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Calcium ion activity in soil solutions as determined by three analytical methods

by

Gerald W. Lutwick

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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(SIGNED) Gerald Lutwick

PERMANENT ADDRESS:

1906 - 25 Avenue North

LETHBRIDGE, Alberta

T1H 4V4

DATED Sept. 16 1986

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Calcium ion activity in soil solutions as determined by three analytical methods submitted by Gerald W. Lutwick in partial fulfilment of the requirements for the degree of Master of Science in Soil Chemistry.

G.R. Webster

Supervisor

W.J. Rendall

Byron Kotchorek

Craig J. Lake

Date Sept 16, 1986

ABSTRACT

Three methods for determining calcium ion activity, (Ca^{+2}), were compared with respect to the agreement among the three (Ca^{+2}) estimates. Calcium activity in 37 soil solutions was determined using species calculation, potentiometric, and colourimetric methods.

The species calculation method used a computer program to determine the distribution of aqueous species in an electolyte solution of known total ionic composition. Thirty-six ion pairs were considered in the calculation. These ion pairs are reported in the literature to be representative of the major ion pairs which form in natural waters and soil solutions between the cations Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, H^{+}, Al^{+3}, Mn^{+2}, and Fe^{+3} and the anions SO_4^{-2}, CO_3^{-2}, HCO_3^{-}, OH^{-}, NO_3^{-}, Cl^{-}, $H_2PO_4^{-}$, and HPO_4^{-2}. The calculation determines the concentration, activity coefficient, and activity of each of the 52 aqueous species considered.

The potentiometric method used an Orion calcium ion-selective electrode to determine (Ca^{+2}). No attempt was made to control ionic strength in either standard or soil solutions. Calibration was in terms of EMF as a function of (Ca^{+2}). For the purpose of electrode calibration, calcium ion activity was calculated using the species calculation method to distribute the aqueous species in $CaCl_2$ solutions of known total ionic composition.

The colourimetric method used the dye tetramethylmurexide. This dye complexes selectively with

calcium to form a coloured complex. The degree of formation of this complex was measured using a dual-wavelength technique. Sodium ion also forms a coloured complex with this dye and, so, interferes with (Ca^{+2}) determination. Therefore, the presence of sodium in solution must be accounted for.

Agreement of (Ca^{+2}) estimations was tested by comparing each of the potentiometric and colourimetric methods to the species calculation method. Good agreement was observed between (Ca^{+2}) estimates using the potentiometric and species calculation methods. Percent relative error was less than 5% for 54% of the soil extracts and 81% of the (Ca^{+2}) estimates agreed to less than 10% relative error. The majority of the differences are thought to be related to the presence of H^+, Na^+, K^+, and Mg^{+2} in solution and to errors in estimating activity coefficients at high ionic strength. The colourimetric and species calculation methods agreed poorly in their estimates of (Ca^{+2}) in soil solutions. Less than 50% of the estimates agreed to less than 15% relative error; about 10% of the estimates differed by 50 to 70% relative error.

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I. INTRODUCTION

This study was initiated because of recent efforts by soil chemists to express the chemical character of soil solutions on the basis of chemical thermodynamics. Thus, it is increasingly popular to express the amount of an ion in solution in terms of its activity instead of its concentration. For example, soil fertility specialists express soil calcium deficiency for a given plant as a minimum value of the ratio of calcium ion activity to the sum of the activities of all cations in solution (Khasawneh, 1971; Beckett, 1972; Adams, 1974; Sparks, 1984). Land reclamation efforts and irrigation water recommendations require a knowledge of the ion exchange properties of soils. The sodium adsorption ratio(SAR) of a soil solution in equilibrium with soil solids can be used to indicate the need of amendments such as gypsum or lime which should be added to sodic soils to increase agricultural productivity, or as an indication of the sodium hazard of an irrigation water. Recent indications are that the calculation of SAR should use ion activities rather than the historically popular use of ion concentrations(Sposito and Mattigod, 1977; Bresler *et al*, 1982). In the course of calculating activity, appropriate corrections are made to free ion concentration and ionic strength because of ion pairing; these corrections affect the value of calculated SAR(Alzubaidi and Webster, 1983). Mineral weathering and surface properties studies also require a knowledge of ion

activity (Kittrick, 1971; Sposito, 1984).

Two common methods for determining calcium ion activity use species calculation and ion-selective electrodes. The more popular approach has been the calculation of the distribution of aqueous species in a solution of known total ionic composition. The species calculation method uses successive approximation to solve a set of simultaneous equations. Each of these equations is constrained by, and the solution of the set of equations must satisfy, two conditions: 1)the total concentration of an ionic species is the sum total of all aqueous species containing the ionic species(mass balance), and 2)the contribution of each species to the total concentration of an ionic species is governed by a mass action equation. Ion selective electrodes are available which respond to calcium ion activity. These electrodes have been used by soil chemists infrequently, and the usual measurement is of calcium ion concentration in a solution of known ionic strength. For example, exchangeable calcium has been determined from a measurement of calcium concentration in a 1 M ammonium acetate extract(Woolson *et al*, 1970).

An alternative method for detecting free calcium is a colourimetric method based on the absorbance of the complex calcium-tetramethylmurexide(Ca-TMM). It has been used to measure free calcium ion concentration in biological fluids and might be adapted to measure calcium ion activity in soil solutions.

Objectives of this study are:

1) to use a species calculation method to calculate calcium ion activity in soil solutions of known total ionic composition,
2) to use a calcium ion-selective electrode to measure calcium ion activity in soil solutions,
3) to adapt a colourimetric method to the measurement of calcium ion activity in soil solutions, and
4) to compare the results of the three methods for agreement with respect to the measures of calcium ion activity in soil solutions.

II. LITERATURE REVIEW

Calcium in soil solutions has been most commonly studied using species calculation and potentiometric methods.

Species calculation methods are used to describe the distribution of species in electroyte solutions. Nordstrom *et al* (1979) have published a review of the popular methods which have been used to perform these calculations.

Potentiometric methods have used an ion-selective electrode to measure ionic calcium concentration by comparing EMF in prepared solutions against EMF in standard solutions (Fertl and Jessen, 1969; Woolson *et al*, 1970; Cheng *et al*, 1973) or to indicate the endpoint of a complexometric titration (Tackett, 1969; Hulanicki and Trojanowicz, 1973). Two papers were published in 1969 describing ion exchange on clays (McLean and Snyder, 1969) and plant uptake of calcium (McLean *et al*, 1969). In these papers, a Ca ion-selective electrode was used and (Ca^{+2}) was determined by comparing EMF in prepared solutions against EMF in standard solutions. No attempt was made to control ionic strength. Electrode calibration used $CaCl_2$ solutions; no mention is made of correcting for the formation of the $CaCl^+$ ion pair.

The following discussion indicates some of the attempts to use species calculation and potentiometric methods for the measurement of (Ca^{+2}). When important, mention is made of how techniques are used and what assumptions have been

made in this study.

A. Species calculation methods

Ion activities can be found directly if the free ion concentrations and respective activity coefficients are known. This information can be gained by calculating the distribution of aqueous species in an electrolyte solution. Aqueous species considered by such a calculation must include simple ions and those species which exist because of the association of two or more simple ions(ion pairs). The coexistence of ions and ion pairs is accommodated in such calculations by consideration of mass balance and chemical equilibrium. Thus, the distribution of aqueous species in an electrolyte solution is a description of the most thermodynamically stable arrangement of the dissolved components in an aqueous system of known total ionic composition.

The major ions existing in soil solutions represent very complex systems in terms of the large number of ion pairs that are considered to coexist with the major simple ions. Describing the equilibrium state of the dozens of ion pair formations in natural waters and soil solutions invariably uses computer-assisted calculations. WATEQ(Truesdell and Jones, 1974), SOLMNEQ(Kharaka and Barnes, 1973), and GEOCHEM(Mattigod and Sposito, 1978) are the names of some computer programs which have been used to calculate the distribution of aqueous species in such

solutions. The properties and abilities of these three programs are representive of the many computer programs which have been used for similar purposes. The differences among the programs represent the different preferences of the authors and suitability to different applications(Nordstrom *et al*,1979; Baham,1984).

The calculation performed by each of these programs is iterative and ends when some condition has been achieved(usually when a certain ion concentration changes, over an iteration, by less than a predetermined amount). The information then available includes the concentration, activity coefficient, and activity of each aqueous species considered by the program. The main limitations of species calculation methods are: 1)the number of aqueous species considered(some important species may be neglected), and 2)the quality of the data used to determine ion pair formation constants(Amacher,1984).

