Jackson, either from NaOH or NaHCO. In the NaOH system, there were gradual changes in pH and a well-regulated high oxidation potential of 0.7 N. However, the theoretical value of 1.12 V. was never reached in their extraction system.

TABLE 3:7

pH AND OXIDATION POTENTIAL OF DITHIONITE CITRATE SYSTEMS WITH VARYING AMOUNTS OF NaHCO and NaOH

Addition of 1 m. $NaHCO_3$					Addition of 1 m. NaOH				
Volume	After 2 Minutes		After 5 Minutes		Volume	After 2 Minutes		After 5 Minutes	
ml.	pH	ox. pot. (v)	pH	ox. pot. (v)	ml.	pH	ox. pot. (v)	pH	ox. pot. (v)
0.0	6.50	0.37	6.00	0.36	0.0	6.50	0.37	5.95	0.34
2.5	7.10	0.65	6.70	0.61	1.0	11.30	0.51	6.45	0.50
3.7	7.50	0.68	6.90	0.65	1.5	11.70	0.58	6.75	0.56
5.0	7.75	0.72	7.25	0.69	2.0	11.90	0.58	7.56	0.56
10.0	8.35	0.73	8.15	0.73	4.0	12.15	0.59	12.10	0.61

Mehra and Jackson also found that "the order in which the reagents were mixed and the resulting pH greatly influenced the rate of dissolution of iron oxides and the precipitation or non-precipitation of S and FeS" Mehra and Jackson (1962).

Mehra and Jackson found that as the pH was increased to 6.4, the free iron oxides dissolved completely, but FeS and S precipitation occurred. As the pH was increased further, the percentage of iron dissolved decreased steadily. The oxidation potential increased sharply up to 8.0 (pH) and then levelled off. The solubility of free iron oxides decreased rapidly above pH 7.0, with the pH curves intersecting at 7.3, suggesting that this was the optimum pH for the most effective and rapid removal of free iron oxides.

The order in which the reagents are added in Mehra and Jackson's method was based largely on Deb's and Haladane's procedures. The substitution of 5 ml. of 1M. NaHcO buffer for the sodium hydroxide in the adjustment in the 40 ml. of sodium citrate overcame the difficulty of S and FeS precipitation, maintained a high oxidation potential and was, according to the authors, "completely effective for dissolution of free iron oxides".

3:8 Comparison of Methods

The method proposed by Mehra and Jackson has been compared to those proposed by Deb, Truog, and Haladane. The proposed method removes approximately 6 to 8 percent of the free iron oxides, as compared to 2 percent for the H S method and slightly more for the others.

The proposed methods dissolved a considerable amount of Al_2O_3 and SiO . The determination of Al and Si is very difficult in Deb's and Haladane's procedures, owing to the excess of sodium dithionite and oxalate respectively. Also, the proposed method was found to be much more rapid -- 1.0 hour in comparison to the 4.8 hours of several of the other methods.

Another important test on an iron extraction method, aside from its being effective, is its effect on the cation exchange properties of the soil minerals. Some soils are more susceptible to decreases in exchange capacity than are others, and a soil to be employed to test the effects of an iron extraction on exchange capacity should be somewhat attackable. In their study, Mehra and Jackson used a Miami silt loam and found that the decrease in exchange capacity was directly proportional to the amount of iron oxide removed, until 48 percent of the exchange capacity had been destroyed and 28 percent of free iron oxides had been removed. Mehra and Jackson thus attribute one-half of the exchange capacity of the mineral portion of the soil to the iron layer silicates.

The proposed method was tested on several soils and two clays by the authors, and compared to Deb's method. A dilute acid and alkali treatment was employed on the soil samples and on a control, causing 1.6 m.e. loss in exchange capacity. The Deb method removed only 1.2 percent of free iron oxides, but caused very little change on the exchange capacity as compared to the control. The proposed method caused about the same decrease in exchange capacity as Jefferies method, but removed twice as much iron as any other procedure.

More tests were carried out on the soil samples in order to determine the effect of the treatments upon the cation exchange capacity (C.E.C.). From these tests, Mehra and Jackson concluded that any method for the removal of free iron oxides will have some destructive effect upon the layer silicate colloids, with a consequent loss in cation exchange capacity. However, the authors state that their method seems to cause as little destruction as many other methods and much less than some.

Mehra and Jackson's proposed method of buffering the dithionite citrate systems with $NaHCO_3$, gives freedom from S, FeS , zinc oxalate and other unwanted precipitates. It is a rapid system requiring 30 to 60 minutes, as compared to the several hours required in earlier methods. It is highly effective in the dissolution of free iron oxides, owing to the maintenance of a slightly alkaline pH, which keeps a high oxidation potential in the sodium dithionite system in marked contrast to earlier acid less buffered dithionite systems. The determination of Fe, Al, and Si in the extract is much easier and simpler. Above all, the treatment has almost no destructive effect upon iron silicate clay minerals.

3:9 Coffin's Method

One of the most modern procedures for the removal of free iron oxides was proposed by D. E. Coffin in 1963. This procedure was developed for the Canadian Department of Agriculture, and is the procedure that the Department feels is most suitable for the extraction of free iron oxides from Canadian soils.

Coffin's study was undertaken to evaluate the efficiency of some of the more widely used hydrosulphate methods, to determine the role of such factors as pH, temperature, and reagent concentration in the removal of free iron from soils, and to develop a system for the removal of free iron oxides from the soils.

3:10 Effect of pH on the Extraction of Fe_2O_3 according to Coffin

To determine the effects of pH on the extraction of iron, Coffin's soils were extracted at 40°C. with a 5 percent solution of sodium hydrosulphite in citrate solutions of 0.1, 0.2, and 0.3 M. sodium citrate and a series of solutions containing sodium citrate and citric acid, in which the total citrate concentration was 0.2 M.

Coffin found that these latter solutions gave extractions with different pH values, in which the effect of varying the citrate concentration was eliminated. His table for the pH of all citrate solutions and the citrate solutions plus hydrosulphite are shown in Table 3:8. He notes that the pH of the citrate solution plus the hydrosulphite is the pH which prevails during the extraction, and Table 3:8 illustrates the fact that there is not necessarily any direct relationship between the pH of the citrate solution and the pH which exists during extraction.

TABLE 3:8

THE EFFECT OF THE ADDITION OF SODIUM HYDROSULPHITE ON THE pH OF THE CITRATE BUFFER SOLUTION

Concentration of Sodium Citrate (M)	Concentration of Citric Acid (M)	pH of Citrate Solution	pH of Citrate plus Sodium Hydrosulphite
0.100	0.000	7.99	4.98
0.100	0.100	4.22	4.24
0.125	0.075	4.48	4.53
0.150	0.050	4.60	4.75
0.175	0.025	5.80	4.98
0.200	0.000	7.83	5.44
0.300	0.000	7.74	5.68

Coffin (1963)

Coffin's Figure 5 shows the relationship between the pH of the extracting system and the amount of iron removed

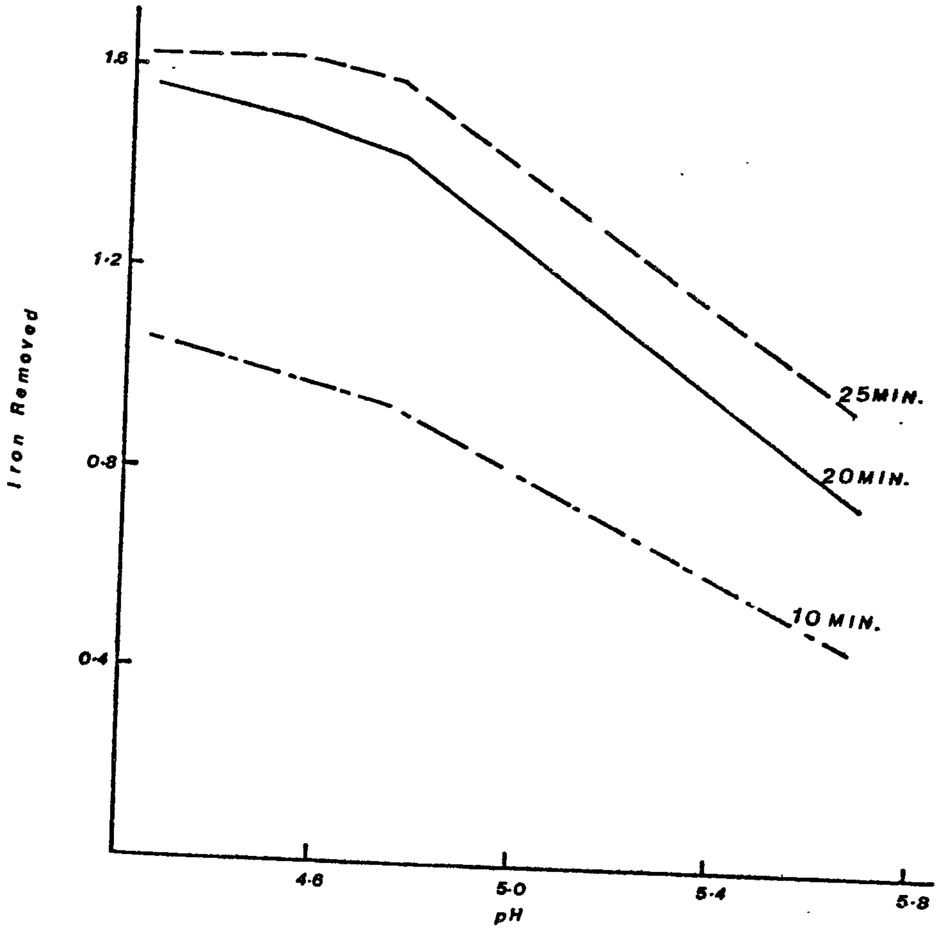


FIGURE: 5

Coffin 1963

from a sample of Charlottetown soil. At pH 4.24 and 4.53, sulphur was precipitated from the extracting solution, but there was no evidence of sulphur precipitation from any other of his extracting systems employed. Coffin found that, except at low pH values, the amount of iron removed from the soil was inversely proportional to the pH prevailing during the extraction, but there was no relation between the pH of the citrate solution and the amount of iron removed. Coffin felt that the effective reduction of the concentration of the reducing agent, due to the precipitation of sulphur, could account for the observed deviation at low pH from the direct relationship between iron removal and pH.

From these results, Coffin was able to conclude that the extractant which was 0.15 M. to sodium citrate and 0.05 M. to citric acid was superior to all others, for it resulted in a pH of 4.75 during extraction -- a pH which gave the most rapid extraction of iron.

Coffin experienced some difficulty in obtaining samples of ferric oxide minerals which would resist physical breakdown of the particles during extraction, as required for his study of the rate of chemical decomposition. He was able to find only one sample of hematite suitable for his purpose. The rates of removal of iron from this hematite by a 5 percent solution of hydrosulphite in the citrate solution, at three temperatures, are shown in Figure 5.

Coffin took the amount of iron remaining undissolved, expressed it as a percent of the sample, and plotted this on a logarithmic scale against time of extraction on a linear scale. He discovered that the energy of activation for the removal of iron from hematite calculated from the differences in the slopes of the curves at different temperatures, was 14.8 k cal/mole/°C.

In Figures 6 and 7, Coffin's rates of removal of iron from the Charlottetown soil, with the same extractant as was employed for the hematite, is shown. He notes that the iron was removed much more rapidly from the soil than from the hematite, and Coffin found it necessary to use lower temperatures to obtain the same rates. This was probably due to the fact that the iron removed from the soils was present in the form of coatings on the mineral grains, rather than as discrete particles. Also, the curves for the removal of free iron oxides from the soils exhibit two distinct slopes; these slopes can be explained in the following manner. The shape of the curves in Figures 6 and 7 exhibits two types of iron being removed from the soil. Coffin determined that in the rapid initial removal of iron the energy of activation was 8.6 k cal/mole/°C., while the rate of removal for the rest of the iron was 22.4 k cal/mole/°C. Coffin carried out similar tests on other soils, coming up with similar results to those shown by the