GEOCHEM uses the Davies equation to calculate activity coefficients in solutions up to ionic strength=0.5(Mattigod and Sposito,1978). When ionic strength is greater than 0.5, GEOCHEM, WATEQ(Truesdell and Jones,1974), and SOLMNEQ(Kharaka and Barnes,1973) use a modified Stokes-Robinson equation. This modified Stokes-Robinson equation combines the extended Debye-Huckel equation and the MacInnes assumption, as proposed by Helgeson(1969):

$$-\log \gamma = \frac{Az^2 I^{1/2}}{1+BaI^{1/2}} - bI$$

where: γ is a single-ion activity coefficient
A and B are Debye-Huckel parameters
z is the charge on the ion
I is ionic strength
a is an ion size parameter found empirically using mean salt activity coefficients.
b is a curve-fitting parameter found empirically; it is $0.3Az^2$ when I is less than 0.5, and is 0.1 for neutral species

MacInnes(1939) assumed, for the purpose of calculating single-ion activity coefficients from mean salt activity coefficients($\gamma_\pm$), that $\gamma_{K^+} = \gamma_{Cl^-} = \gamma_{\pm,KCl}$. Generally, $\gamma_+\gamma_- = \gamma_\pm^2$;

$$\gamma_{Na^+} = \frac{\gamma^2_{\pm,NaCl}}{\gamma_{\pm,KCl}}, \text{and}$$

$$\gamma_{Ca^{+2}} = \frac{\gamma^3_{\pm,CaCl_2}}{\gamma^2_{\pm,KCl}}.$$

The assumption allows accurate calculation of activity coefficients as long as the salts used for comparison(e.g. NaCl and $CaCl_2$ above) do not form ion pairs. The ion-pair $CaCl^+$ is in fact considered to form, and this modified Stokes-Robinson equation may give erroneous values for the activity coefficient of calcium.

The Davies equation is a simplification of this Stokes-Robinson equation using Ba=1 and $b=0.3Az^2$ (Davies, 1962):

$$-\log \gamma = Az^2\left(\frac{I^{1/2}}{1+I^{1/2}} - 0.3I\right)$$

The value of B is a function of the dependence on

temperature of the dielectric constant of water; at 25°C, B=0.33. Davies considers the "distance of closest approach", a, to be approximately 3 Angstroms. Therefore, the value of Ba is near 1, and good estimates of single-ion activity coefficients are given if $b=0.3Az^2$. Significant errors in estimating activity coefficients might be made for large ions such as Mg^{+2}, Al^{+3}, and Fe^{+3} (i.e. when a is greater than 3).

This study uses the Davies equation regardless of the magnitude of the ionic strength. It is considered that comparing the calcium ion activity of two solutions, one of ionic strength slightly less than 0.5 and one slightly greater than 0.5, is inappropriate. An apparent difference in (Ca^{+2}) may be the result of using different equations to calculate the activity coefficient rather than a genuine difference in (Ca^{+2}). Another advantage of using the Davies equation rather than the Debye-Huckel equation is the absence of an ion size parameter. This omission allows easy algebraic elimination of variables in derivation of expressions for (Ca^{+2}).

Stability constants are used in one of two ways; the choice seems to depend on the author's preference rather than on relative ease of programming or speed of calculation execution. GEOCHEM calculates conditional stability constants based on estimates of activity coefficients; the concentrations of aqueous species are then calculated directly. WATEQ and SOLMNEQ use thermodynamic stability

constants. Ion activities are calculated and then concentrations are found using estimates of activity coefficients. The program used in this study is the same as WATEQ and SOLMNEQ in its use of stability constants.

The number of mass action considerations included in each mass balance depends on the complexity of the system being described. The simplest system is one in which only one electrochemical association is considered. Examples of such a system include: 1)an incompletely dissociated salt, and 2)a completely dissociated salt in ion exchange equilibrium with a clay suspension. The system becomes more complex when other effects are included, such as redox reactions, precipitation, dissolution, adsorption, and coexistence of many salts in one electrolyte solution. This study describes a relatively simple solution — the major ions and ion pairs considered to occur in soil extracts. No redox, precipitation, dissolution, or adsorption phenomena are considered to affect chemical equilibrium once a soil solution has been extracted and contained separate from the soil solids.

B. Potentiometric methods

Potentiometry measures ion activities directly. However, the accuracy of the results of this method depend on the validity of the assumptions made regarding electrode calibration. These assumptions have to do with separating a mean salt activity coefficient into single ion activity

coefficients and are based on relative experimental values(Bates and Guggenheim,1960; Bates and Alfenaar,1969). Neither the MacInnes convention nor the Stokes-Robinson(hydration) convention accurately predicts single ion activity coefficients when ionic strength is greater than about 0.1, when ion pairing occurs; or when ion charge exceeds 1. No other convention has proved to be better than either of these two conventions and, so, a convention has not been accepted for calculating single ion activity coefficients. There is no standard method available for calibrating ion-selective electrodes(Pytkowicz,1979; Covington,1979). To maintain consistency in derived values for (Ca^{+2}), this study uses the species calculation method to distribute the aqueous species in $CaCl_2$ solutions. This use allows electode calibration in terms of EMF as a function of (Ca^{+2}).

C. Colourimetric methods

A colourimetric method for determining (Ca^{+2}) would provide another option for the analytical chemist and would, for the purpose of this study, provide another estimate of (Ca^{+2}) against which the other estimates could be compared. The utility of such a procedure depends on: 1)an accurate estimate of the formation constant of the coloured complex used to determine (Ca^{+2}), 2)an anion which complexes specifically and to a small extent with calcium, and 3)a complex which forms to the same extent regardless of pH.

Gysling and Schwarzenbach(1949) first reported the preparation and use of such a dye(tetramethylmurexide - TMM). Jeremy(1975) used TMM to measure the concentration of ionic calcium. Ohnishi(1978a and 1978b) presented a dual-wavelength spectrophotometric method for studying the colourimetric properties of metal-dye complexes. This technique is especially useful when using TMM or any other dye which absorbs light at the same wavelength as does the metal-dye complexes. The use of a colourimetric method to determine (Ca^{+2}) in soil solutions has not been reported and it is hoped the methodology can be adapted for use in this determination.

III. MATERIALS AND METHODS

A. Methods of determining calcium ion activity

Three methods of determining calcium ion activity in soil solutions were used:

1)calculation of the distribution of aqueous species in solutions of known total ionic composition,

2)potentiometric measurement using a calcium ion-selective electrode,and

3)colourimetric measurement of the degree of formation of a calcium complex using the dye tetramethylmurexide

These methods provide independent estimates of calcium ion activity because of the different measured parameters used. Method 1 requires analysis of a soil solution for pH, electrical conductivity, and the total concentration of major cations and anions. Method 2 requires the measurement of electrical potential between a measuring and a reference electrode with the electrode assembly immersed in a soil solution. Method 3 requires analysis of a soil solution for electrical conductivity(in order to estimate ionic strength), total concentration of sodium, and the optical density of a prepared solution.

A description of the derivation of expressions for calcium ion activity used in each method follows.

1) Calculation of the distribution of aqueous species

The distribution of aqueous species refers to a partitioning of the total amount of an ion in solution among the various forms in which it is assumed to occur. Thus, the mass balance for an ion includes the concentrations of the free ion and all ion pairs or complexes in which the ion occurs. Within a mass balance expression, mass action equations describe the equilibrium states of the various forms. Equivalent expressions of mass balance and mass action for the major cations and anions present in a soil solution are solved simultaneously to describe the equilibrium state of all electolytes in solution.

The calculation used here is similar to that suggested by Adams(1971) which accounts for ion pairing and for ionic strength effects on ion activities. The formation of complexes is considered to be negligible for the major species present in soil solutions. Ion activity is described as the product of the ion concentration and the single ion activity coefficient. Calculation of activity coefficients requires knowledge of the solution ionic strength, which in turn requires accurate estimates of the concentrations of ionic species. Subtraction of the sum of the concentrations of ion pairs from total ion concentration gives the concentration of free ion. Ion pair concentrations are expressed using mass action equations, which require free ion activities. The cyclic nature of this derivation of an expression for ion activity is used to make successive

approximations of solution parameters(ionic strength and concentrations of free ions and ion pairs) and to then calculate ion activities.

A computer program similar to that used by Feagley(1979) was used in this study to calculate the distribution of aqueous species. Figure 1 is a flow diagram showing the mathematical manipulations performed; the computer program, called SALT, is listed in Appendix 1. Four sections are evident in Figure 1: data aquisition, initial estimates of ionic strength and cation activity coefficients and activities, successive approximation of ionic strength and aqueous species concentration, and output of results.

Data required for calculation of the distribution of aqueous species is electrical conductivity(EC,expressed in dS/m), pH, and total concentrations([ ]'s, expressed in me/L) of major cations(Na^+, K^+,Ca^{+2},Mg^{+2},NH_4^+, Al^{+3},Fe^{+3}, and Mn^{+2}) and anions($CO_3^{-2}+HCO_3^-$,SO_4^{-2},Cl^-,NO_3^-, and PO_4^{-3}). A computer program was used to facilitate the input of data in the form required for calculation by SALT(a listing of the computer program SALTIN is provided in Appendix 2).

The calculation is initiated by estimating some solution parameters. Electrical conductivity is used to estimate ionic strength(I; Griffin and Jurinak,1973). Major cation activity coefficents, denoted γ, and activities, denoted ( ), are then estimated:

$$I=EC\cdot 0.013$$

$$-\log\gamma=Az^2((I^{1/2}/(I^{1/2}+1))-0.3I)$$

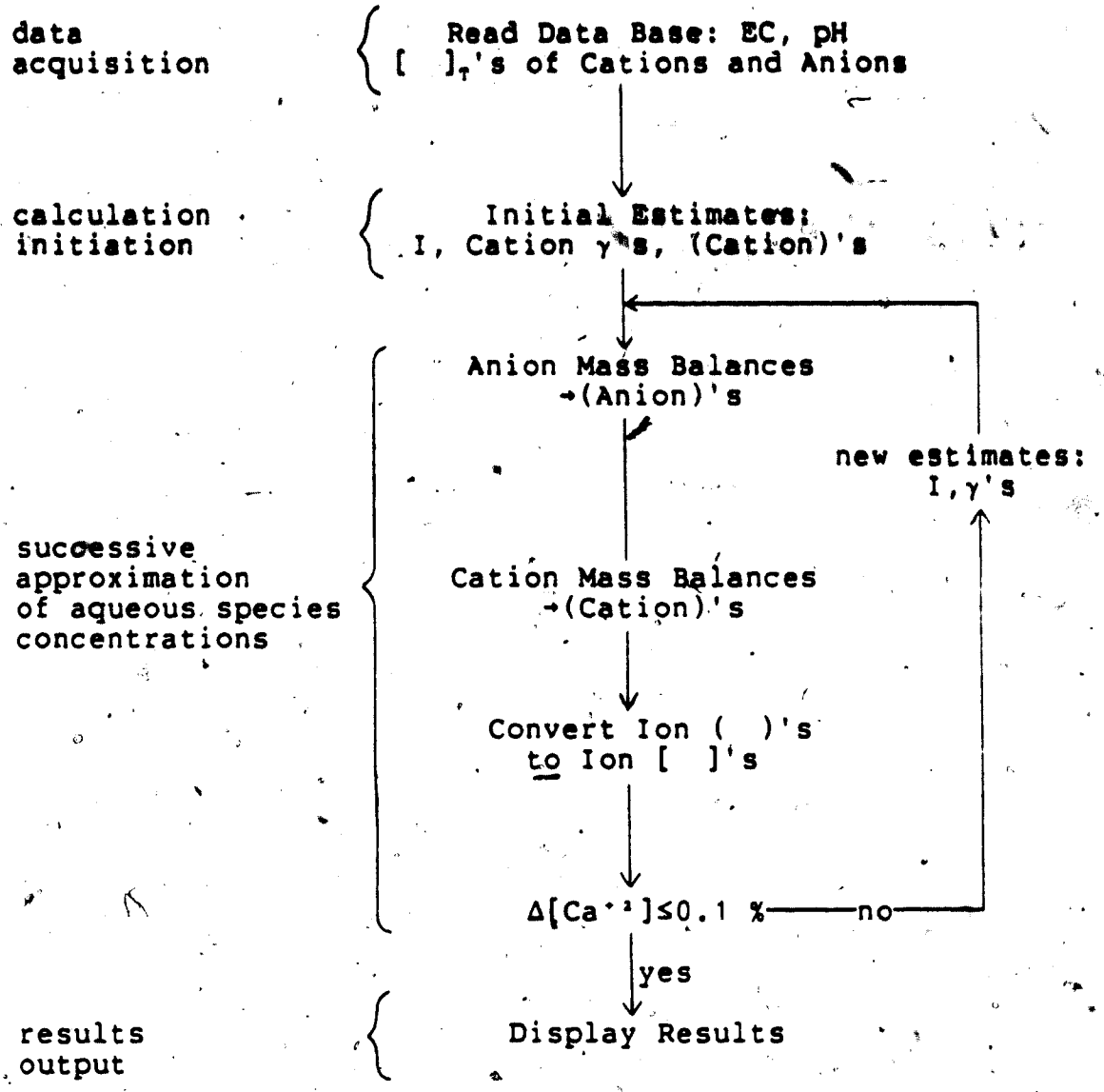

Figure 1. Flow diagram for calculating the distribution of aqueous species.

$( ) = \gamma \cdot [ ]$

Where: A is a function of the dielectric constant of water, and

z is ion valence.

Carbonate and bicarbonate concentrations are estimated using soil solution pH and the amount of acid required to titrate to pH 4.5(if pH of the soil solution is greater than 8.3, consideration is made for carbonate species requiring two protons). These first estimates of solution parameters provide for initiation of the calculation and, if the estimates are accurate, allow rapid convergence of the successively approximated values of aqueous species concentrations.

Successive approximation of the concentrations of aqueous species refers to the above mentioned cyclic calculation of free ion activities, aqueous species concentrations, ionic strength, activity coefficients, free ion activities, etc. The calculation continues until the change in the calculated values of solution parameters is less than a predetermined limit. The primary equation used in this section of the calculation is an expression of free ion activity derived from mass action relationships in a mass balance equation. For example, the sulphate mass balance, including the predominant ion pairs assumed to form in soil solutions, is:

$$[SO_4^{-2}]_T = [SO_4^{-2}] + [NaSO_4] + [KSO_4] + [CaSO_4] + [MgSO_4] + [FeSO_4] + [MnSO_4] + [AlSO_4]$$

The derived expression from this mass balance is for sulphate ion activity, so each contribution to the total sulphate concentration is expressed in terms of sulphate ion activity:

$$[SO_4^{-2}]_T = \frac{(SO_4^{-2})}{\gamma_{SO_4^{-2}}} + \frac{K_{NaSO_4^-}(SO_4^{-2})(Na^+)}{\gamma_{NaSO_4^-}} + \frac{K_{KSO_4^-}(SO_4^{-2})(K^+)}{\gamma_{KSO_4^-}}$$

$$+ \frac{K_{CaSO_4^\circ}(SO_4^{-2})(Ca^{+2})}{\gamma_{CaSO_4^\circ}} + \frac{K_{MgSO_4^\circ}(SO_4^{-2})(Mg^{+2})}{\gamma_{MgSO_4^\circ}}$$

$$+ \frac{K_{FeSO_4^+}(SO_4^{-2})(Fe^{+3})}{\gamma_{FeSO_4^+}} + \frac{K_{MnSO_4^\circ}(SO_4^{-2})(Mn^{+2})}{\gamma_{MnSO_4^\circ}}$$

$$+ \frac{K_{AlSO_4^+}(SO_4^{-2})(Al^{+3})}{\gamma_{AlSO_4^+}} ;$$

where: K_{IP} is the value of the thermodynamic formation constant of an ion pair(where IP is $NaSO_4^-$, KSO_4^-, etc.).

Sulphate ion activity is then collected algebraically as a common factor:

$$(SO_4^{-2}) = \frac{[SO_4^{-2}]_T}{\left[\frac{1}{\gamma_{SO_4^{-2}}} + \frac{K_{NaSO_4^-}(Na^+)}{\gamma_{NaSO_4^-}} + \frac{K_{KSO_4^-}(K^+)}{\gamma_{KSO_4^-}} + \frac{K_{CaSO_4^\circ}(Ca^{+2})}{\gamma_{CaSO_4^\circ}} + \frac{K_{MgSO_4^\circ}(Mg^{+2})}{\gamma_{MgSO_4^\circ}} + \frac{K_{FeSO_4^+}(Fe^{+3})}{\gamma_{FeSO_4^+}} + \frac{K_{MnSO_4^\circ}(Mn^{+2})}{\gamma_{MnSO_4^\circ}} + \frac{K_{AlSO_4^+}(Al^{+3})}{\gamma_{AlSO_4^+}}\right]}$$

Thus, sulphate ion activity is expressed as the ratio of total sulphate concentration to the sum of the weighting factors which describe the relative contributions of each aqueous species to total sulphate concentration. These weighting factors change as a function of changing cation activity and activity coefficient with successive approximations. Expressions of anion activity, such as that shown above for SO_4^{-2}, use estimates of cation activity. Likewise, estimates of anion activities are used in expressions of cation activity. The calcium mass balance, including species assumed to be present in soil solutions, is:

$$[Ca^{+2}]_T = [Ca^{+2}] + [CaHCO_3^+] + [CaCO_3^\circ] + [CaSO_4^\circ] + [CaOH^+] + [CaNO_3^+] + [CaCl^+] + [CaH_2PO_4^+] + [CaHPO_4^\circ]$$

and

$$(Ca^{+2}) = \frac{[Ca^{+2}]_T}{\left[\frac{1}{\gamma_{Ca^{+2}}} + \frac{K_{CaHCO_3^+}(HCO_3^-)}{\gamma_{CaHCO_3^+}} + \frac{K_{CaCO_3^\circ}(CO_3^{-2})}{\gamma_{CaCO_3^\circ}}\right.}$$

$$+ \frac{K_{CaSO_4^\circ}(SO_4^{-2})}{\gamma_{CaSO_4^\circ}} + \frac{K_{CaOH^+}K_w}{\gamma_{CaOH^+}(H^+)}$$

$$+ \frac{K_{CaNO_3^+}(NO_3^-)}{\gamma_{CaNO_3^+}} + \frac{K_{CaCl^+}(Cl^-)}{\gamma_{CaCl^+}}$$

$$\left. + \frac{K_{CaH_2PO_4^+}(H_2PO_4^-)}{\gamma_{CaH_2PO_4^+}} + \frac{K_{CaHPO_4^\circ}(HPO_4^{-2})}{\gamma_{CaHPO_4^\circ}}\right]$$

where: K_w is the thermodynamic dissociation constant of water.