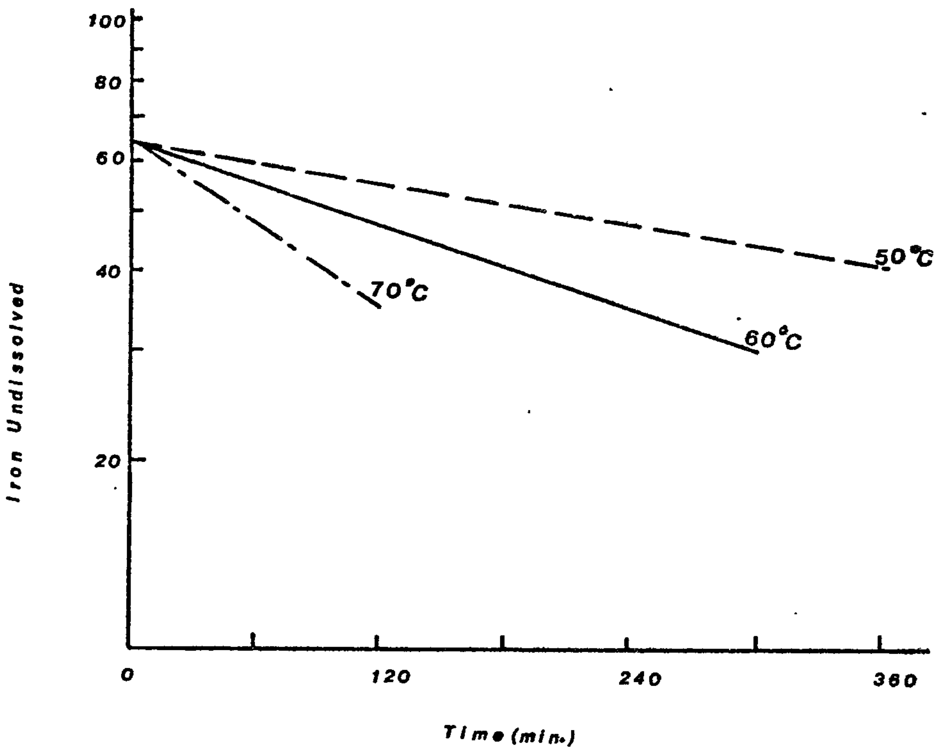


FIGURE: 6

Coffin 1983

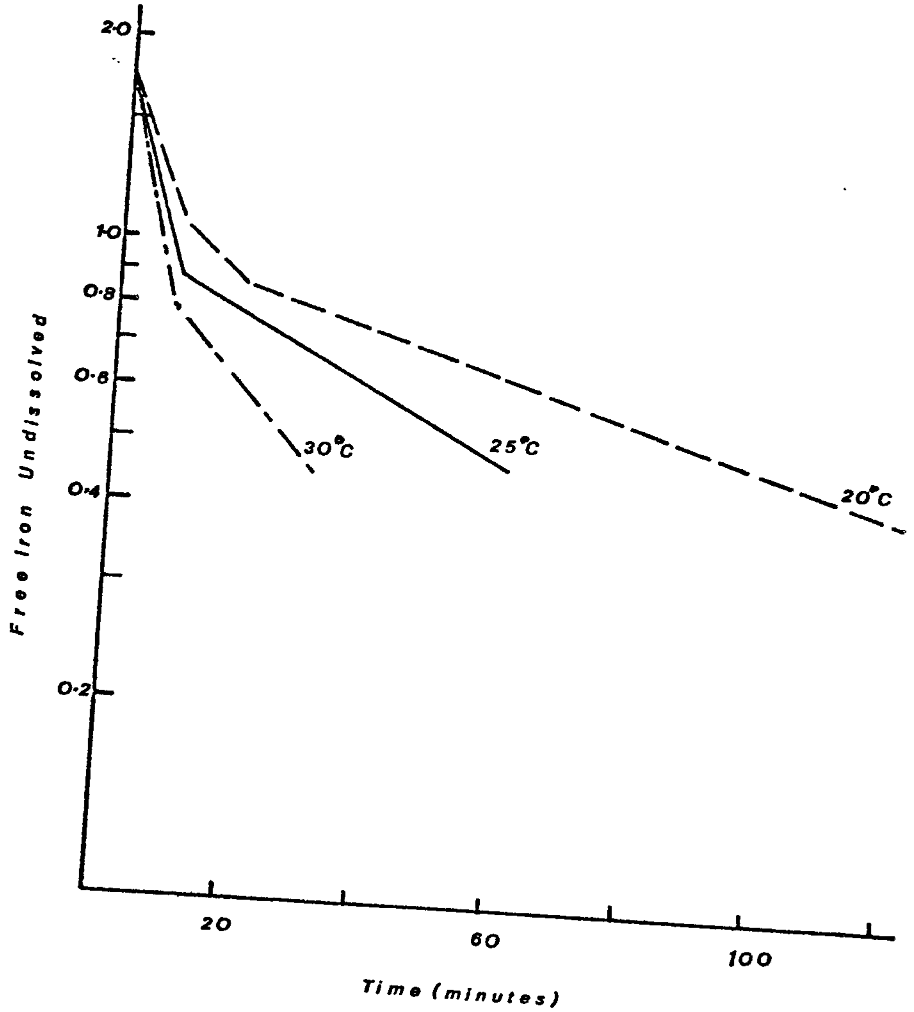


FIGURE: 7

Coffin 1963

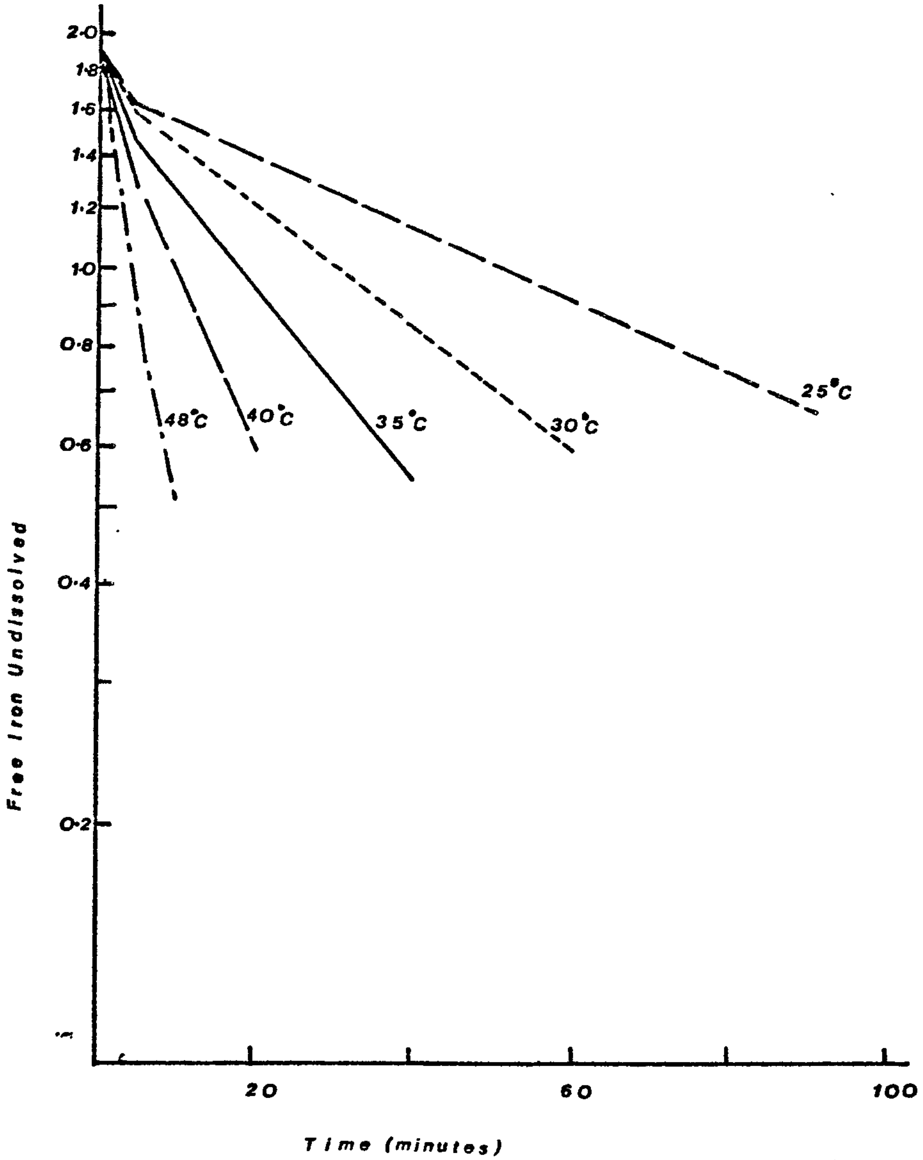


FIGURE: 8

Coffin 1963

Charlottetown experiment; these studies showed that not only because of the above fact, but also that because the energies for activation did differ so considerably from the values for the hematite, the free iron could not have existed in the soil in the form of discrete particles.

Coffin employed 19 horizons of podzolic soil and performed free iron extraction at 40°C. and 50°C. with a 5 percent solution of sodium hydrosulphite in a citrate solution. He found that at 40°C., 45 to 60 minutes were required to reach a point where no more iron could be removed from the soil, while only 15 to 30 minutes were required to reach the same point at 50°C. Moreover, he noted that successive extractions were of no advantage over single extractions over the same time period.

The results indicated that at 50°C., all the free iron coatings could be removed from the soil grains by one 30-minute extraction.

Coffin performed his extraction method on several soils. Also, extraction time for these soils was extended well over the 30-minute time period. Table 3:9 shows the results of this work. The table shows that the free iron was completely removed from these soils by one 30-minute extraction, and that no more iron could be removed by extracting up to 16 hours.

The maximum amount of soil extracted from these soils, according to Coffin, did not, in any instance, approach the total content of the soils.

TABLE 3:9

THE AMOUNTS OF IRON REMOVED BY APPLICATION
OF THE PROPOSED PROCEDURE FOR VARYING TIMES

	Iron Removed		
Soil	30 minutes	60 minutes	16 hours
Charlottetown 1	1.71	1.73	1.73
Charlottetown 2	1.28	1.28	1.28
Charlottetown 3	1.42	1.39	1.42
Queens 1	1.40	1.42	1.42
Queens 2	1.87	1.87	1.89
Alberni 1	3.07	3.05	3.07
Alberni 2	2.31	2.27	2.29

Coffin (1963)

Coffin believed that the above results indicated that this procedure removed only free iron from the soils, and that iron was not slowly removed from the crystal lattice of the silicates present in the soil.

Finally, Coffin subjected his procedure to a number of clays, in order to determine the destructive effect, if any, on a variety of clay minerals.

The amount of iron and aluminum removed from five clays and their cation exchange capacity before and after extraction is shown in Table 3:10. Coffin found that the exchange capacity of the clays was not appreciably altered by the procedure. No magnesium was detected in the free iron extracts from hectorite, which is a clay containing large amounts of magnesium. Coffin concluded, therefore, that the procedure does not cause any appreciable destruction of the clay minerals.

TABLE 3:10

Clay	Total Iron %	Free Iron %	Total Al	Al Removed	Cation Exchange Capacity	
					Before	After
Clauconite	15.88	4.62	6.28	0.03	20	19
Hectorite	0.23	0.04	0.11	0.00	57	56
Illite	3.62	0.23	9.74	0.06	33	34
Montmorillonite						
Chambers	1.02	0.06	8.96	0.12	115	113
Otay	0.66	0.06	8.39	0.02	115	114

Coffin (1963)

Coffin compared his procedure with those developed by Anguilera and Jackson, Mehra and Jackson, and Mitchell and Mackenzie; the results of his tests are found in Table 3:11.

TABLE 3:11

PERCENT IRON REMOVED BY VARIOUS METHODS

Soil	Percent Iron Removed			
	Anguilera & Jackson	Mehra & Jackson	Mitchell & Mackenzie	Proposed
Charlottetown 1	1.72	1.74	0.75	1.73
Charlottetown 2	1.29	1.28	0.60	1.28
Queens 1	1.89	1.87	0.83	1.87
Alberni 2	2.28	2.30	1.84	2.28

Coffin (1963)

The results of "this Table combined with the fact that it failed to bleach many of the samples, demonstrates that the procedure proposed by Mitchell and Mackenzie is not satisfactory for the removal of free iron from these soils" Coffin (1963). The other procedures removed equal amounts of free iron oxides.

3:11 Conclusions on the Useful Methods of Extracting Free Iron Oxides

In the preceding discussion, the advantages and disadvantages of the most popular procedures for extracting free iron oxides have been discussed at length. The analysis which has been undertaken will now permit the selection of the most useful procedure for free iron oxide removal. The most useful procedure, in my opinion, is Coffin's method.

(a) This procedure requires a single 30-minute extraction at 50°C., in contrast to a single 60-minute extraction in Deb's case, and two 15-minute extractions and a 1-hour 80°C. wash required by Aguilera and Jackson and Mehra and Jackson.

(b) The great accuracy and excellent results (re: large amounts of iron extracted) obtained by Mehra and Jackson can be obtained by Coffin's method in a much shorter time span.

(c) The destruction of the crystal lattice of the clay minerals is much greater in Mehra and Jackson's procedure than it is in Coffin's. Therefore, some of the iron extracted by Mehra and Jackson could have been removed from the crystal lattice, thus making Coffin's extraction more useful.

(d) In tests by Coffin, only the free iron coatings were removed from the mineral grains and the procedure did not remove any iron from the crystal lattice of the silicates present, thus proving the validity of point (c).

(e) The precipitation of FeS and S is not encountered by Coffin's procedure, while this is a problem in Deb's and, to some extent, in Mehra and Jackson's procedure.

(f) The necessity of having a high oxidation potential to precipitate all available free iron oxides is not necessary in Canadian soils because of low free iron oxide content. Thus, the great problems of maintaining a pH of 7.3 are not necessary, and a major complexity may be negated by using Coffin's method with excellent results. Also, Mehra and Jackson's idea of buffering the solution was an added complication which could have more easily been accomplished by adding additional citrate, for citrate and HCO are both proton acceptors at the pH they required. This tends to suggest unnecessary complication and poor experimental results in their procedure.

For the above reasons, Coffin's procedure will be accepted from the literature as being the most useful method of extracting free iron oxides available, at the present time.

3:12 Holmgren's Procedure

In order to effect a complete discussion of the available procedures, there is one final procedure which has not been discussed up to this point. This procedure was really a modification of an earlier one which had its roots in the procedure proposed by Deb. The earlier procedure was one developed by J. Kilmer (1960), while G. A. Holmgren (1967) was responsible for the latest one. Both of these procedures were developed in the Soil Survey Laboratory of the United States Department of Agriculture. The Holmgren Procedure was not performed in the soil science laboratories at McMaster University because chemicals needed to perform it were only available from companies in the United States on special order, which would have meant a long delay while awaiting delivery. For this reason, the procedure was not performed. However, it is a useful procedure, as it is the one employed by the U.S.D.A. and, therefore, warrants a brief discussion.

The Holmgren Procedure, a later development of one proposed by Kilmer (the latter used in the soil laboratories at McMaster University) is really a modification of Deb's. The principle modification is the removal of iron oxides at room temperature, rather than at elevated temperatures. While the rate of iron removal is slower at room temperature, the attention of the worker is not required.

Some workers, Kilmer says, may prefer a colorimetric procedure for estimating iron, rather than titration by dicromate as described by this procedure. However, Kilmer believes that the titration has a distinct advantage where soils of diverse iron oxide content are routinely examined, for its range is practically unlimited and dilution of the iron solution is unnecessary.

Holmgren's study was undertaken to develop an extractable iron method that would incorporate improved reliability over the procedure then used by the U.S.D.A., yet one that would also be rapid and adaptable to routine use. The principle innovation of Holmgren's procedure was the incorporation of a citrate buffer into an overnight shaking with a single extraction. The use of an automatic pipette and a floculating agent, the volumetric calibration of the shaking bottles, along with the use of a modified orthophenanthroline iron procedure resulted in a rapid procedure which is "adequately" precise for the purpose.

Holmgren reasoned that the extent of the extraction depends upon the amount of citrate present rather than the pH. The high pH, he said, was necessary to prevent the decomposition of dithionite as detected by sulphur dioxide fumes.

The procedure developed by Holmgren does have certain advantages over the Kilmer procedure, as outlined here:

(1) The citrate solution bleaches the soil, whereas the Kilmer procedure does not.

(2) The two procedures are both acceptable on soils containing less than 5 percent extractable free iron; however, on

soils containing large amounts of free iron, the results using either method, tend to be variable and often incomplete.

(3) The second extraction in Holmgren's procedure removed only 2 percent more free iron, while Kilmer's procedure removed up to 40 percent more iron on the second extraction. Thus, Kilmer's procedure requires two extractions to remove similar amounts of free iron oxides as compared to the one extraction by Holmgren's procedure.

(4) Kilmer or Holmgren presented very little data to support their particular procedures, thus raising doubts as to the usefulness of their respective methods.

(5) The values of extraction by Kilmer's method are generally less, and their standard deviation greater, than in Holmgren's method.

3:13 Conclusions

This chapter has been written to give the reader some measure of understanding concerning the various procedures of free iron extraction available, the theory behind them, and their relative merit in comparison to other procedures available to the researcher. The procedures presented in this chapter, except

Holmgren's procedure, have been used on arctic podzols in the soil laboratories at McMaster University, and the results of this study will be presented in the following chapter. From the data presented in Chapters III and IV, a suitable method for determining free iron oxides in Canadian soils can be defined.

CHAPTER IV

MULTIPLE STEPWISE REGRESSION
AND
FACTOR ANALYSIS
OF THE ORIGINAL SOIL DATA

4:1 Multiple Stepwise Regression

This section of the chapter deals with the multiple stepwise regression of the original soil data, in an attempt to determine which variable is the most dependent variable in the extraction of free iron oxides by a particular extraction procedure.

The analysis was undertaken to separate the variable-dependent procedures from the procedures which are not dependent upon any particular variable or combination of variables for the extraction of free iron oxides from soil samples.

Each of the four procedures analysed in the laboratory were subjected to two extractions, with the second extraction being undertaken to determine the amount of free iron left by the first extraction. Also, it was hoped that different variables which had not played a major role in the first extraction would interact on the second extraction. Therefore, for each procedure there is a regression analysis for the first extraction, the second extraction, and the sum of the two extractive procedures. This will allow the most dependent variables for each extraction to be determined, and the effects of these extractions on the crystal structures of the layer silicates will also be discovered. Therefore, by summing the results of the two extractions, it is hoped that the most dependent variable can be determined, as well as its effect upon the extractive procedure.

4:2 Deb's Procedure

Deb's Procedure is the most established of any of the procedures tested in the soil labs. On the first extraction, the multiple regression analysis showed that the most dependent variable was the lower limit of the soil horizon. From this, it can be assumed that, as the lower limit of the iron-rich horizon increases, the amount of iron extracted on the first extraction decreases significantly. This would seem to suggest that Deb's Procedure is only able to remove the iron oxide coatings at shallow depths. As the depth increases, the chemical bonds existing between the iron oxides and the layer silicates minerals strengthens, and this extractive procedure is not able to break these bonds in order that the free iron oxides may be extracted and their relative percentages determined. The relationship between Deb's first extraction and depth can be seen in Table 4:1.

In the second extraction, the effect of the subsequent extraction upon the same soil sample by the test procedure is clearly brought out. In this case, the procedure is dependent not upon the depth at which the soil sample was taken, but rather upon the cation exchange capacity (C.E.C.) of the soil sample.

In this case, the procedure is causing the breakdown of the silicate mineral structure, which results in the removal of iron from the borders of the layer silicates. Therefore, with repeated extractions, employing this procedure as illustrated in Table 4:2, the chain structure of the silicate minerals is disturbed, iron is removed, and this iron becomes part of the overall free iron extracted. Therefore, an incorrect percentage of free iron oxides results, due to the incorporation of iron other than free iron in the final analysis.

In the overall analysis, however, the variable which seems to be most important in the extraction of free iron oxides, according to Deb's Procedure, is the depth of the sampling horizon. Table 4:3 shows quite clearly that, as depth increases, the amount of iron removed by this procedure decreases. This is primarily due to the fact that as soil water passes down through the soil capillaries, it gives off the free iron oxides leached from the above

TABLE 4:1

FREE IRON OXIDE EXTRACTION

MULTIPLE REGRESSION SUMMARY

Dependent Variable: Deb - first extraction

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE R	BETA
DEPTL#	.048	.40398	-.15446048E-01
CEC	.224	.52407	.21287824
PH	.573	.55122	-.31098631
DEBPH	.654	.57065	.13296058
DEPTU	.747	.58315	.10944752E-01
CONSTANT			1.5874545

\# Variables are designated by computer symbols ----
See Appendix C for key.

TABLE 4:2

FREE IRON OXIDE EXTRACTION

MULTIPLE REGRESSION SUMMARY

Dependent Variable: Deb - second extraction

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE Q	BETA
CEC#	.052	.39434	-.20188140E-01
DEBPH	.397	.45740	.32058121E-02
DEPTL	.500	.50024	-.17262877E-02
DEPTU	.146	.68638	.18352017E-02
CONSTANT			.43722425E-01

\# Variables are designated by computer symbols ---
See Appendix C for key.

TABLE 4:3

FREE IRON OXIDE EXTRACTION

MULTIPLE REGRESSION SUMMARY

Dependent Variable: Deb

VARIABLE	SIGNIFICANCE	MULTIPLE R	BETA
DEPTL#	.045	.41359	-.17172336E-02
CEC	.264	.51569	.19269010
PH	.567	.54359	-.31782670
DEBPH	.676	.56081	.13616639
DEPTU	.711	.57751	.12779954E-01
CONSTANT			1.6311769

\# Variables are designated by computer symbols ---
See Appendix C for key.

horizons. At greater depths, the clays and uncharged oxides on which the oxides precipitate are undersaturated in oxides. The bonds holding the thin oxide coatings are much stronger than is the case when the oxide coatings are very thick. Thus, at increasing depth, the extractive procedure is not able to break the bond and extract significant amounts of iron oxide; this opinion is verified by Russel (1961). Therefore, this system has an inherent weakness in that it does not reliably extract free iron oxides from soils taken from great depths. Thus, it would seem that this procedure would be useful only for the extraction of iron oxides from horizons of shallow depths.

Other factors not included in the regression analysis was the time necessary to perform the extractive procedure; this is of critical importance when the researcher has many samples to run in a specified time period. In Deb's case, the time required to perform extraction technique was, on the average, four hours.

The second factor which must be investigated is the difficulty in performing the procedure. As a researcher, it is my experience that a straight-forward procedure is less likely to confuse or cause problems than is a very complicated one. In this regard, Deb's procedure is very straight-forward and could be handled by anyone with even the most rudimentary knowledge of chemistry.

Therefore, from the multiple regression analysis, it can be assumed that Deb's procedure is not completely suitable for free iron extraction, (a) due to the variable results encountered at varying depths, and (b) due to the effect of the procedure upon the outer chain silicate minerals under repeated extractions and the possible incorporation of iron from the chain silicates into the extract solution causing incorrect results.

4:3 Kilmer's Procedure

Kilmer's procedure, it may be remembered, is really an early adaptation of Holmgren's, the procedure currently employed by the U.S.D.A. In Kilmer's procedure, the dependent variable according to Table 4:4 is the pH of the soil extract after the procedure is performed on the soil sample. This would suggest that as the pH of the solution increases, the amount of iron that is possible for the procedure to take into solution decreases. This will result, as the pH increases, in the precipitation of foreign precipitates into the extract, which can drastically affect the overall determination of free iron oxides in the soil solution. This point is well-illustrated in Chapter III of this thesis.

The increase of the pH during extraction leads not only

TABLE 4:4

FREE IRON OXIDE EXTRACTION
MULTIPLE REGRESSION SUMMARY

Dependent Variable: Kilmer - first extraction

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE R	BETA
KILPH#	.061	.37310	1.7806546
PH	.214	.50500	- .80898882
CEC	.272	.60211	.56631732
DEPTU	.824	.60643	.96236072E-02
DEPTL	.877	.60907	- .76704588E-02
CONSTANT			-3.3973957

Variables are designated by computer symbols --
See Appendix C for key.

to complication, as mentioned above, but also results in such problems as determining the normality of the solution needed for subsequent extraction in order that the pH may be returned to its optimum position so that precipitation of precipitates other than free iron oxides does not increase proportionally as the pH continues to increase.

Kilmer's procedure is a useful one, for it is not dependent upon the depth of the sampling horizon or upon the cation exchange capacity. Therefore, it does not affect the layer silicates resulting in the incorporation of iron other than free iron into the final extract, nor are variable results encountered at varying depths. However, the fact that the dependent variable in the first, second, and summation extraction is the pH (after extraction), can often result in precipitation of other precipitates, making this a very hazardous procedure to employ in free iron oxide extraction.

This procedure is one of the most time-consuming of any of the procedures available for free iron oxide extraction. It involves a 16-hour shaking period and up to 6 hours of laboratory analysis, to determine free iron oxide content. However, as the results of Table B-1 of Appendix B show, this is a useful procedure for it does present a good set of results which compare favourably with the other extractive techniques.

Finally, this procedure does have one important fault. It incorporates in its procedure the titration of the extract to a specific colour end point. This, I feel, is a poor technique, for it involves the judgement of the researcher in determining when that end point is reached, which may or may not be correct. Therefore, I feel that more accurate results could be obtained with the use of a spectrophotometric technique replacing the titration procedure currently employed by this procedure.

Kilmer's procedure is unsuitable for free iron extraction because of the following reasons:

(a) The dependency of the extraction upon pH could cause the introduction of foreign precipitates into the extract, resulting in inaccurate results.

(b) In my opinion, the results obtained by use of titration rather than spectrophotometric techniques, are inaccurate.

(c) There is a large time factor involved in performing this extractive technique.

4:4 Mehra and Jackson's Procedure

This procedure is proclaimed by many researchers in the soil sciences to be one of the most effective systems for the extraction of free iron oxides in soils. However, the results of experiments performed in the McMaster Laboratories employing this extraction technique contradict this belief. The multiple regression analysis performed on the first extraction shows a definite dependency existing between the amount of iron extracted and the lower limit of the sampling horizon. (See Table 4:6) In this relationship, as the depth of the soil horizon from which the soil sample was obtained increases, the amount of iron extracted from the sample decreases. By contrast, the upper limit of the sampling horizon plays no major role in determining the amount of iron removed.

This can be explained during the first extraction, in the following manner. As the soil water percolates through the overlying organic and mineral (A) horizons, it takes into solution, among other substances, free iron. This solution percolates down through the soil until it reaches the B horizon, where it is deposited in the form of coatings on the silicate minerals present in that horizon. These coatings tend to be more well-developed in the upper zone of that horizon; thus, the upper limit tends not to be a major variable. However, as the water solution continues to percolate down through the soil capillaries, there are fewer mineral precipitates available to come out of solution to form coatings on the mineral grains. In the upper layers of the

TABLE 4:5

FREE IRON OXIDE EXTRACTION

MULTIPLE REGRESSION SUMMARY

Dependent Variable: Kilmer

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE R	BETA
KILPH#	.063	.36760	1.8215859
PH	.211	.50256	- .84055584
CEC	.255	.60659	.58688838
DEPTU	.801	.61207	.7393694Z3-02
DEPTL	.915	.61333	- .54240861E-02
CONSTANT			-3.4347624

\# Variables are designated by computer symbols -- see Appendix C for key.

TABLE 4:6

FREE IRON OXIDE EXTRACTION

MULTIPLE REGRESSION SUMMARY

Dependent Variable: Mehra and Jackson - first extraction

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE R	BETA
DEPTL#	.095	.30980	- .21705601E-01
CEC	.145	.50108	.5897319
PH	.266	.60095	-1.4529873
MJPH	.454	.64745	1.1032094
DEPTU	.614	.67190	.17609429E-01
CONSTANT			2.0269067

Variables are designated by computer symbols -- See Appendix C for key.

horizon, the coatings become very thick; the bonds that exist between the coatings and the mineral grains are weaker than when thin coatings exist as in the lower layers of the horizon, and these bonds (the thicker ones) can be broken, and the free iron oxides removed much more easily than when the bonds are very strong, as exist in the lower limits of the horizon. This results in the need for multiple extraction of soil samples at greater depth in order to achieve effective removal of the free iron oxide coatings when sampling from very deep horizons.

The preceding discussion is further exemplified by Table 4:7. This table is based on the second extractive procedure, and shows that after the first extraction is performed employing this method, the dependent variable is no longer the lower limit of the sampling horizon, but rather the upper limit becomes the dependent variable. This change in dependent variable is due to the removal of much of the free iron oxides on the silicate grains during the first extraction. This results in a much stronger bond existing between silicate mineral and the coating, which in turn causes samples taken at shallow depth to perform in a similar manner to samples taken at great depth. Therefore, on repeated extraction, the thick coatings of iron oxides are removed, a stronger bond exists between the two mediums, which results in the multiple regression analysis determining that the upper limit is the dependent variable.

TABLE 4:7

FREE IRON OXIDE EXTRACTION
MULTIPLE REGRESSION SUMMARY

<u>Dependent Variable: Mehra and Jackson - second extraction</u>

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE R	BETA
DEPTU#	.017	.53035	.11156277E-01
CEC	.209	.63105	-.14941564
MJPH	.404	.67468	.60686352
PH	.638	.69017	-.50852814
DEPTL	.904	.69144	-.30804316E-02
CONSTANT			-.17131476

\# Variables are designated by computer symbols --
See Appendix C for key.

In reality, the real dependent variable is the strength of the bond which exists between coating and mineral grain.

Another variable which can lead to discrepancies in the results obtained, employing Mehra and Jackson's technique, is the cation exchange capacity (Table 4:6). This dependency shows quite clearly that this extractive technique is not attacking the coatings of free iron oxide but rather the chain structures of the silicate minerals, resulting in possible inaccuracies in the amount of free iron oxides found in the final extract.