Similar expressions are derived for carbonate, bicarbonate, nitrate, chloride, phosphate, sodium, potassium, magnesium, iron, aluminum, and manganese.

Table 1 shows the formation constants for those ion pairs which are assumed to form in soil solutions and which have been included in the mass balance equations used in this study.

The second section of Figure 1 shows that the calculation is initiated using estimates of cation activities. Successive approximation begins with calculation of anion activities using these cation activity estimates; then cation activities are calculated using these estimates of anion activities. The weighting factors for charged

Table 1. Values of thermodynamic formation constants(log K_f) at I=0 and 25°C for the ion pairs assumed, in this study, to form in soil solutions.

	SO_4^{-2}	CO_3^{-2}	HCO_3^-	OH^-	$(OH^-)_2$	NO_3^-	Cl^-	$H_2PO_4^-$	HPO_4^{-2}
Ca^{+2}	2.31	3.15	1.02	1.30		0.68	0.60	1.40	2.74
Mg^{+2}	2.23	2.88	0.95	2.58					
Na^+	0.65	0.55	0.16						
K^+	0.85	1.30	-0.25						
H^+		10.33	6.36					2.15	7.20
Al^{+3}	3.20			8.98	18.70				
Mn^{+2}	2.26		1.80	3.05			0.61		
Fe^{+3}	4.15			11.81	22.31	1.00	1.48	5.43	10.91

These values are collected from: Nakayama(1971), Smith and Martell(1976), Lindsay(1979), Sposito and Mattigod(1979), and Hogfeldt(1982).

Blank spaces indicate that ion pair formation is considered to be negligible.

aqueous species are then used to calculate the concentrations of species contributing to ionic strength. Calculation continues cyclically with successive approximation of ionic strength, single ion activity coefficients, anion activities, cation activities, and aqueous species concentrations until the concentrations of free calcium and phosphate change, through the previous iteration, by less than 0.1 percent.

Single ion activity coefficients are calculated using the Davies equation(Davies,1962). It is considered that this equation estimates activity coefficients equally as well as do other equations such as the extended Debye-Huckel equation. The Davies equation is preferred to other equations because it does not include a variable ion size parameter - this allows algebraic elimination of variables

in derivation of an expression for calcium ion activity for the colourimetric method and, to be consistent, is used in the calculation of the distribution of aqueous species. Activity coefficients for neutral species are calculated using the Setchenow equation which is a simplification of the Davies equation:

$\log\gamma = KI$

where K is a salting coefficient(ion pairs form because of decreased water activity) set at 0.1(Sposito,1981).

The results of the calculation are arranged for hard copy printing. This information includes ionic strength, the anion/cation charge balance(the ratio of the sum of anion concentrations to the sum of cation concentrations), pH, electrical conductivity, the number of iterations required for convergence, the total concentrations of major ions, and the concentration and activity of each aqueous species considered.

2) Potentiometry using a calcium ion-selective electrode

Calcium ion activity is determined by first measuring the electrical potential between a measuring(calcium ion-selective) electrode (Orion,Model 93-20) and a reference electrode(Orion, Model 90-01) with the electrode assembly immersed in a soil solution. Activity is then found by comparing the measured potential to a calibration curve.

There is no accepted convention by which the activity coefficient of the aqueous calcium ion can be calculated.

Therefore, a standard method is not available for calibrating the electrode assembly in terms of electrical potential as a function of calcium ion activity. In this study, the species calculation method is used to calculate the distribution of Ca^{+2}, Cl^{-}, and $CaCl^{+}$ in prepared solutions of $CaCl_2$. The derived calcium activities in these solutions were used in preparing a standard curve.

3) Colourimetry using tetramethylmurexide(TMM)

This method is based on a determination of the extent of formation of the Ca-TMM complex. TMM is used as the NH_4 salt which gives a purple solution. The active portion of the dye is a monovalent anion and the 1:1 complex that forms with Ca^{+2} is a monovalent cation, the solution of which is orange. Formation of the Ca-TMM complex is insensitive to pH (at values ≥ about 3.5); and the molar absorptivity coefficient of the complex is high(small amounts of dye can be used, little calcium is complexed, and the distribution of calcium species at equilibrium is relatively undisturbed).

a) selection of analytical wavelengths

Absorption spectra of TMM and Ca-TMM were measured in solutions of $3 \cdot 10^{-5}$ M TMM in water and 1 M $CaCl_2 \cdot 2H_2O$, respectively, using a Bausch and Lomb Spectronic 100 spectrometer equipped with a flow through cell(Figure 2). A significant separation between the wavelengths of maximum absorbance is evident(528 nm for TMM and 489 nm for Ca-TMM),

and the molar absorptivity coefficients are different at all but one wavelength. At any wavelength, the measured absorbance is the sum of the absorbances of free TMM and Ca-TMM complex. Use of a dual-wavelength procedure, as suggested by Ohnishi(1978), eliminates the absorbance due to the uncomplexed dye and the uncertainty in estimating the molar absorptivity coefficient of TMM. Selection of wavelengths consists of choosing one wavelength (Figure 2, 554 nm) where the difference between the absorbances of the free dye and the Ca-TMM complex is greatest(on the high wavelength side of the TMM curve, where the absorbance due to Ca-TMM is lower). The second wavelength (Figure 2, 507 nm) is then chosen so that the molar absorptivities of free dye at the two wavelengths are equal. The difference between the absorbances measured at the two wavelengths represents the absorbance due to only the Ca-TMM complex.

b) selection of $[TMM]_T$

The total concentration of TMM used in this study was $5 \cdot 10^{-5}$ M because, over the range of $[Ca^{+2}]_T$ used(0 to 100 me/L), errors in measuring absorbance are kept to a minimum (absorbance is ≤ 1 at 507 nm and ≥ 0.2 at 554 nm).

c) determination of the effect of Na and Mg

A solution $5 \cdot 10^{-5}$ M in TMM was prepared in 0.1 M Na_2SO_4 or 0.05 M $MgSO_4 \cdot 5H_2O$. The absorbance was measured at 507 and 554 nm using a Bausch and Lomb Spectronic 100 spectrophotometer equipped with a 1 cm flow-through cell.

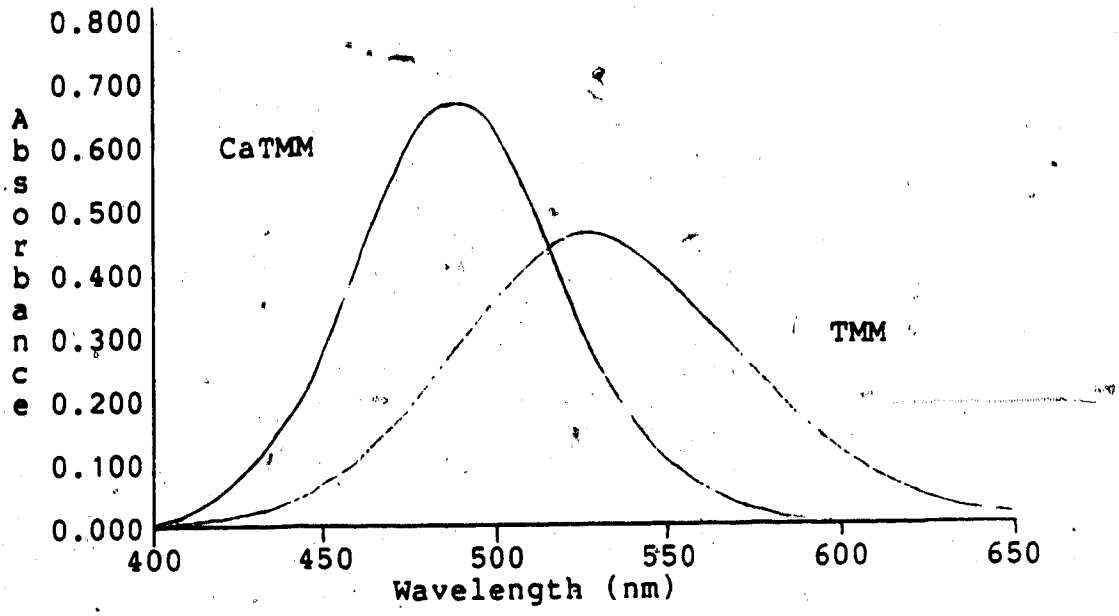

Figure 2. Absorbance spectra of TMM and Ca-TMM.