Time is not a critical factor in this procedure. It was determined that this procedure could easily be performed in 2.5 to 3.0 hours, which makes this the most rapid procedure yet discussed. However, one great difficulty in the procedure is the maintenance of a high pH as called for by the authors. The pH was not found to be a dependent variable in the multiple regression analysis. However, I believe this is because, on the whole, the soils are very low in free iron oxides. If the soils were latesols, with a very high free iron oxide content, this would have been a dependent variable. In their paper, the authors demonstrated the need for a high pH when they stated that in order to maintain a high oxidation potential to allow sodium dithionite to extract to its maximum, a high pH was necessary. However, in soils low in free iron oxides, this high oxidation potential is not necessary, for sodium dithionite can easily remove the coatings as demonstrated by previous procedures using sodium dithionite at low pH. The maintenance of a high pH can also be detrimental in that, if the pH is in the range of 5 to 8, oxidized iron cannot remain in solution and thus goes out of solution, bonding itself on to clays, uncharged oxides, or mineral complexes. This can result in a significant loss in total free iron oxides extracted by the procedure. This point is well demonstrated by Hem and Cooper in a paper (1959). Thus, Mehra and Jackson complicate their procedure by specifying a high pH, which is difficult to maintain when there is really no need to maintain such a high pH, except in special cases.

In conclusion, Mehra and Jackson's procedure is not suitable for the removal of free iron oxides from Canadian soils, because:

(a) The extraction of iron oxides is directly dependent upon the depth at which the sample is taken. If the sample is taken at great depths, the bonding which exists may be so strong that this procedure is not able to remove significant amounts of free iron oxides to obtain reliable results.

(b) The cation exchange capacity, being a dependent variable, tends to demonstrate that this procedure attacks forms of iron other than free iron, and can result in inaccuracies due to this problem.

(c) The maintenance of a high oxidation potential, through the use of a high pH, is a time-consuming and unnecessary procedure on Canadian soils.

Thus, for the above reasons, this procedure is not recommended for use as an extractive technique for free iron oxides.

4:5 Coffin's Procedure

At the beginning of this chapter, the definition of a suitable iron extraction technique was given. It stated that a good free iron oxide extraction procedure should be completely independent of any variables. In the multiple linear regression analysis performed on the four extraction techniques, none of the procedures tested were totally independent of external variables. This, however, does not mean that a suitable method for free iron oxide extraction was not determined by the research carried out for this thesis. A technique was found that has a significance value high enough to recommend it as the most useful method of determining free iron oxide percentages in Canadian soils. The method was proposed by D. E. Coffin, and is the method currently employed by the Canadian Department of Agriculture.

The procedure is suitable for the following reasons:

(a) The procedure is virtually independent of any variable tested against it, as shown by Table 4:8. It is also independent of multiple extractions on similar soil samples, as shown by Tables 4:8, 4:9, and 4:10.

(b) The procedure is very rapid, requiring only 2.0 to 2.5 hours to extract as great a percentage of free iron oxides as was extracted in the combined first and second extraction of several other techniques.

(c) The problems resulting from multiple extraction need not be encountered when this technique is employed, for as much free iron oxides are extracted when employing this technique on the first extraction as on multiple extractions using other techniques. Also, this procedure resulted in minimal variation in the cation exchange capacity and pH (Table B-2), proving conclusively that the results obtained employing this method are useable and not influenced by foreign precipitates and foreign types of iron.

(d) This procedure does have the disadvantage that it does employ titration and equation conversions rather than the more

TABLE 4:8

FREE IRON OXIDE EXTRACTION
MULTIPLE REGRESSION SUMMARY
Dependent Variable: Coffin (first extraction) Procedure

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE R	BETA
COFPH#	.659	.02552	- .84224964E-01
CEC	.761	.03929	.15829153
DEPTL	.752	.05653	- .92159363E-02
DEPTU	.856	.06339	.86084099E-02
CONSTANT			1.0737306

\# Variables are designated by computer symbols --
See Appendix C for key.

TABLE 4:9

FREE IRON OXIDE EXTRACTION
MULTIPLE REGRESSION SUMMARY

Dependent Variable: Coffin - second extraction

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE R	BETA
CEC#	.232	.17271	- .81288725E-02
PH	.348	.27706	- .49738520E-02
DEPTU	.447	.34884	.57116137E-03
DEPTL	.452	.43427	.46786966E-03
CONSTANT			.30105148E-01

\# Variables are designated by computer symbols --
See Appendix C for key.

TABLE 4:10

FREE IRON OXIDE EXTRACTION
MULTIPLE REGRESSION SUMMARY

Dependent Variable: Coffin's Procedure

VARIABLE ENTERED	SIGNIFICANCE	MULTIPLE R	BETA
COFPH#	.650	.02704	- .89137070E-01
CEC	.776	.03909	.15016128
DEPTL	.759	.05539	- .96836206E-02
DEPTU	.846	.06324	.91795066E-02
CONSTANT			1.1035387

Variables are designated by computer symbols -- See Appendix C for key.

reliable spectrophotometry and calibration curves. However, this is a minor disadvantage which can be easily corrected by employing a new technique of colorimetry replacing titration, making this system the most useful system tested up to this point in time.

4:6 Factor Analysis

The second technique applied to the data was factor analysis. With a large number of soil variables to interpret, simplification of the data makes the relationship between soil variables easier to interpret. Factor analysis is one technique whereby soil variables which are similar in nature or which respond in a similar manner to environmental changes can be grouped into a smaller number of discrete independent factors, which facilitates the interpretation of the multiple regression.

The same correlation matrix used to construct the multiple regression was used in the factor analysis. Means and standard deviations were also entered into the factor programme. Due to the degree of intercorrelation in the data, the largest of the diagonal elements in the correlation matrix was used as the initial communality estimate. Only factors with eigenvalues greater than 1.0 are reported and interpreted. Only one type of factor analysis from the S.P.S.S. programme Laboratory, Nic et al. (1970), was used, which was an orthogonal factor analysis with oblique rotation. A delta value of zero, which gives a moderately well-correlated solution, was used with the oblique rotation.

4:7 Interpretation of Oblique Factor Structure Matrix After Rotation

Factor analysis was performed on the data in order to determine which variable or variables are the most dependent which, it was hoped, would help to clarify and strengthen the data presented by the multiple regression analysis. Secondly, it was performed to allow the separation of the various variables in order to simplify the procedure of determining which free iron oxide extraction technique is most suitable for use on Canadian soils.

Before the results of the factor analysis are presented, the reader must remember that due to the limited number of cases (10) for each extraction technique, the correlation matrix is ill-conditioned and the factor score coefficients may not be reliable.

Factor 1 (Tables 4:11, 4:12, C:2, and C:3) consists of free iron extraction procedures proposed by Deb, and Mehra and Jackson. These factors are the most dependent factors as shown by the percent variation of 47.5 (Table 4:11). Included in this factor is the weak dependency of Kilmer's procedure and the very weak dependency of Coffin's procedure. However, of prime concern in this factor is the fact that Mehra and Jackson's and Deb's procedures are strongly dependent variables.

Factor 2 consists of the strong dependency of Kilmer's procedure and the less dependent Coffin's procedure. These first two factors are iron factors, and will be referred to as iron 1 (factor 1) and iron 2 (factor 2). In both cases, the iron factors seem to be correlated to a limited extent with the time necessary to achieve maximum removal of free iron oxides from the soil.

Factor 3 exists as an independent factor, pH which ranks third on the list of dependent factors with a percent variation of 13.6 (Table 4:11). This factor tends to show that pH is not a dominant dependent variable in any of the extraction procedures, but rather it is an independent variable which can, under certain circumstances as noted in the regression analysis, act as a dependent variable.

Factor 4 also exists as an independent factor consisting of the cation exchange capacity (C.E.C.) of the soil sample. This factor is the least dependent, according to the percent variation of 9.0 from Table 4:11. This tends to show that the procedures do not often interfere with the chain silicate minerals but, due to a weak dependency, the C.E.C. can be affected, which means inaccurate results may result under certain circumstances.

4:8 Comparison of Different Factor Solutions

The factor analysis clearly demonstrates that there are two dependent factors consisting primarily of the four extractive procedures and two independent factors, pH and C.E.C.

The dependency of the iron extraction techniques does clearly demonstrate that any particular free iron oxide extraction technique will be dependent, to some degree, upon some variable. Therefore, no technique can be expected to give completely uniform results on any soil at any particular point in time. However, the particular procedure which is least dependent upon any single or group of variables can be determined from this research. In analyzing the factor matrix (Table C:3), it can be seen that Coffin's procedure is the least dependent of the four procedures tested. This procedure, therefore, can be assumed to be the most useful technique for free iron oxide extraction, for it is much less dependent upon a specific variable or group of related variables than are the other three procedures. This fact would tend to assure the researcher of more consistent results and fewer inaccuracies due to

TABLE 4:11

FREE IRON OXIDE EXTRACTION

FACTOR ANALYSIS SUMMARY

FACTOR	EIGEN VALUE	PERCENT OF VARIANCE	CUMULATIVE PERIOD
1#	11.77126	47.5	47.5
2	7.41932	29.9	77.4
3	3.37612	13.6	91.0
4	2.23361	9.0	100.0

Factors correlate with computer symbols --
See Appendix C for key to factors.

TABLE 4:12

FREE IRON OXIDE EXTRACTION
FACTOR ANALYSIS SUMMARY
FACTOR PATTERN CORRELATIONS

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
FACTOR 1#	1.00000	.14472	- .19801	.08750
FACTOR 2	.14472	1.00000	.06410	- .02170
FACTOR 3	- .19801	.06410	1.00000	- .08199
FACTOR 4	.08750	- .02170	- .08199	1.00000

\# Factor correlation is given in computer symbols -- for key, see Appendix C.

the interaction of outside variables on the extraction of iron oxides from the soil sample.

Factors 3 and 4 are both independent factors which, if the factor analysis is correct, do not tend to influence the extraction of free iron oxides to any great extent. However, these factors do become important when multiple extractions on the soil sample are necessary. In these cases, the pH of the solution, for example, can cause the iron oxides in solution to oxidize and re-attach themselves to clay minerals or uncharged oxides. This is particularly the case where the pH of the solution is allowed to rise into a 5 to 8 range. In turn, the oxidation can cause a change in the type of iron present. The oxidation of iron (II), a reduced iron by oxidation, can lead to the development of iron (III), an iron sulphate, which results in a further drop in the pH; this results in the precipitation of other precipitates into the extract. By employing a factor analysis, the two independent factors, pH and C.E.C., have been shown to be dependent variables in multiple extractions only. However, since most of the procedures require multiple extractions, these two seemingly independent factors become important in the overall analysis.

The factor pattern correlation exhibits two important results (Table 4:12). It shows that the iron factors and pH can be weakly related in some cases, verifying that which has been stated previously. Secondly, it demonstrates that the two iron extraction factors are related. Due to the fact that all four systems are somewhat closely related according to amounts of iron removed, time for removal, etc., this would tend to result in a weak relationship.

4:9 Summary

The analysis of iron data by multiple regression and factor analysis was undertaken in order to determine which of the four procedures tested was the most useful procedure for free iron oxide extraction. A definition of a useful procedure was given as the procedure which was least dependent upon specific variables. The following conclusions can be drawn from the preceding analysis.

(a) Deb's procedure is a very dependent procedure which does not give consistently accurate results from a series of soil samples. It is chiefly dependent upon the depth from which the soil sample was taken, and can, under multiple extractions, result in destruction of the chain silicates with the incorporation of liberated foreign iron into the extract.

(b) Mehra and Jackson's procedure has also been found to be a very dependent procedure, giving poor results and not being recommended for use in extracting free iron oxides.

(c) Kilmer's procedure is a less dependent procedure and could, under certain conditions, be suitable for use in free iron oxide extraction. However, under multiple extractions it can cause the pH to become a dependent variable, resulting in precipitation of foreign precipitates into solution. Also, it is a very time-consuming procedure, which tends to make it less attractive than one that can be performed more rapidly with equal or better results.

(d) Cation exchange capacity and pH are normally independent variables but can, under specific circumstances such as multiple extractions, become dependent. When this occurs, large inaccuracies can result.

(e) Coffin's procedure from the multiple regression analysis was considered to be the most independent procedure available. Factor analysis shows this procedure to be somewhat dependent upon certain variables, as most procedures are; however, it is still the least dependent of any procedure tested. It is a rapid and highly successful method of removing free iron oxides and, therefore, can be considered as the best procedure available at the present time for the extraction of free iron oxides from soils containing small percentages of free iron oxides.

CHAPTER V

CONCLUSIONS

In soil science research, as in any applied science, it is imperative that there be a continual review of the procedures employed by that science to extract the necessary information in order to complete the research under investigation at any particular point in time. Unfortunately, it is often the case whereby, rather than testing their procedures against more modern ones, the scientist may often continue to employ the older method in order to save the time which would be necessary to test the new method. This can often result in inferior results, which could be avoided by employing a different method. This thesis was undertaken to test the various procedures available for free iron oxide extraction and to determine which of these procedures is the most useful procedure for the Canadian soil laboratories.

This research did produce some very interesting results, which should aid researchers in choosing a method of extracting free iron oxides from soils. The following conclusions can be reached from the preceding study:

(1) The technique which proved to be the most useful procedure for extracting free iron oxides (from podzolic soils) was developed by D. E. Coffin and is currently employed by the Canadian Department of Agriculture.

(2) A measure of the reliability of a free iron oxide extraction procedure can be obtained by determining the percentage of free iron oxide removed by the procedure during multiple extractions, and the effect of the multiple extraction on the pH and C.E.C. of the soil sample.

(3) A useful procedure for free iron oxide extraction has been determined from this research as one which is least dependent upon outside variables such as pH, C.E.C., time necessary for extraction, and depth of the soil horizon.

(4) This research has shown that various procedures cannot be used effectively on all types of soils. This can be determined by the amount of free iron oxides present; for example, if the soil is rich in coatings of free iron oxide, a procedure with a high oxidation potential is the most effective system to use in order to allow the sodium dithionite to achieve its maximum potential. However, if the percentage of free iron oxides is low, as is the case in most Canadian soils, then a technique employing a high oxidation potential, with its related problems,

is not necessary. Therefore, the procedure used for extracting free iron oxides must be tested on local soils in order to determine whether or not it is the best procedure for the particular soil group under investigation.