Absorbance due to the presence of the Na-TMM or Mg-TMM complexes is expressed as the arithmetic difference between the measured absorbances.

d) effect of pH on absorbance measurements

Significant concentrations of Al, Mn, and Fe are expected in soil extracts of low pH. Of the three metals, Al^{+3} is most easily hydrolysed and can be in solution when the pH is not low enough to hydrolyse Fe^{+3} and Mn^{+2} to a significant extent. Efforts to show the effects of Al on the measurement of the absorbance of a TMM solution were frustrated because of steadily decreasing absorbance readings. Solutions were prepared in an effort to determine if the effect was because of high proton concentration. Solutions of $AlCl_3$ or HCl were added to $5 \cdot 10^{-3}$ M TMM to prepare solutions of pH 3, 3.5, 4, 4.5, and 5. Absorbance was measured at 528 nm(wavelength at which TMM absorbs most

strongly) over a 15 minute time period using a Bausch and Lomb Spectronic 21 spectrophotometer.

e)stability of Ca-TMM complex

A $3 \cdot 10^{-3}$ M solution of TMM was prepared in 1 M $CaCl_2 \cdot 2H_2O$ and the absorbance of this solution was measured at 489 nm every 5 minutes over a 1 hour time period using a Bausch and Lomb Spectronic 100 spectrophotometer fitted with a 1 cm flow-through cell.

f)determination of the formation constant and the molar absorptivity coefficient of the Ca-TMM complex

Ohnishi(1978) reports values for the conditional formation constants(K_f^*) of the Ca^{+2},Na^+, and Mg^{+2} complexes of TMM(pH buffered at 7 using HEPES):

	K_f^*	K_f
Ca-TMM	360	970
Na-TMM	8	13
Mg-TMM	16	43

These values were determined at an ionic strength of 0.1. The Davies equation was used in my study to calculate first the activity coefficient of calcium and then the thermodynamic formation constant(K_f) of the Ca-TMM complex(i.e. K_f at I=0):

$$K_f = \frac{(Ca\text{-}TMM^+)}{(Ca^{+2})(TMM^-)} = \frac{[Ca\text{-}TMM^+]\gamma_{TMM^-}}{[Ca^{+2}]\gamma_{Ca^{+2}}[TMM^-]\gamma_{TMM^-}} = \frac{K_f^*}{\gamma_{Ca^{+2}}},$$

where: K_f^* is the conditional stability constant.

Ohnishi(1978) used $[Ca]_T$ up to 10 mM in determining the formation constant of Ca-TMM; $[Ca]_T$ up to about 50 mM is expected in soil solutions. Therefore, the value of the formation constant of Ca-TMM was determined over a wide range of $[Ca^{+2}]_T$ as verification of Ohnishi's value and to test if complexes other than 1:1 Ca:TMM form at higher $[Ca^{+2}]_T$. Values of K_f^c for the Na and Mg complexes of TMM are much lower than that for the Ca complex; Ohnishi's values are accepted as being accurate. Although the concentrations of Na and Mg used to determine the conditional stability constants were not reported, the highest concentrations used were very likely much larger than those anticipated in soil solutions.

Formation constants were determined, using the method of Ohnishi(1978), at each of six ionic strengths. Optical density was measured, at 554 and 507 nm, of solutions containing $5 \cdot 10^{-5}$ M TMM and 0, 0.5, 1; 1.5, 3, 5, 10, 15, 20, 25, 30, 35, or 50 mM $CaCl_2$. The appropriate volume of a solution of NH_4Cl was added to adjust the ionic strength to 0.025, 0.050, 0.075, 0.100, 0.125, or 0.150. The concentration of TMM was chosen to be $5 \cdot 10^{-5}$ M on the basis of the concentration which gave an absorbance of close to but not greater than 1 at 507 nm and greater than 0.2 at 554 nm. A maximum of 0.15 M NH_4Cl was added; the contribution by this salt to the absorbance is small at this concentration. When the difference in absorbance at the two wavelengths is calculated, the value for TMM alone is 0.000 and when 1 M

NH_4Cl is present the value is 0.007. The higher calcium concentrations were sometimes greater than the desired ionic strength and could not be used; the number of calcium concentrations used ranged from 5 at I=0.025 to 12 at I=0.150. Solutions representing each combination of total calcium concentration and ionic strength were prepared in triplicate.

The amount of NH_4Cl required to bring a solution of $CaCl_2$ to a given ionic strength was calculated using mass balance and ionic strength expressions in the equation for the formation constant of the $CaCl^+$ ion pair:

$$K = \frac{(CaCl^+)}{(Ca^{+2})(Cl^-)} = \frac{[CaCl^+]}{[Ca^{+2}][Cl^-]} \cdot \frac{\gamma_{CaCl^+}}{\gamma_{Ca^{+2}}\gamma_{Cl^-}} .$$

Assuming $\gamma_{CaCl^+}=\gamma_{Cl^-}$,

$$K\gamma_{Ca^{+2}} = \frac{[CaCl^+]}{[Ca^{+2}][Cl^-]} ,$$

where: $[CaCl^+]=[Ca^{+2}]_T-[Ca^{+2}]$

$$[Cl^-]=[NH_4^+]+2[Ca^{+2}]_T-[CaCl^+]$$

$$=[NH_4^+]+[Ca^{+2}]_T+[Ca^{+2}]$$

$$I=0.5([NH_4^+]+[Cl^-]+4[Ca^{+2}]+[CaCl^+])$$

$$[NH_4^+]=I-[Ca^{+2}]_T-2[Ca^{+2}] \qquad (1)$$

Then, $$K\gamma_{Ca^{+2}} = \frac{[Ca]_T-[Ca^{+2}]}{[Ca^{+2}](I-[Ca^{+2}])} .$$

gives:

$$[Ca^{+2}] = \frac{1+K\gamma_{Ca^{+2}}I}{2K\gamma_{Ca^{+2}}} - \left[\left(\frac{1+K\gamma_{Ca^{+2}}I}{2K\gamma_{Ca^{+2}}}\right)^2 - \frac{[Ca^{+2}]_T}{K\gamma_{Ca^{+2}}}\right]^{1/2}$$

where: $[Ca]_T$, K, and I are known

$\gamma_{Ca^{+2}}$ is calculated using Davies equation.

Then, the concentration of NH_4Cl required to bring the solution to I is found using equation (1). At any I, the formation constant is found by extrapolating the linear relationship between a log function of optical density and $\log[Ca^{+2}]$ to $\log[Ca^{+2}]=0$.

$$K_{f,CaTMM} = \frac{(Ca_n\text{-}TMM)}{(Ca^{+2})^n(TMM^-)} = \frac{[Ca_n\text{-}TMM]}{(Ca^{+2})^n[TMM^-]} \cdot \frac{\gamma_{Ca_nTMM}}{\gamma_{TMM}}$$

$$= \frac{[Ca_n\text{-}TMM]}{(Ca^{+2})[TMM^-]}$$

where: $[TMM^-]=[TMM^-]_T-[Ca_n\text{-}TMM]$,

$[TMM^-]_T=A_\infty/a_{Ca_nTMM}$,

$[Ca_n\text{-}TMM]=A/a_{Ca_nTMM}$,

A is the difference between the absorbances at 554 and 507 nm,

A_∞ is the difference between the absorbances at 554 and 507 nm when all dye is complexed, and

a_{Ca_nTMM} is the difference in the molar absorptivities of Ca_nTMM at 554 and 507 nm.

$$\log K_f = \log[Ca_n\text{-}TMM]-n\log(Ca^{+2})-\log[TMM^-]$$

$$= \log[Ca_n\text{-}TMM]-n\log(Ca^{+2})-\log([TMM^-]_T-[Ca_n\text{-}TMM])$$

$$= \log(A/a_{CaTMM})-n\log(Ca^{+2})-\log((A_\infty-A)/a_{CaTMM})$$

$$= -n\log(Ca^{+2})+\log(A/(A_\infty-A))$$

$$= -n\log(Ca^{+2}) + \log(A/(A_\infty - A))$$

Therefore, when $\log(Ca^{+2})=0$, $\log K_f = \log(A/(A_\infty - A))$. The formation constant is not dependent on I, and the determination of K at different ionic strengths allows for the detection of inconsistencies in the method and/or inaccuracies in the values of $\gamma_{Ca^{+2}}$ and/or $K_{f,CaCl^+}$. This approach is general in that it does not assume that only a 1:1 Ca:TMM complex is formed. If this is, indeed, the only complex formed, then n equals 1.

g) derivation of an expression for (Ca^{+2})

Sodium also forms a coloured complex with TMM and this contribution to measured absorbance must be accounted for when estimating (Ca^{+2}). The measured absorbance is the sum of the absorbances of the calcium and sodium complexes of TMM:

$$A_T = A_{CaTMM} + A_{NaTMM}$$

$$= a_{CaTMM}[Ca\text{-}TMM^+] + a_{NaTMM}[Na\text{-}TMM]$$

Using mass action equations to describe the concentrations of complexes gives:

$$A_T = \frac{a_{CaTMM} K_{f,CaTMM} (Ca^{+2})[TMM^-]\gamma_{TMM^-}}{\gamma_{CaTMM}} + \frac{a_{NaTMM} K_{f,NaTMM} [Na^+][TMM^-]\gamma_{Na^+}\gamma_{TMM^-}}{\gamma_{NaTMM}}$$

The intent is to use the measured total concentration of sodium and activity coefficients calculated using values of

I estimated from measured electical conductivity. Activity coefficients calculated using the Davies equation are the same at a given I for all univalent ions(regardless of sign), for all divalent ions, etc. Therefore, γ's for TMM^- and Ca-TMM^+ are the same at any I, and the above expression for total absorbance simplifies with algebraic elimination of these γ's in the first part of the right hand side of the equation. Also, the activity coefficients for Na^+ and TMM^- are equal at any I, and γ for $NaTMM^\circ$ is taken to be 1. The equation has two unknown quantities, calcium ion activity and concentration of free dye. Rearranging to express $[TMM^-]$ gives:

$$[TMM^-]=\frac{A_T}{a_{CaTMM}K_{f,CaTMM}(Ca^{+2})+a_{NaTMM}K_{f,NaTMM}[Na^+]\gamma_{Na^+}\gamma_{TMM^-}}$$

The concentration of free dye is part of a mass balance equation for the dye:

$$[TMM]_T=[TMM^-]+[Ca\text{-}TMM^+]+[Na\text{-}TMM^\circ]$$
$$=[TMM^-]+K_{CaTMM}(Ca^{+2})[TMM^-]+K_{NaTMM}[Na^+][TMM^-]\gamma_{Na^+}\gamma_{TMM^-}.$$

Rearranging gives an expression for $[TMM^-]$ which can be substituted into the above equation. That equation then has only one unknown quantity(calcium ion activity). The derived expression for calcium ion activity is:

$$(Ca^{+2}) = \frac{[TMM]_T(a_{NaTMM}K_{f,NaTMM}[Na^+]\gamma^2_{Na^+} - A(1+K_{f,NaTMM}[Na^+]\gamma^2_{Na^+})}{K_{CaTMM}(A_T-[TMM]_T a_{CaTMM})}.$$

h) measurement of absorbance in prepared soil solutions

Saturated paste extracts were prepared and collected by standard methods (McKeague, 1978). Solution preparation involved pipetting 10 mL of soil extract into a test tube, adding 0.2 mL of $2.55 \cdot 10^{-3}$ M TMM (using an Eppendorf pipette), and mixing. Absorbance was measured at 507 and 554 nm using a Bausch and Lomb Spectronic 100 spectrophotometer equipped with a 1 cm flow-through cell. The absorbance due to organic staining was measured in soil solutions with no added TMM. This absorbance was subtracted from the absorbance measured with added TMM.

B. Soil Samples Collected For Study

An attempt was made to include soils which represented a wide variety of kinds and concentrations of salts. It was considered that a rigorous test of the suitability and accuracy of the methods used for determining (Ca^{+2}) required inclusion of soil solutions representing variety in terms of ionic strength, fraction of total calcium as ion pairs, and concentration of interfering aqueous species (Mg^{+2}, Na^+, H^+, organic matter).

1) High sulphate systems

a)The Ccasa horizon of a Brown Solodized Solonetz(Hemaruka series) from near Enchant, Alberta was sampled. The major soluble minerals in this sample are mirabolite and gypsum. The crystal state of the sodium sulphate salt depends on ambient temperature and humidity after sampling and is usually not as highly hydrated as mirabolite. The sample is also calcareous, so the pH should be about 8. A profile description is given in Appendix 4.

b) Gypsum was mixed into the surface 20 cm of the soil along an oil pipeline right-of-way near Redwater, Alberta where a pipeline rupture resulted in oil and saline water being discharged to the surface. A sample of the surface 20 cm was collected one year after the oil/water spill. The sample was of a loamy texture. Although a smell of petroleum was evident, the sample did not appear to be heavily contaminated; decomposition of oil may have been well advanced. Because this sample was taken from a pipeline right-of-way, the soil profile was disturbed; thus, a profile description is not given. According to Soil Survey Report No.21, nearby soils are Eluviated Black and Orthic Black Chernozems developed on alluvial lacustrine materials(Bowser *et al*, 1962).

c) Samples of the Ap, Bnt1, Bnt2, Csk1, and Csk2 horizons of a Black Solonetz(Daugh series) from another

study(Alzubaidi and Webster, 1983) were available. The samples were from a plot area near Chipman, Alberta where the effects of tillage practices and calcium additions on the chemical and physical properties of a Solonetzic soil are being studied. Most samples were too small, so the samples from plots representing different replications of the same treatment were combined to provide sufficient sample for this study. Some of these composite samples required combining the Bnt1 and Bnt2 horizons or the Csk1 and Csk2 horizons to provide sufficient sample. In this way, 24 samples were prepared representing the following combinations of treatments and soil horizons:

tillage practice	normal	deep plowing
calcium addition	none, $CaSO_4$, $CaCO_3$	none, $CaSO_4$, $CaCO_3$
horizon represented	Ap, Bnt, Csk1, Csk2	depths equivalent to the Ap, Bnt1 Bnt2, Csk horizons

2) Highly soluble calcium salts

a) Additions of calcium nitrate and ammonium nitrate were mixed into the surface 20 cm of the soil along an oil pipeline right-of-way near Redwater, Alberta to inhibit the effects of spilled oil and saline water. A sample of the surface 20 cm was collected 2 months after the spill. The sample was of a loamy sand texture. An oily smell and appearance was evident; oil decomposition is presumed to

have progressed to only a very small extent. Because this sample was taken from a pipeline right-of-way, the soil profile was disturbed; thus, a profile description is not given. According to Soil Survey Report No.21, nearby soils are Orthic Regosols developed on aeolian material(Bowser *et al*, 1962).

b) Calcium chloride was added to the surface of a soil material at the site of an abandoned coal mine near Bow City, Alberta. The material was drastically disturbed because of mining operations, and efforts were made to return the area to agricultural production. The surface 10 cm was sampled. A soil profile description is not provided for this material because the profile was destroyed during mining operations.

3) Low total salt content

Two samples representing soils with low salt contents are included. One is from near Medicine Hat, Alberta and one is from near Beaverlodge, Alberta. Soil profile descriptions are provided in Appendix 4.

a)the Cca of an Orthic Brown Chernozem(Maleb series)

b)The Cca of an Orthic Gray Luvisol(Culp series)

4) Low pH

a)The Cs horizon of a Podzolic Gray Luvisol(Boundary complex) was sampled. The pH of this sample was expected to be about 4. A profile description is given in Appendix 4.

b)The BCg horizon of a Luvic Gleysol(Josephine series) was sampled. The pH of this sample was expected to be about 3.5 to 4(Pawluk,1971). A profile description is given in Appendix 4.

c)Seventeen surface and near-surface soil samples were collected from sites near the sulphur blocks at two southwest Alberta gas plants. It was intended that sampling would represent a range of pH(2-7); samples were collected at varying distances from the sulphur blocks(100m-1km) and from either the surface(0-1 cm) or near-surface(1-2 or 1-3 cm). Profile descriptions are not given for the sites represented by these samples. Acidification is anthropomorphic and no association is made between the pH of these samples and soil forming processes.

C. Methods of Preparing and Analysing for the Major Ion Content of Soil Solutions

1)Saturated pastes were prepared and the extracts were collected using standard techniques (McKeague,1978).

2)Analyses included the following parameters and techniques:

Parameter	Technique	Reference
Electrical conductivity	conductivity bridge	Markson, 1978
Na,K	flame photometry	Corning, 1978
Ca,Mg,Al, Fe,Mn	AAS	Perkin-Elmer, 1982
NH_4	colourimetry	Technicon, 1977
pH,CO_3,HCO_3	acid titrimetry	Metrohm, 1982
SO_4	colourimetry	Technicon, 1972
Cl	colourimetry	Technicon, 1976
NO_3	colourimetry	Technicon, 1978
PO_4	colourimetry	Technicon, 1973

All analyses were performed on duplicate subsamples. Equipment calibration was checked after each group of nine samples by taking measurements on a standard reference sample.

The results of these analyses are reported in Appendix 3.

IV. RESULTS AND DISCUSSION

For the purpose of comparing the three methods used here, one method should be selected against which the other two can be compared. A standard method for measuring calcium ion activity has not been accepted. The species calculation method was used in this study as the standard for comparison for the following reasons:

1) it is most commonly reported in the literature for estimating calcium ion activity,
2) interferences in the measurement of total concentration are better understood than are the interferences in the measurement of activity by potentiometric and colourimetric methods, and
3) the colourimetric method has not been tested for measuring calcium ion activity.