(5) In the colorimetry section of the extraction procedure, spectrophotometry was found to give far more consistently reliable results than did the older titration system and is, therefore, recommended for incorporation into extraction procedures employing titration in its colorimetry.

This research was undertaken to subject a number of the most widely-used free iron oxide extraction techniques to critical examination in order to determine which system was most useful for performing its assigned task. I hope that the preceding research has accomplished this goal, and that it will enable Canadian soil scientists to better determine which system is most useful for their particular research.

APPENDIX A

LABORATORY RESEARCH TECHNIQUES FOR FREE IRON OXIDE EXTRACTION

1. Deb's Method of Free Iron Oxide Extraction.
2. Kilmer's Method of Free Iron Oxide Extraction.
3. Mehra and Jackson's Method of Free Iron Oxide Extraction.
4. Coffin's Method of Free Iron Oxide Extraction.
5. Procedure for Determining Cation Exchange Capacity.

APPENDIX A

LABORATORY RESEARCH TECHNIQUES FOR FREE IRON OXIDE EXTRACTION

1. Deb's Method

Reagents

1. Sodium Acetate: 1 N (82 gm. in 1 litre of H O)
2. Sodium Tartrate: 0.2 N (46 gm. in 1 litre of H O)
3. Hydrochloric Acid: 0.02 N (20 ml. of 1N HCl, make 1:1 in H O)
4. HCl + 50% HNO: 3:1 solution (Aquaregia)
5. Potassium Thiocynate 10%: (10 gm. of K.S.C.N in 100 ml. of H_2O)
6. Hydrogen Peroxide: H O (30% solution)
7. Sodium Dithionite Powder: $Na_2S_2O_4$

Procedure

1. Place 1 gm. of soil in a 100 gm. centrifuge tube.

2. Add 25 ml. of sodium acetate and 25 ml. of sodium tartrate to the above soil solution.

3. Place the above solution on a shaker, seal the top of the centrifuge tube with a rubber stopper, and shake the solu-

tion for 20 minutes at 200 r.p.m. on a mechanical shaker.

4. Remove the solution from the shaker and add 2 gm. of sodium dithionite powder to the tube (this must be performed rapidly as sodium dithionite decomposes rather rapidly in solution).

5. Place the above solution (still contained in the centrifuge tube) in a water bath at 40°C. for 30 minutes. Stir the solution occasionally when it is in the water bath as this will aid in the bleaching of the solution.

6. Remove the solution from the water bath and place it into a centrifuge. Centrifuge the solution at 2200 r.p.m. for approximately 10 minutes. Pour the clear supernatant, after centrifuging in a 100 ml. flask.

7. Treat the soil remaining in the centrifuge tube with 30 ml. of 0.02 N Hydrochloric acid. Shake this solution at 200 r.p.m. for 10 to 15 minutes to allow complete bleaching of the soil.

8. Centrifuge the above solution for 10 minutes at 2200 r.p.m. Pour the resulting clear liquid into the 100 ml. flask containing the previous centrifuged solution and make the resulting solution to 100 ml. This is known as solution 1.

9. Pipette 10 ml. of solution 1 and put it in a 100

ml. flask; then add 90 ml. H_2O. This becomes solution 2.

10. Pipette 10 ml. of solution 2 and put it in a 100 ml. flask; add 2 ml. of aquaregia and make the solution to 50 ml. by adding H_2O.

11. To the above solution add 10 ml. K.S.C.N (10%) and 2 drops of hydrogen peroxide.

12. Pipette a suitable aliquot of the above solution into a test tube suitable for use in the spectrophotometer. After calibrating the instrument with a blank (see below) read the iron sample at 475 Å on the spectrophotometer; maximum colour is reached in 30 minutes.

13. Prepare a blank by repeating steps 2 and steps 6 through 12.

Calibration Curve

1. Weigh 0.1 gm. of iron and dissolve this sample in 20 ml. of concentrated HCl and 5 ml. of H_1O.

2. Pour the above solution, when the iron sample is totally dissolved, into a 1000 ml. flask and dilute to volume.

3. Aliquots of 5, 10, 20, 30, and 40 ml. of the above solution are placed in beakers and steps 9 through 12 (from the

above procedure) are performed on the samples. Read the samples at 475 Å in the spectrophotometer and construct the calibration curve from these readings.

DEB'S CALIBRATION CURVE

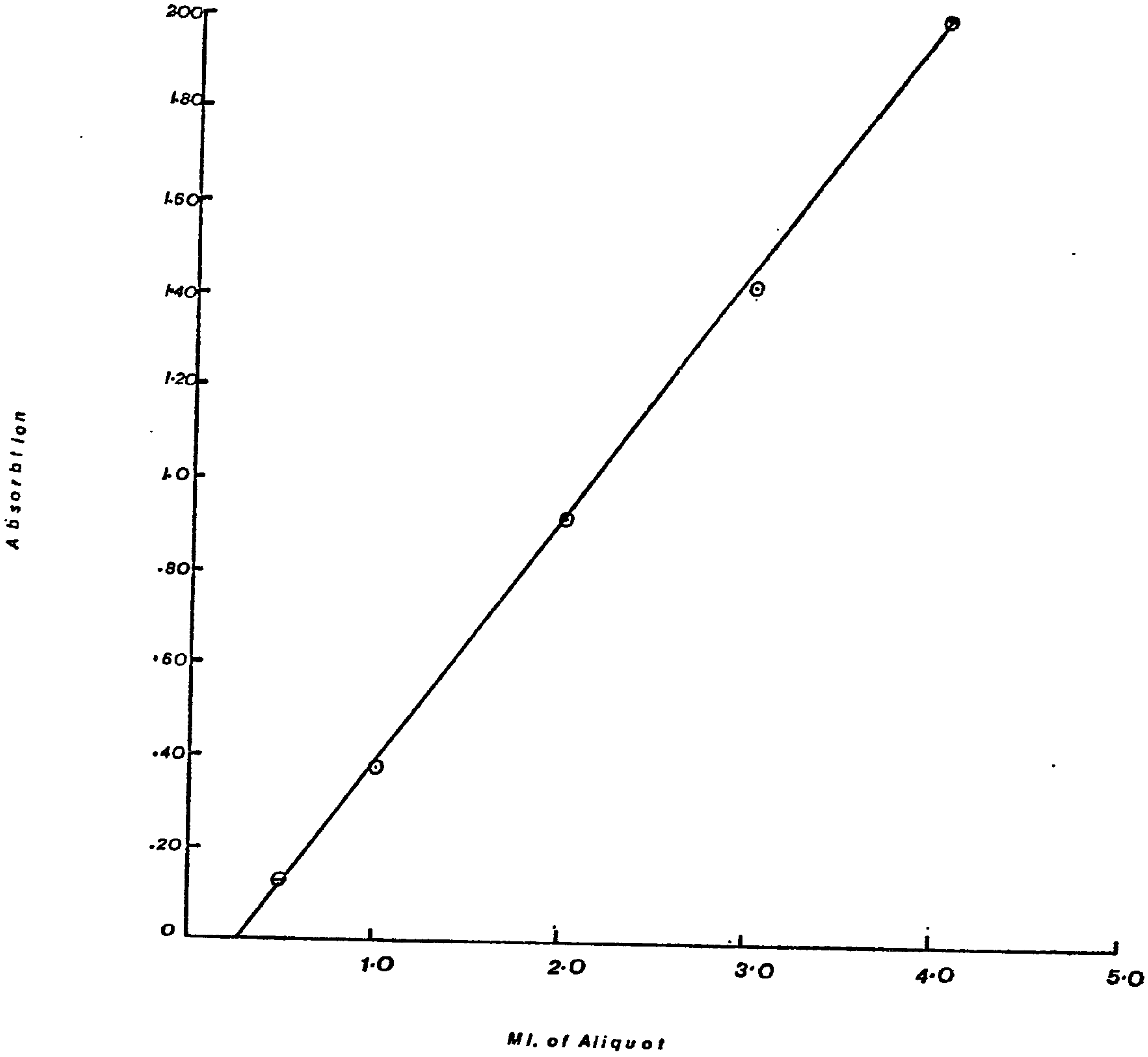


Figure: 9

2. Kilmer's Method

Reagents

1. Sodium Dithionite Powder: ($Na_2S_2O_4$)
2. Hydrochloric Acid: (HCl) 1 N -
3. Hydrogen Peroxide: (H_2O_2) 30% solution
4. Potassium Ferricyanide: (($K_3Fe(CN)_6$)) 0.1% -- a new solution must be prepared each time
5. Ammonia Hydroxide: (NH_4OH) 7 N -
6. Hydrochloric Acid: (HCl) 6 N -
7. Stannous Chloride: ($SnCl_2$) - 1 gm. in 3 ml. of HCl and dilute with 50 ml. H_2O - fresh each time.
8. Mercuric Chloride: ($HgCl_2$) saturated aqueous sol.
9. Orthophospheric Acid: 85 percent solution
10. Potassium Dicromate: ($k_2Cr_2O_7$) 0.1 N -
11. Barium Diphenylamine: .16 percent aqueous solution

Procedure

1. Place 5 gm. of soil in a flask and add 5 gm. sodium dithionite powder and 100 ml. of H_2O. Stopper and shake the above

solution for 16 hours. The shaking must begin no longer than 20 minutes after the water is added, as sodium dithionite decomposes rather rapidly in solution.

2. After shaking for 16 hours, transfer the above solution to a 250 ml. beaker and adjust the pH to 3.5 - 4.0 using 1 N hydrochloric acid. Let the solution stand for not less than one hour, stirring it 4 to 5 times during that period.

3. Transfer the preceding solution to a 250 ml. flask, dilute to volume, stopper, and shake at 200 r.p.m. on the mechanical shaker for 15 minutes.

4. Transfer the above solution to a 100 ml. centrifuge tube and centrifuge at 2000 r.p.m. for 10 minutes. Using a mechanical source of suction due to the presence of a dangerous gas, transfer 50 ml. of the supernatant liquid to a 100 ml. beaker. Add 15 ml. of hydrogen peroxide, then dilute to volume.

5. Cover the beaker with a watch glass and warm the solution on a hot plate until the reaction begins. Remove the beaker from the hot plate, let the reaction subside, then bring the solution to the boil for 10 to 15 minutes.

6. Place 2 to 3 drops of the above solution on a hot plate and add 1 to 2 drops of potassium ferricyanide to test for iron.

7. If iron is present, add another 5 ml. of hydrogen peroxide to the above solution and boil 5 to 10 minutes more.

8. To the above solution, add a slight excess of 7 N ammonia hydroxide and boil the solution for a further 10 to 20 minutes.

9. Now dissolve the Fe $(OH)_3$ precipitate by adding 15 ml. of 6 N hydrochloric acid through the lip of the covered beaker.

10. Heat the solution to 90°C. and reduce the iron by adding stannous chloride dropwise with stirring until the yellow colour just disappears.

11. Add 4 drops of stannous chloride in excess, cool the solution to room temperature, and add 15 ml. of saturated mercuric chloride rapidly from a volumetric cylinder.

12. A light, silky precipitate should form if the proper amount of stannous chloride was added; if it does not form, the solution is useless and the procedure must be repeated on a fresh sample.

13. If a silky precipitate does form, dilute the solution to 125 ml., then add 5 ml. of 85% orthophospheric acid and 10 drops of barium diphenylamine sulphate.

14. Titrate the above solution with standardized 0.1 N potassium dicromate to a violet blue endpoint.

Calculations

Free Iron Oxides as % Fe 0 = ml. of $k_2Cr_2O_2$ used x normality of $k_2Cr_2O_2$ x 7.92

3. Mehra and Jackson's Method

Reagents

1. Sodium Citrate: 0.3 M
2. Sodium Chloride: Saturated Solution
3. Sodium Dithionite Powder
4. Sodium Bicarbonate: 1 M
5. Acetone

Procedure

1. Weigh 4 gm. of soil into a 100 ml. centrifuge tube and add 40 ml. of sodium citrate (0.3 M) and 5 ml. (1.0 M) sodium bicarbonate.

2. Bring the above solution to 80°C. in a water bath.

3. Remove the solution from the water bath and add 1 gm. sodium dithionite, stirring constantly for 1 minute, then occasion-

MEHRA & JACKSON'S CALIBRATION CURVE

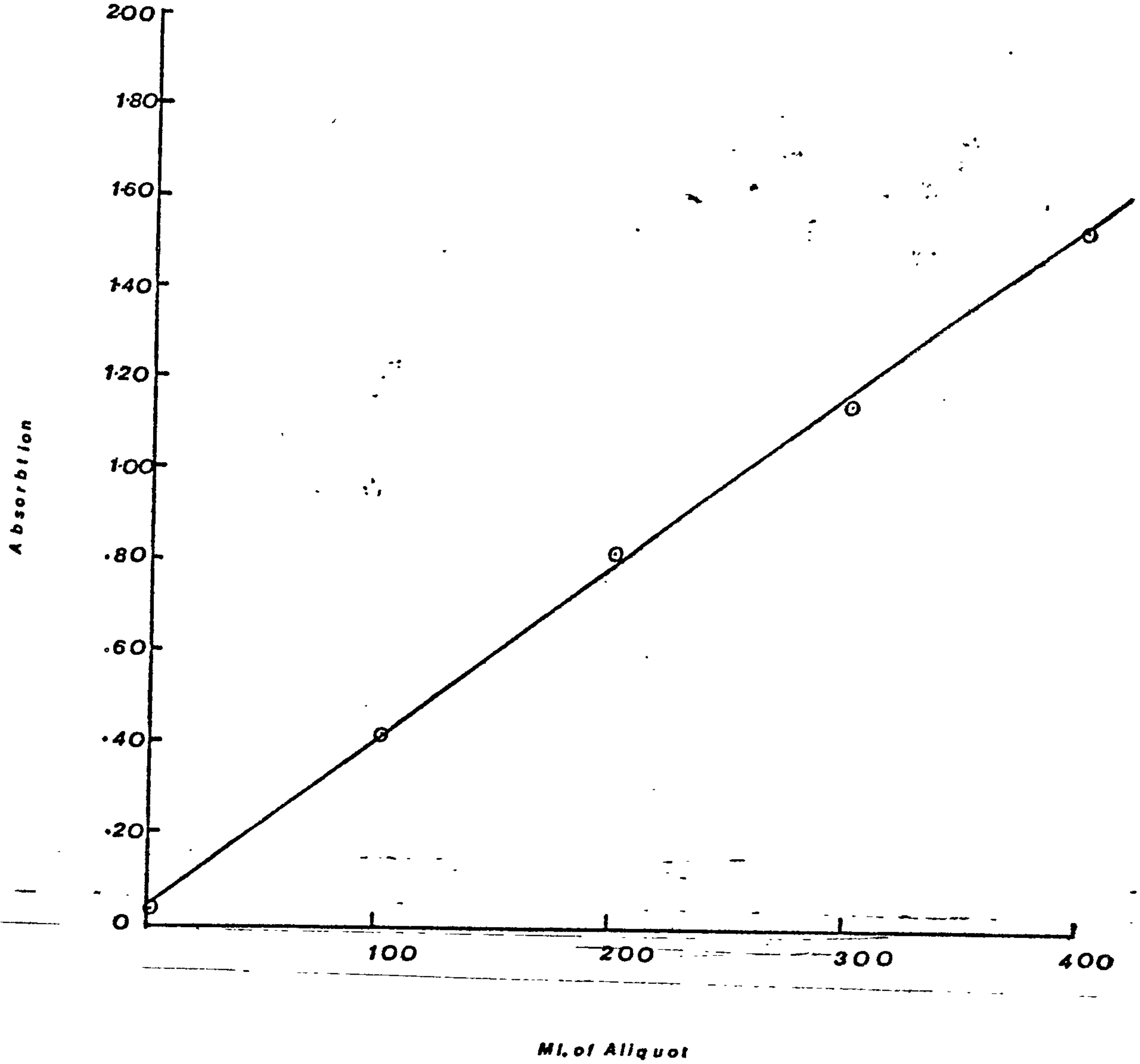
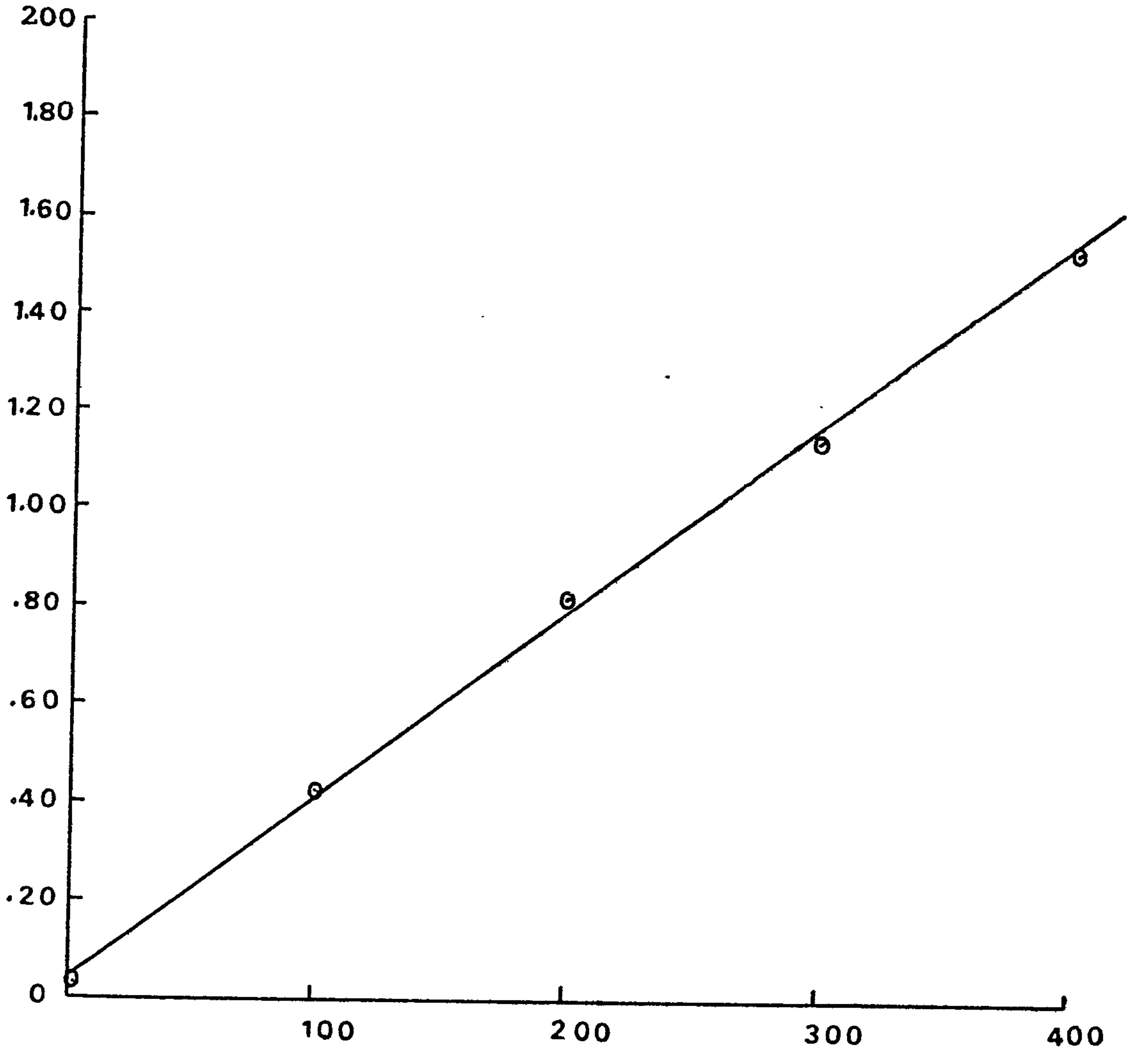


Figure: 10


200
1.80
1.60
1.40
1.20
1.00
.80
.60
.40
.20
0
100
200
300
400

ally for 15 minutes.

4. Add 10 ml. of sodium chloride solution and 10 ml. of acetone to promote floculation.

5. Mix the above solution, then warm it in a water bath. The solution is then centrifuged for 5 minutes at 1600 to 2000 r.p.m.

6. Decant the clear supernatant liquid into a 500 ml. flask and make to volume with distilled water.

Colourmetric Procedure for Mehra and Jackson

Reagents

1. Hydrochloric Acid: 6 N
2. Potassium Thiocyanate: 20 %
3. Hydrogen Peroxide: 30 %

Procedure

1. Transfer a suitable aliquot (0.5 to 3.0 p.p.m.) to a 50 ml. flask. Add 35 ml. of H_2O.

2. To the above solution, add 1 drop of hydrogen peroxide and 5 ml. of potassium thiocyanate.

3. Make the above solution to volume.

4. Transfer a suitable aliquot of the above solution to a test tube suitable for use in a spectrophotometer. Read the absorption of the solution on the spectrophotometer at 490 M.

Calculations

1. $\text{Fe(pct)} = \frac{\text{mg/l of Fe from curve}}{\text{gm. of sample}} \times \frac{\text{ml. extract}}{\text{ml. aliquot}} \times 0.005$

2. Fe 0 (pct) = Fe(pct) x 1.43

4. Coffin's Method

I. Reagents

1. Citrate Buffer Solution: 10.5 gm./litre citric acid monohydrate and 174 gm. sodium citrate
2. Sodium Dithionite Powder
3. Perchloric Acid: concentrated

Procedure

1. Place 0.5 gm. of 0.15 (100 mesh) soil into 15 ml. centrifuge tube and add 10 ml. of the citrate buffer solution.

2. To the above solution, add 0.5 gm. of sodium dithionite powder; stopper and shake the solution at 50°C. in a water bath for 30 minutes.

3. Centrifuge the above solution, then digest a suitable aliquot of the supernatant liquid in a tall form beaker with 2 ml. of perchloric acid until nearly dry.

4. Take up the above residue in hydrochloric acid diluted to standard volume and analyse for iron.

II. Reagents

1. Potassium Dicromate Solution: dry potassium chromate at 120°C. and cool in a dessicator, dissolve 4.904 gm. in water and dilute to 1 litre.
2. Barium Diphenylamine Sulphate: 0.16% solution (aqueous)
3. Orthophospheric Acid: concentrated
4. Tin (II) Chloride Solution: 12 gm. pure tin dissolved in 100 ml. concentrated hydrochloric acid and diluted to 200 ml.
5. Mercury (II) Chloride Solution: saturated

Procedure

1. Iron must be in divalent state -- use a Jones reductor

or tin II chloride solution.

2. Take 25 ml. aliquot of the test solution--containing approximately 0.1 gm. of iron--and make about 5 molar with respect to hydrochloric acid; heat to 70 to 90°C.

3. Add tin chloride from a burrette, stirring until the yellow colour has almost disappeared.

4. Then, add dilute tin chloride solution (1 volume tin chloride solution to 5 volume of 5 M hydrochloric acid) dropwise with shaking until the solution becomes faintly green.

5. Protect the solution from the atmosphere and cool rapidly to 20°C. Then add 10 ml. of mercury (II) chloride solution; a slightly white precipitate should form. If the colour is dark or heavy, then the experiment must be discarded and started over.

6. Allow the reduced solution to stand for 5 minutes. Then, dilute with 200 ml. of water containing 5 ml. of hydrochloric acid.

7. Add 5 ml. of phospheric acid and 0.5 ml. barium diphenylamine solution to the above solution.

8. Titrate the solution with potassium dicromate to a permanent violet-blue endpoint.

Calculations

1. 1 ml. of M/60 $k_2Cr_2 0_2$ = 0.005585 gm. Fe
2. Fe x 1.14 = Fe 0 (pct)

5. Cation Exchange Capacity

Reagents

1. Ammonia Acetate: 68 ml. ammonium hydroxide and 57 ml. acetic acid to 1 litre of water. Adjust to pH 7.0 with ammonium hydroxide or acetic acid.
2. Boric Acid: 4% solution. Dissolve 40 gm. of boric acid in 1 litre of distilled water.
3. Sodium Hydroxide: 1 N. Dissolve 50 gm. sodium hydroxide in 1 litre of distilled water.
4. Hydrochloric Acid: 0.2 N. Dissolve 36.5 ml. of hydrochloric acid in 1 litre of distilled water.
5. Mixed indicator: Mix 1.250 gm. methyl red and 0.825 gm. methylene blue in 1 litre of 95% ethanol.
6. Brom Cresol Green: (0.1%) Mix 0.1 gm. brom cresol green in 100 ml. of distilled water.

Procedure

1. Weigh 25 gm. air dry less than 2 mm. soil into a 250 ml. erlenmeyer flask and add 50 ml. ammonia acetate solution. Stopper, shake the flask, and allow to stand overnight.

2. Transfer the contents of the flask to a buchner funnel fitted with No. 42 moist filter paper. Filter, using gentle suction. Leach with 200 ml. ammonia acetate, adding small amounts at a time.

3. Gradually leach the ammonia-saturated soil remaining on the buchner funnel with 100 ml. 95% ethanol.

4. Transfer the ammonia-saturated soil on the filter paper to a kjeldahl flask. Add 200 ml. of distilled water, 25 ml. of sodium hydroxide, and a zinc granule to the flask. Spray anti-foam on the surface.

5. Connect the flask with the condensor and distill 20 drops into a 50 ml. of boric acid solution. The solution in the kjeldahl flask should boil for 20 minutes.

6. Add 10 drops of mixed indicator and 2 drops of brom cresol green to the distillate.

7. Titrate the distillate with 0.2 N hydrochloric acid with swirling to the first tinge of purple.

Calculations

1. $\text{C.E.C. (meq/100 gm.)} = \frac{\text{ml. HCl}}{\text{gm. sample}} \times \text{N of Acid} \times 100$

APPENDIX B

SOIL SAMPLE PROFILE DESCRIPTIONS AND DATA SUMMARIES

TABLE B-1	EXTRACTION OF FREE IRON OXIDES EMPLOYING DIFFERENT METHODS AND MULTIPLE EXTRACTION
TABLE B-2	SOIL ANALYSIS PERFORMED ON SOIL SAMPLES AFTER EXTRACTION BY THE ABOVE TECHNIQUES
TABLE B-3	TIME NECESSARY FOR MAXIMUM EXTRACTION EMPLOYING DIFFERENT EXTRACTION TECHNIQUES
TABLE B-4	SOIL SAMPLE PROFILE DESCRIPTIONS

TABLE B-1

Extraction of free iron oxides from arctic soil samples by different methods, with each method performed twice on each sample of soil. Data given in % Fe_2O_3 present.

SAMPLE NUMBER	DEB		KILMER		MEHRA AND JACKSON		COFFIN	
	A	B	A	B	A	B	A	B
1.	.572	.017	.312	.004	.321	.121	.574	.001
2.	.872	.020	1.181	.021	.568	.338	1.021	.004
3.	.500	.006	.550	.007	.075	.487	.560	.002
4.	.486	.001	1.100	.031	.193	.634	.701	.009
5.	.614	.004	.553	.021	.371	.248	.617	.004
6.	.614	.006	.390	.003	.380	.084	.409	.008
7.	.715	.021	.471	.002	.403	.307	.713	.010
8.	.943	.005	.790	.028	.750	.193	.972	.001
9.	.572	.021	.712	.036	.307	.334	.715	.005
10.	.572	.007	.550	.024	.204	.284	.528	.003

A is the first extraction on a measured soil sample.

B is the second extraction performed on the same soil sample.

TABLE B-2

Soil analysis performed on soil samples after extraction by free iron oxide extractive techniques.