A. Synthetic solutions

1) Potentiometric method

Repeated observation with the Orion calcium ion-selective electrode used here (Orion, model 93-20) showed that the slope of the electrode response was 31±1.5 mV per decade change in calcium ion activity. This slope is slightly higher than the manufacturer's claim (29.08 mV per decade at 25°C) and may be associated with errors in electrode calibration or with the history of this particular electrode. The calculation used in the species calculation method was also used to calculate calcium ion activity in $CaCl_2$ solutions; information so gained was used to prepare a calibration curve. Any inaccuracy in the value of the formation constant for the $CaCl^+$ ion pair or in estimating activity coefficients is reflected in estimations of calcium ion activity. If a real difference exists between the theoretical and observed slopes for electrode response, then estimates of activity coefficients are too low and/or the value used for the formation constant for $CaCl^+$ is too high. In either case, a slope which is higher than expected results because a range of calcium ion activity greater than one decade is treated as if it were one decade. The observed slope of the electrode response is about 5 percent more than the theoretical slope. This difference can easily arise in the species calculation method - the value of the formation constant for $CaCl^+$ used here is $10^{0.6}$; if this value is 5

percent high, then the real value is 10$^{0.11}$. The uncertainty in estimating this value is likely at least 5 percent. Differences in electrode calibration are observed when two sets of standard solutions are used (one set prepared using $CaCl_2$, the other using $Ca(NO_3)_2$; Table 2).

Table 2. EMF in solutions of $CaCl_2$ or $Ca(NO_3)_2$ and calculated values of (Ca^{+2}) in each solution.

	——$CaCl_2$——		——$Ca(NO_3)_2$——	
$[Ca]_T$ (me/L)	EMF (mV)	(Ca^{+2}) (mM)	EMF (mV)	(Ca^{+2}) (mM)
1.3	58.4	0.5319	58.9	0.5315
2.1	63.6	0.8161	63.9	0.8152
3.1	68.4	1.1454	68.4	1.1435
4.7	73.1	1.6288	73.3	1.6250
7.0	77.8	2.2568	77.6	2.2497
12.0	83.7	3.4436	83.0	3.4279
18.0	87.9	4.6617	86.6	4.6335
28.0	92.6	6.3937	90.1	6.3423
50.0	98.6	9.4957	95.5	9.3864
57.0	100.0	10.3612	96.8	10.2319

Using linear regression analysis, the following relationships were calculated:

1) $CaCl_2$ solutions

$$E=66.6 + 32.4 \log (Ca^{+2}) \; ; r=0.9997 \qquad (2)$$

2) $Ca(NO_3)_2$ solutions

$$E=66.9 + 29.5 \log (Ca^{+2}) \; ; r=0.9998 \qquad (3)$$

The slope of the electrode response was, on that day and for $CaCl_2$ solutions, 32.4 mV per decade change in (Ca^{+2}). This slope was the highest observed throughout this study. On the same day, for $Ca(NO_3)_2$ solutions, the slope was 29.5 mV/decade change in (Ca^{+2}). This slope is close to the manufacturer's claim(29.1 mV at 20°C). The electrode exhibits daily variations in its response. No significance is attributed to the similarity of the theoretical and observed slopes for the electrode response in $Ca(NO_3)_2$ solutions ; this similarity is considered to be coincidental. The point to be made here is that electrode response is calculated to be so much different in solutions of $CaCl_2$ and $Ca(NO_3)_2$. The data in Table 2 suggest that electrode operation was normal because $r \simeq 1$ and EMF measurements were reproducible. The difference in calculated electrode response is probably associated with errors in calculation of the distribution of aqueous species in $CaCl_2$ and/or $Ca(NO_3)_2$ solutions. Inaccurate values for the formation constants for $CaCl^+$ and/or $CaNO_3^+$ ion pairs would give the observed difference in calculated electrode response. No effort was made here to verify the values of the formation constants for the $CaCl^+$ and $CaNO_3^+$ ion pairs. Solutions of $CaCl_2$ were used in preparing all calibration curves.

Cations other than calcium may interfere in measurements with the calcium electrode by increasing the measured electrical potential according to the relationship

(Simon, *et al.*, 1978):

$$E = E^{\circ} + s \cdot \log[(Ca^{+2}) + \Sigma K^{Pot}_{CaM}(M)^{2/Z_M}] \qquad (4)$$

where E is cell electrical potential

E° is the reference electrical potential

s is the slope of the electrode response

(Ca^{+2}) is calcium ion activity

K^{Pot}_{CaM} is the potentiometric selectivity coefficient in response to interfering metal ion, M

(M) is metal ion activity

Z_M is the charge on the metal ion

Various values for K^{Pot}_{CaM} are found in the scientific literature. Powley *et al* (1980) published values (Table 3) which can be used to calculate the levels of interferences causing a 10 percent error in the analysis of calcium concentration as published by the manufacturer of the calcium ion-selective electrode. The numbers published by Powley *et al* (1980) suggest a larger interference from aqueous sodium and potassium than from aqueous magnesium. However, the electrode should be more selective to divalent than monovalent cations, and magnesium should give a greater interference than sodium or potassium. The operation manual for the calcium ion-selective electrode (Orion, 1979) does not include information about the ion exchanger used in the electrode. The scientific literature too does not state this information directly, but enough information is given to

suggest that the ion exchanger is the calcium salt of di-n-octylphenylphosphoric acid dissolved in di-n-octylphenylphosphonate. Simon *et al.*(1978) published values of K^{Pot}_{CaM} for an electrode based on this ion exchanger; those values(Table 3) support a higher selectivity for magnesium than for sodium or potassium.

Table 3. Values of K^{Pot}_{CaM} for Na^+, K^+, and Mg^{+2}.

	1	2
Na^+	0.025	0.0000063
K^+	0.0062	0.000002
Mg^{+2}	0.0001	0.00025

1 from Powley *et al*, 1980
2 from Simon *et al.*, 1978

The extent to which Na^+, K^+, and Mg^{+2} interfere in the analysis of (Ca^{+2}) was investigated using the calcium ion-selective electrode and a single junction reference electrode. Electrical potential was measured in solutions containing 2 or 10 me/L $CaCl_2$ or $Ca(NO_3)_2$ and 100 me/L of one of the nine salts obtained by combining Na^+, K^+, or Mg^{+2} with Cl^-, NO_3^-, or SO_4^{-2}.

Sodium, potassium, and magnesium are all observed to interfere with calcium ion activity analysis using the calcium ion-selective electrode(Table 4, column 2).

Correction of EMF[1] using the values for K^{Pot}_{CaM} published by Powley *et al*(1980) reduced relative error(Table 4, column 3); sometimes the correction was too large and predicted values of (Ca^{+2}) were less than those calculated using the species calculation method. The values for K^{Pot}_{CaM} published by Simon *et al*.(1978) are too small for use with the electrode used here; corrections are usually less than 0.1 mV in solutions which require reductions of 1 to 5 mV to reduce relative error to zero. Values of K^{Pot}_{CaM} which reduce relative error to zero(Table 4, column 4) are similar to those published by Powley *et al*(1[illegible]) and higher than those published by Simon *et al*.([illegible]). The data in Table 4, column 4 also indicate errors in [illegible]ting (Ca^{+2}). The value of K^{Pot}_{CaM} which corrects for Na^{+}, K^{+}, or Mg^{+2} seems to depend on (Ca^{+2}) and the predominant anion; this observed dependence suggests that errors are inherent in the species calculation method. These errors are probably in the values used for the formation constants for ion pairs involving calcium with chloride, nitrate, and/or sulphate.

Errors in electrode calibration and in correcting for cation interference are thought to be because of inaccurate

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[1]Correction of EMF uses equation 4 and the relationship

$$E = E^{\circ} + s \cdot \log(Ca^{+2}) \qquad (5)$$

Subtracting equation (5) from equation (4) gives an expression for the amount by which EMF changes because of the presence of an interfering ion:

$$E_c = \frac{s \cdot \log[1 + K^{Pot}_{CaM}(M)^{2/Z_M}]}{(Ca^{+2})}$$

where E_c is the change in measured EMF

Calculation of the values in Table 4 also uses equations (2) and (3).

Table 4. Values of (Ca^{+2}) calculated using a species calculation method and the relative error of (Ca^{+2}) predictions using the calcium ion-selective electrode with and without correction for the effect on measured EMF of Na^{+}, K^{+}, or Mg^{+2}.