Profile Number	pH of Soil Before Fe_2O_3 Extraction Techniques	pH of Soil After Deb's Method	pH of Soil After Kilmer's Method	pH of Soil After Mehra and Jackson's Method	pH of Soil After Coffin's Method	C.E.C.
1.	4.305	4.278	4.005	4.125	4.300	.240
2.	4.516	4.500	4.510	4.504	4.508	.160
3.	4.820	4.615	4.325	4.718	4.816	.420
4.	4.325	4.015	4.289	4.295	4.323	.185
5.	4.135	3.955	4.032	3.984	4.130	.624
6.	4.404	4.201	4.001	4.395	4.402	.301
7.	4.086	3.099	4.070	3.970	4.078	.180
8.	4.155	4.005	3.878	4.015	4.147	.640
9.	4.486	4.284	4.315	4.378	4.480	.360
10.	4.343	4.108	4.217	4.297	4.339	.120

TABLE B-3

The amount of time needed for each extractive procedure to achieve maximum free iron oxide percentages.

SAMPLE NUMBER	DEB'S METHOD			KILMER'S METHOD			MEHRA AND JACKSON'S METHOD			COFFIN'S METHOD		
	A	B	C	A	B	C	A	B	C	A	B	C
1.	.572	.574	.575	.300	.312	.313	.305	.321	.323	.574	.575	.575
2.	.572	.584	.584	1.012	1.181	1.182	.542	.568	.569	1.021	1.023	1.024
3.	.500	.532	.532	.432	.550	.550	.064	.075	.075	.560	.560	.560
4.	.486	.484	.485	.989	1.100	1.100	.093	.193	.193	.701	.702	.702
5.	.614	.628	.630	.359	.553	.556	.273	.371	.373	.617	.617	.618
6.	.614	.632	.632	.285	.390	.390	.281	.380	.380	.409	.409	.409
7.	.715	.725	.725	.378	.471	.476	.304	.403	.403	.713	.717	.718
8.	.903	.913	.913	.651	.790	.790	.648	.750	.752	.972	.975	.975
9.	.572	.582	.583	.595	.712	.712	.208	.307	.308	.715	.718	.718
10.	.572	.574	.574	.403	.550	.551	.158	.204	.204	.528	.530	.530

The above data is from the first extraction on a soil sample, with A representing 30 minutes, B representing 60 minutes, and C representing 16 hours.

TABLE B-4

Soil profile descriptions for soil samples employed in the study.

SOIL SAMPLE	HORIZON	DEPTH	SOIL PROPERTIES
1(J78817)	L	9 - 7 cm.	Surface composed of a vegetational cover of lichen, scattered birch trees, and clumps of labrador tea, blueberries, on a 3 slope at the foot of a drumlin.
	F	7 - 4 cm.	Many fine roots; very fibrous. Penetration force 0.0
	H	4 - 0 cm.	Coarse, granular soil with medium fine roots running through it. Penetration force 0.3
	Ae	0 - 8 cm.	Colour of soil 7.5 Y.R. 6/2, medium-sized grains of grey to dark grey soil. Few fine roots and an undulating boundary; penetration force 0.8
	Bh	8 - 10 cm.	Colour of soil 10 Y.R. 3/4, dark brown sandy loam. Frequent fine roots and some clay present; penetration force 0.5
"Sampling horizon" No. 10	Bfe	10 - 20 cm.	Colour of Soil 5 Y.R. 3/3, dark red brown sandy soil. Clay is present; penetration force 1.3
"Sampling horizon" No. 1	Bfe	20 - 25 cm.	Colour of Soil 5 Y.R. 5/6, gravelly sandy loam; penetration force 1.1

SOIL SAMPLE	HORIZON	DEPTH	SOIL PROPERTIES
	B_3	25 - 36 cm.	Colour of Soil 10 Y.R. 5/6, fine sandy soil. Moist horizon with few roots and some nodules present. Penetration force 1.1
	C	36 - 46 cm.	Bedded fine gravels and coarse gravels below 50 cm. Penetration force 1.0 - 1.3
2(J79518)	L	7.5 - 5 cm.	Vegetational cover of spruce trees up to 25 feet, with a floor cover of lichen, moss, and labrador tea.
	F	5.0 - 2.5 cm.	Many roots present.
	H	2.5 - 0.0 cm.	
	Ae	0.0 - 3.75 cm.	Distinct boundary layer composed of a grey gravelly deposit with some organic fragments and few roots.
	Bf	3.75 - 6.0 cm.	Medium red/brown sandy soil with a diffuse boundary layer.
"Sampling horizon"	Bfe	6 - 12 cm.	Dark red brown mottled soil with a wavy boundary layer.
	Bf_1	12 - 32.5 cm.	Distinct boundary layer with a light yellow red brown soil with distinct mottles and concretions.
	C	32.5 +	Moist light grey coarse gravelly soil.
3(J79371)	L	12 - 8 cm.	Vegetational cover of moss, lichen and spruce trees of 10 - 15 feet in height.

SOIL SAMPLE	HORIZON	DEPTH	SOIL PROPERTIES
	F	8 - 6 cm.	Many fine roots, horizon colour being dark brown.
	H	6 - 0 cm.	Soil colour dark brown to black with fine roots and charcoal fragments.
	Ae	0 - 11 cm.	Loose medium-coarse gravelly soil with frequent mottles of iron and organic matter. The colour is dominantly light grey.
	B_1	11 - 32 cm.	Light brown in colour with an undulating boundary layer.
"Sampling horizon"	Bfe	32 - 40 cm.	A yellow brown horizon with a loose sand gravel texture.
4(J07124)	Ah	0 - 2 cm.	Vegetational cover of lichen, labrador tea, blueberries, and spruce (20 feet). Soil is black sandy muck.
	Ae	0 - 12 cm.	Dark grey mud with an undulating boundary layer.
	Bf_1	12 - 55 cm.	Yellow brown soil, medium fine texture.
"Sampling horizon"	Bf_2	55 - 65 cm.	Deep red yellow pocket of medium fine sandy soil.
	C	65 + cm.	Soil colour is yellow grey with a sandy texture.
5(J09328)	L	4 - 2 cm.	Vegetational cover of spruce (10 to 20 feet), labrador tea, lichen on a 10 north slope.
	H	2 - 0 cm.	Black coloured soil with many lateral roots.

SOIL SAMPLE	HORIZON	DEPTH	SOIL PROPERTIES
	Ah	0 - 1.5 cm.	Very dark brown fine-grained sandy loam, with a diffuse boundary layer.
	Ae	1.5 - 12.5 cm.	Light grey fine sandy loam, with some roots present.
	Bf_1	12.5 - 30 cm.	Orange brown fine gravelly soil with some roots and a diffuse boundary layer.
"Sampling horizon"	Bf_2	30 - 40 cm.	Dark yellow brown fine sandy soil.
	CB	40 - 44.5 cm.	Yellow grey brown transitional horizon with vughs (1 cm.) and stones (10 to 12 cm.) present
	C	44.5 + cm.	Yellow grey gravelly soil.
6(J47991)	L	7 - 6 cm.	Vegetational cover of spruce (15 to 20 feet), labrador tea, and white and yellow lichen in a flat area with several rock outcrops.
	F	6 - 4.5 cm.	
	H	4.5 - 0 cm.	Very friable soil with many fine roots present.
	Ae	0 - 7 cm.	Light grey slightly clay-dominated horizon, with fine roots and an irregular boundary layer.
	Bfe	7 - 12 cm.	Dark red brown soil with a loose sandy (fine) composition.
	Bfe_2	12 - 19 cm.	Light brown fine sandy loam with some roots present.
	B_2g	19 - 36 cm.	Dominantly a fine sand with quartz, gravel and mica flecks present. Root channels have an iron coating.

SOIL SAMPLE	HORIZON	DEPTH	SOIL PROPERTIES
	B	36 - 44 cm.	Similar to B g.
	BC	44 - 48 cm.	
	C	48 + cm.	
7(J10105)	L	6 - 5 cm.	Vegetational cover of labrador tea, grass, moss, some lichen, and spruce trees (3 to 10 feet). 20 paces from the edge of a recent burn.
	H	5 - 0 cm.	Burnt, charred horizon with few root ends and a very straight boundary layer.
	Ae	0 - 5 cm.	Light grey soil with a slightly irregular boundary.
	B_1	5 - 8 cm.	Light yellow brown soil with a straight boundary.
"Sampling horizon"	Bfe	8 - 10 cm.	Dark red brown fine-grained sandy soil with roots and humus-lined channels.
	B_2	10 - 13 cm.	Light yellow brown coarse sand with some gravel present.
	B_3	13 - 21 cm.	Pale yellow brown coarse sandy loam with some mottling present.
	C_1	21 - 30 cm.	Yellow grey sandy loam with some gravel and clay present.
	C_2	30 + cm.	Pale yellow grey gravelly soil with granite fragments present.
8(J20715)	L	5.5 - 3.5 cm.	Vegetational cover of lichen, labrador tea, and spruce (20 to 40 feet) on a slope of 5 in a boulder-strewn area near the edge of a burn.
	H	3.5 - 0 cm.	Very wavy boundary layer.

SOIL SAMPLE	HORIZON	DEPTH	SOIL PROPERTIES
	Ae	0 - 6 cm.	Light grey gravelly soil with a straight boundary layer.
	B_1	6 - 11 cm.	Yellow brown soil with a gravelly texture, root channels and a diffuse boundary layer.
	Bfe	12 - 18 cm.	Dark red brown soil with many medium to fine roots and a diffuse boundary layer.
	B_3	18 - 29 cm.	Pale yellow brown fine sandy loam.
	C	29 + cm.	Yellow grey gravelly soil.
9(J47149)	L	6.25 - 3.75 cm.	Vegetational cover of moss, lichen, labrador tea, blueberries, and spruce (5 to 10 feet). On a down slope area of 5 with frequent boulders and burn debris.
	H	3.75 - 0 cm.	A few fine roots and charcoal fragments.
	Ae	0 - 12 cm.	Light grey gravelly soil with an undulating boundary layer, tonguing into the Bf . Some flakes of organic matter present.
	Bf_1	12 - 30 cm.	Medium yellow red to dark red mottled gravelly soil with an undulating boundary layer.
"Sampling horizon"	Bf_2	30 - 38 cm.	A wavy mottled yellow-red band of sandy material with some organic matter.
	C	37.5 + cm.	Light grey coarse sandy soil with some rocks present.
10(J63471)			Same soil profile as sample number one expert experiments performed on Bfe horizon, 10 to 20 cm. depth.

APPENDIX C

MULTIPLE REGRESSION

AND

FACTOR ANALYSIS SUMMARIES

KEY TO VARIABLE LABELS EMPLOYED IN COMPUTER PROGRAMMES

DEB 1 - Percent Iron Extracted by Deb's Procedure first extraction.

DEB 2 - Percent Iron Extracted by Deb's Procedure second extraction.

DEB - Percent Iron Extracted by the Summation of the first and second extractions employing Deb's procedure.

KIL 1 - Percent Iron Extracted by Kilmer's Procedure first extraction.

KIL 2 - Percent Iron Extracted by Kilmer's Procedure second extraction.

KIL - Percent Iron Extracted by the Summation of the first and second extractions employing Kilmer's procedure.

MJ1 - Percent Iron Extracted by Mehra and Jackson's procedure first extraction.

MJ2 - Percent Iron Extracted by Mehra and Jackson's procedure second extraction.

MJ - Percent Iron Extracted by the Summation of the first and second extractions employing Mehra and Jackson's procedure.

COF 1 - Percent Iron Extracted by Coffin's procedure first extraction.

COF 2 - Percent Iron Extracted by Coffin's procedure second extraction.

COF - Percent Iron Extracted by the Summation of the first and second extractions employing Coffin's procedure.

PH - Initial pH of the Soil prior to Iron Extraction.

DEBPH - pH of the Soil after Deb's Extraction procedure.

KILPH - pH of the Soil after Kilmer's Extraction procedure.

MJPH - pH of the Soil after Mehra and Jackson's Extraction procedure.

COFPH - pH of the Soil after Coffin's Extraction procedure.

CEC - Cation Exchange Capacity of the Soil Sample.

DEPTU - Upper limit of soil horizon in centimeters.

DEPTL - Lower limit of soil horizon in centimeters.

DEBT1 - Deb's Procedure, Iron Removed in 30 minutes.

DEBT2 - Deb's Procedure, Iron Removed in 60 minutes.

DEBT3 - Deb's Procedure, Iron Removed in 16 hours.

KILT1 - Kilmer's Procedure, Iron Removed in 30 minutes.

KILT2 - Kilmer's Procedure, Iron Removed in 60 minutes.

KILT3 - Kilmer's Procedure, Iron Removed in 16 hours.

MJT1 - Mehra and Jackson's Procedure, Iron Removed in 30 minutes.

MJT2 - Mehra and Jackson's Procedure, Iron Removed in 60 minutes.

MJT3 - Mehra and Jackson's Procedure, Iron Removed in 16 hours.

COFT1 - Coffin's Procedure, Iron Removed in 30 minutes.

COFT2 - Coffin's Procedure, Iron Removed in 60 minutes.

COFT3 - Coffin's Procedure, Iron Removed in 16 hours.

TABLE C-1

MULTIPLE REGRESSION ANALYSIS OF IRON DATA

	DEB1	DEB2	KIL1	KIL2	MJ1	MJ2	COF1	COF2
DEB2	.22664							
KIL1	.33074	.15819						
KIL2	.08054	-.22339	.63182					
MJ1	.94685	.15343	.25965	.14204				
MJ2	-.35835	.02738	.61153	.35788	-.49024			
COF1	.78844	.36475	.73751	.45580	.71134	.17992		
COF2	-.19860	.27273	.11964	-.17177	-.15101	.28211	-.16308	
PH	-.34920	-.09221	.14188	-.05807	-.49759	.36411	-.15071	-.25360

	DEB1	DEB2	KIL1	KIL2	MJ1	MJ2	COF1	COF2	PH	DEBPH	KILPH	MJPH
DEBPH	-.14971	-.30012	.20923	.22567	-.19253	.06429	-.02297	-.61555	.78538			
KILPH	-.19821	.32049	.61082	.28333	-.37685	.66012	.23227	.09196	.67239	.44307		
MJPH	-.31911	-.06216	.24531	-.03568	-.47136	.39590	-.13958	-.10840	.97246	.75139	.72999	
COFPH	-.35658	-.09802	.13843	-.05997	-.50307	.36365	-.15976	-.24932	.99993	.78595	.66950	.97343
CEC	.25192	-.02797	-.12562	.17237	.35230	-.21889	.14122	-.41558	-.15741	.07929	-.49308	-.27320
DEPTU	-.63013	-.27065	.29488	.42724	-.54473	.72825	-.12733	.13819	.18395	.13785	.24708	.14426
DEPTL	-.63560	-.33726	.31190	.48182	-.55660	.72540	-.13790	.08922	.20009	.19042	.27132	.16662
DEBT2	.78549	-.10038	-.11424	-.02779	.81571	-.50273	.43967	-.16356	-.56409	-.41533	-.66913	-.59199
DEBT3	.78454	-.10156	-.11467	-.02578	.81600	-.50317	.43953	-.16398	-.56673	-.41626	-.67092	-.59512
KILT1	.29818	.24217	.98596	.60303	.23746	.61966	.73068	.13206	.15533	.20890	.60646	.25240
KILT3	.72490	.20583	.40710	.22101	.57932	-.16350	.68760	-.37928	.19320	.29649	.35536	.19847
COFT2	.78897	.36711	.73579	.45573	.71172	.17902	.99998	-.16119	-.15301	-.02682	.23122	-.14187
COFT3	.78923	.36791	.73555	.45480	.71186	.17879	.99998	-.16036	-.15375	-.02791	.23134	-.14254
MJT1	.96440	.21445	.25589	.08535	.97897	-.50345	.73238	-.28327	-.38895	-.07280	-.30399	-.37809
MJT3	.94831	.15281	.25879	.14295	.99999	-.49112	.71127	-.15352	-.49801	-.19144	-.37779	-.47246
DEB	.99918	.26589	.33393	.07043	.94551	-.36344	.79553	-.18523	-.34946	-.16066	-.18285	-.31926
KIL	.32531	.14486	.99950	.65613	.25862	.61005	.73572	.10944	.13575	.21296	.60630	.23834
MJ	.67443	.18741	.62055	.47319	.61883	.38128	.91664	.09408	-.19962	-.14627	.19522	-.14315
COF	.78713	.37038	.74151	.45407	.71064	.18521	.99986	-.14642	-.15544	-.03355	.23445	-.14181

	COFPH	CEC	DEPTJ	DEPTL	DEBT2	DEBT3	KILT1	KILT3	COFT2	COFT3	MJT1	MJT3
EC	-.15878											
EPTU	.18767	.13138										
EPTL	.20396	.14455	.99288									
EBT2	-.56868	.53129	-.52440	-.54283								
EBT3	-.57131	.53424	-.52174	-.54014	.99998							
ILT1	.15199	-.19843	.32217	.32607	-.14522	-.14580						
ILT3	.18437	.15467	-.53012	-.49515	.32649	.32522	.33870					
OFT2	-.16208	.13920	-.12940	-.14015	.44164	.44149	.72916	.68727				
OFT3	-.15283	.13906	-.12997	-.14074	.44156	.44141	.72875	.68767	1.00000			
JT1	-.39533	.29949	-.60017	-.60913	.76240	.76223	.24104	.65285	.73237	.73249		
JT3	-.50350	.35424	-.54356	-.55536	.81549	.81579	.23662	.57916	.71164	.71178	.97915	
EB	-.35700	.22322	-.63494	-.64311	.77327	.77228	.30519	.72603	.79615	.79644	.96344	.94495
IL	.13231	-.11524	.30461	.32341	-.11236	-.11269	.98562	.40541	.73504	.73477	.25263	.25781
J	-.20585	.17040	.07857	.06341	.41210	.41201	.81034	.46711	.91623	.91619	.58462	.61803
OF	-.16445	.13449	-.12530	-.13674	.43804	.43789	.73487	.68294	.99987	.99988	.72947	.71053

	DEB	KIL	MJ
IL	.32800		
J	.67531	.82412	
OF	.79447	.74054	.92068

ABLE C-2 FACTOR ANALYSIS OF IRON DATA

LATION COEFFICIENTS..

CEB1	CEB2	KIL1	KIL2	MJ1	MJ2	COF1	COF2	PH	DEBPH
1.00000	.22664	.33074	.08054	.94885	-.36835	.78844	-.19860	-.34920	-.14971
.22664	1.00000	.15819	-.22339	.15343	.02738	.36475	.27273	-.09221	-.30012
.33074	.15819	1.00000	.63182	.25965	.61153	.73751	.11964	.14188	.20923
.08054	-.22339	.63182	1.00000	.14204	.35788	.45580	-.17177	-.05807	.22567
.94885	.15343	.25965	.14204	1.00000	-.49024	.71134	-.15101	-.49759	-.19253
-.36835	.02738	.61153	.35788	-.49024	1.00000	.17992	.28211	.36411	.06429
.78844	.36475	.73751	.45580	.71134	.17992	1.00000	-.16308	-.15071	-.02297
-.19860	.27273	.11964	-.17177	-.15101	.28211	-.16308	1.00000	-.25360	-.61555
-.34920	-.09221	.14188	-.05807	-.49759	.36411	-.15071	-.25360	1.00000	.78538
-.14971	-.30012	.20923	.22567	-.19253	.06429	-.02297	-.61555	.78538	1.00000
-.19821	.32049	.61082	.28333	-.37685	.66012	.23227	.09196	.67239	.44307
-.31911	-.08216	.24631	-.03568	-.47135	.39590	-.13958	-.10840	.97246	.75139
-.35658	-.09802	.13843	-.05997	-.50307	.36365	-.15976	-.24932	.99993	.78595
.25192	-.62797	-.12562	.17237	.35230	-.21889	.14122	-.41558	-.15741	.07929
-.63013	-.27085	.29488	.42724	-.54473	.72825	-.12733	.13819	.18395	.13785
-.63560	-.33726	.31190	.48182	-.55660	.72540	-.13790	.08922	.20009	.19042
.78549	-.10038	-.11424	-.02779	.81571	-.50273	.43967	-.16356	-.56409	-.41533
.78454	-.10156	-.11467	-.02578	.81600	-.50317	.43953	-.16398	-.56673	-.41626
.29818	.24217	.98696	.60303	.23746	.61966	.73068	.13206	.15533	.20890
.72490	.20583	.40710	.22101	.57932	-.16350	.68760	-.37928	.19320	.29649
.78897	.36711	.73579	.45573	.71172	.17902	.99998	-.16119	-.15301	-.02682
.78923	.36791	.73555	.45480	.71186	.17879	.99998	-.16036	-.15375	-.02791
.96440	.21445	.25589	.08535	.97897	-.50345	.73238	-.28327	-.38895	-.07281
.94831	.15281	.25879	.14295	.99999	-.49112	.71127	-.15352	-.49801	-.19144
.99918	.26589	.33393	.07043	.94551	-.36344	.79553	-.18523	-.34946	-.16066
.32531	.14486	.99950	.65613	.25862	.61005	.73672	.10944	.13575	.21296
.67443	.18741	.82655	.47319	.61883	.38128	.91664	.09408	-.19962	-.14627
.78713	.37038	.74151	.45407	.71064	.18522	.99986	-.14642	-.15544	-.03355

KILPH	MJPH	COFPH	CEC	DEPTU	DEPTL	DEBT2	DEBT3	KILT1	KILT3
-.19821	-.31911	-.35658	.25192	-.63013	-.63560	.78549	.78454	.29818	.72490
.32049	-.08216	-.09802	-.62797	-.27085	-.33726	-.10038	-.10156	.24217	.20583
.61082	.24631	.13843	-.12562	.29488	.31190	-.11424	-.11467	.98696	.40710
.28333	-.03568	-.05997	.17237	.42724	.48182	-.02779	-.02578	.60303	.22101
-.37685	-.47135	-.50307	.35230	-.54473	-.55660	.81571	.81600	.23746	.57932
.66012	.39590	.36365	-.21889	.72825	.72540	-.50273	-.50317	.61966	-.16350
.23227	-.13958	-.15976	.14122	-.12733	-.13790	.43967	.43953	.73068	.68760
.09196	-.10840	-.24932	-.41558	.13819	.08922	-.16356	-.16398	.13206	-.37928
.67239	.97246	.99993	-.15741	.18395	.20009	-.56409	-.56673	.15533	.19320
.44307	.75139	.78595	.07929	.13785	.19042	-.41533	-.41626	.20890	.29649

KILPH	MJPH	COFPH	CEC	DEPTU	DEPTL	DEBT2	DEBT3	KILT1	KILT3
1.00000	.72999	.66950	-.49308	.24708	.27132	-.66913	-.67092	.60646	.35536
.72999	1.00000	.97343	-.27320	.14426	.16662	-.59199	-.59512	.25240	.19848
.66950	.97343	1.00000	-.15878	.18767	.20398	-.56868	-.57131	.15199	.18437
-.49308	-.27320	-.15878	1.00000	.13138	.14455	.53129	.53424	-.19843	.15487
.24708	.14426	.18767	.13138	1.00000	.99288	-.52440	-.52174	.32217	-.53012
.27132	.16662	.20398	.14455	.99288	1.00000	-.54283	-.54014	.32607	-.49515
-.66913	-.59199	-.56868	.53129	-.52440	-.54283	1.00000	.99998	-.14522	.32649
-.67092	-.59512	-.57131	.53424	-.52174	-.54014	.99998	1.00000	-.14580	.32522
.60646	.25240	.15199	-.19843	.32217	.32607	-.14522	-.14580	1.00000	.33870
.35536	.19848	.18437	.15487	-.53012	-.49515	.32649	.32522	.33870	1.00000
.23122	-.14187	-.16208	.13920	-.12940	-.14015	.44164	.44149	.72916	.68727
.23134	-.14254	-.16283	.13906	-.12997	-.14074	.44156	.44141	.72875	.68767
-.30399	-.37809	-.39533	.29949	-.60017	-.60913	.76240	.76223	.24104	.65285
-.37779	-.47246	-.50350	.35425	-.54356	-.55535	.81549	.81579	.23662	.57916
-.19285	-.31926	-.35700	.22322	-.63494	-.64311	.77327	.77228	.30519	.72603
.60630	.23834	.13231	-.11524	.30461	.32341	-.11236	-.11269	.98562	.40541
.19522	-.14315	-.20585	.17640	.07857	.06341	.41210	.41201	.81034	.46711
.23445	-.14181	-.16445	.13449	-.12530	-.13674	.43804	.43789	.73487	.68294

COFT2	COFT3	MJT1	MJT3	CEB	KIL	MJ	COF
.78897	.78923	.96440	.94831	.99918	.32531	.67443	.78713
.36711	.36791	.21445	.15281	.26589	.14486	.18741	.37038
.73579	.73555	.25589	.25879	.33393	.99950	.82655	.74151
.45573	.45480	.08535	.14295	.07043	.65613	.47319	.45407
.71172	.71186	.97897	.99999	.94551	.25862	.61883	.71064
.17902	.17879	-.50345	-.49112	-.36344	.61005	.38128	.18522
.99998	.99998	.73238	.71127	.79553	.73672	.91664	.99986
-.16119	-.16036	-.28327	-.15352	-.18523	.10944	.09408	-.14642
-.15301	-.15375	-.38895	-.49801	-.34946	.13575	-.19962	-.15544
-.02682	-.02791	-.07281	-.19144	-.16066	.21296	-.14627	-.03355
.23122	.23134	-.30399	-.37779	-.19285	.60630	.19522	.23445
-.14187	-.14254	-.37809	-.47246	-.31926	.23834	-.14315	-.14181
-.16208	-.16283	-.39533	-.50350	-.35700	.13231	-.20585	-.16445
.13920	.13906	.29949	.35425	.22322	-.11524	.17640	.13449
-.12940	-.12997	-.60017	-.54356	-.63494	.30461	.07857	-.12530
-.14015	-.14074	-.60913	-.55536	-.64311	.32341	.06341	-.13674
.44164	.44156	.76240	.81549	.77327	-.11236	.41210	.43804
.44149	.44141	.76223	.81579	.77228	-.11269	.41201	.43789
.72916	.72875	.24104	.23662	.30519	.98562	.81034	.73487
.68727	.68767	.65285	.57916	.72603	.40541	.46711	.68294
1.00000	1.00000	.73237	.71164	.79615	.73504	.91623	.99987
1.00000	1.00000	.73249	.71178	.79444	.73477	.91619	.99988
.73237	.73249	1.00000	.97915	.96344	.25263	.58462	.72947

TABLE C-3

OBLIQUE FACTOR STRUCTURE MATRIX AFTER ROTATION WITH KAISER NORMALIZATION

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
DEB1	.96811	.34213	- .27900	.11243
DEB2	.24848	.15692	- .08746	- .66684
KIL1	.14234	.95968	.19268	- .16295
KIL2	- .03479	.67410	.04636	.29540
MJ1	.91429	.29332	- .42692	.24193
MJ2	- .52191	.61143	.27754	- .23753
COF1	.67217	.81046	- .09747	.00343
COF2	- .26306	.03708	- .31143	- .48071
PH	- .27527	.03576	.97677	- .09280
DEBPH	- .08258	.10809	.85188	.26491
KILPH	- .22712	.49123	.68102	- .50767
MJPH	- .26715	.08833	.95223	- .20862
COFPH	- .28011	.03085	.97627	- .09189
CEC	.21546	.02681	- .16775	.81588
DEPTU	- .77477	.40077	.10547	.21266
DEPTL	- .78064	.40626	.14560	.25416
DEBT2	.76661	- .00351	- .58264	.45378
DEBT3	.76534	- .00298	- .58499	.45656
KILT1	.11748	.95133	.18991	- .22129
KILT3	.73297	.36897	.29018	.01632
COFT2	.67302	.80924	- .10023	.00117
COFT3	.67329	.80894	- .10091	.00019
MJT1	.95402	.27500	- .29747	.20289
MJT3	.91396	.29310	- .42693	.24426
DEB	.96955	.34505	- .28067	.07569
KIL	.13655	.96349	.18940	- .14437
MJ	.47839	.87888	- .20157	.03140
COF	.66888	.81345	- .10448	- .00736

DELTA = 0.000

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