		$CaCl_2$ solutions				$Ca(NO_3)_2$ solutions			
		1	2	3	4	1	2	3	4
	C	0.3205	53	4	.011	0.3204	30	-12	.0077
	D	0.3125	37	-8	.0075	0,3124	14	-23	.0044
	E	0.1706	32	-24	.0042	0.1705	2	-42	.0016
	F	0.3205	41	26	.0084	0.3204	20	7	.0056
A[6]	G	0.3125	27	14	.0057	0.3124	3	-8	.0027
	H	0.1761	32	13	.0046	0.1761	1	-14	.0016
	I	0.2912	67	66	.0044	0.2910	43	42	.0034
	J	0.2845	49	48	.0034	0.2844	28	28	.0024
	K	0.2005	38	38	.0028	0.2004	10	9	.0014
	C	1.5484	34	22	.034	1.5447	39	26	.035
	D	1.5119	4	-5	.0047	1.5083	5	-5	.0034
	E	0.8643	15	0	.011	0.8630	9	-5	.0076
	F	1.5484	24	21	.025	1.5447	30	27	.028
B	G	1.5119	-3	-5	-[5]	1.5083	-2	-4	-[5]
	H	0.8912	12	9	.0093	0.8899	8	4	.0069
	I	1.4210	44	44	.015	1.4178	54	53	.016
	J	1.3899	13	12	.0046	1.3869	15	15	.048
	K	1.0050	21	21	.0077	1.0034	18	18	.0071

1 values of (Ca^{+2}) using species calculation method ($x10^3$)

2 % relative error in estimating (Ca^{+2}) when EMF is not corrected for Na, K, Mg

3 % relative error in estimating (Ca^{+2}) when EMF is corrected for Na, K, Mg using the values of K^{Pot}_{CaM} from Powley *et al* (1980)

4 value of K^{Pot}_{CaM} which corrects for Na, K, Mg to give no error in estimating (Ca^{+2})

5 - means values of K^{Pot}_{CaM} can not be calculated because relative error is negative

6 group A is 2 me/L of $CaCl_2$ or $Ca(NO_3)_2$
group B is 10 me/L of $CaCl_2$ or $Ca(NO_3)_2$
C to K indicates the addition of one of the following salts at 100 me/L

C is NaCl D is $NaNO_3$ E is Na_2SO_4
F is KCl G is KNO_3 H is K_2SO_4
I is $MgCl_2$ J is $Mg(NO_3)_2$ K is $MgSO_4$

values for the formation constants for some of the ion pairs which are considered in the species calculation method. Small errors in these values can cause large errors in (Ca^{+2}) predictions. No effort is made here to verify the values of the formation constants for the $CaCl^{+}$, $CaNO_3^{+}$, or $CaSO_4^{\circ}$ ion pairs. As stated earlier, solutions of $CaCl_2$ were used to prepare all calibration curves. Comparisons of the predictions of (Ca^{+2}) in soil solutions using the species calculation and potentiometric methods will use the potentiometric predictions with and without correction for interfering cations. Correction will use the appropriate values from Table 4, column 4. The major anion will probably be sulphate, and use of the values derived for 2 and 10 me/L $CaCl_2$ will depend on total calcium in the soil solutions. The value 5 me Ca^{+2}/L was chosen arbitrarily and was used to determine which value for K^{Pot}_{CaM} will be used to correct EMF - that value calculated using the lower(2 me/L) or higher(10me/L) total calcium concentration.

2) Colourimetric method

a) value of $K_{f,CaTMM}$

The value of log K was determined to be 2.833±0.070 (uncertainty is expressed as the 95% confidence limit);

i.e. $p(800 \geq K_{f,CaTMM}=681 \geq 580)=0.95$

Figure 3 shows a plot of log K as a function of I. Although a positive slope is suggested, the error associated with the calculation of K is great enough that a dependence of K on I

can not be confirmed. The total dye concentration was $5 \cdot 10^{-5}$ M and the maximum absorbance(the difference in the absorbances at 554 and 507 nm of a solution $5 \cdot 10^{-5}$ M TMM in 2 M $CaCl_2$) was 0.851. Thus, the value of the molar absorptivity coefficient for the Ca-TMM complex was determined to be 17000.

The forgoing values for the formation constant and molar absorptivity coefficient for the Ca-TMM complex are lower than those published by Ohnishi(1978). However, the value for $K_{f,CaTMM}$ is very similar to the value published by Gysling and Schwarzenbach(1949):

	K	a
Ohnishi	970	18000
G + S	617	*
This study	681	17000

*in the study reported by G + S, molar absorptivity was not determined using dual wavelength spectrophotometry

The absorbance measurements used in this determination of $K_{f,CaTMM}$ were made using a Bausch and Lomb Spectronic 21 spectrophotometer. Later absorbance measurements, using a Bausch and Lomb Spectronic 100, determined the maximum absorbance of $5 \cdot 10^{-5}$ M TMM. The difference in the absorbances measured at 504 and 554 nm in a solution $5 \cdot 10^{-5}$ M TMM and 2 M $CaCl_2$ was 0.900 which gives the same value as Ohnishi for the molar absorptivity coefficient of the Ca-TMM complex. Possible sources of errors in determining $K_{f,CaTMM}$ using the Bausch and Lomb Spectronic 21 include the effects on measured absorbance of inaccurate wavelength calibration

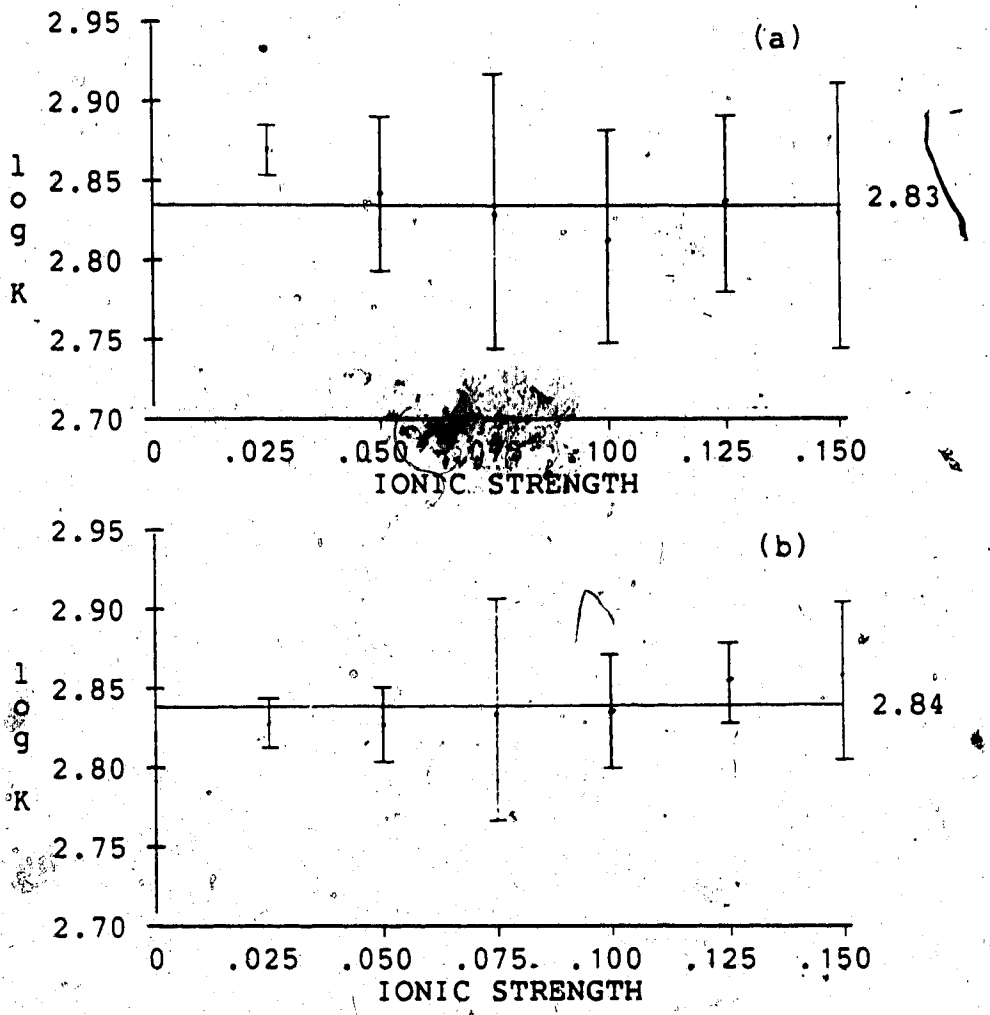

Figure 3. Calculated values of the formation constant of the Ca-TMM complex as a function of ionic strength using (a)absorbance data not corrected for inaccurate wavelength calibration or stray light and (b)corrected absorbance data.

and stray light.

Inaccurate wavelength calibration is suggested by the wavelength(502.5 nm) found here(using the Bausch and Lomb Spectronic 21) which gave the same molar absorptivity coefficient as did 554 nm. Ohnishi(1978) used 554 and 507 nm(a difference of 47 nm). The appropriate correction to be made is to find two wavelengths on the TMM absorbance spectrum which are separated by 47 nm and which give the

same molar absorptivity coefficient, and to then correct measured absorbances accordingly. The wavelengths thus determined were 551.7 and 504.7 nm, and measured absorbances were corrected using the following data taken from the Ca-TMM absorbance spectrum using $2.74 \cdot 10^{-4}$ M TMM in 2 M $CaCl_2$:

Abs(502.5)	Abs(554)	Abs(502.5)-Abs(554)
0.597	0.078	0.519
Abs(504.7)	Abs(551.7)	Abs(504.7)-Abs(551.7)
0.578	0.090	0.488

Measured absorbances were multiplied by 0.488/0.519 to give the absorbance that would have been measured had wavelength calibration been accurate.

The forgoing absorbances were corrected again for the effects of stray light. The correction assumes that stray light is a fraction of the incident light and bases the correction on increasing the absorbance of $5 \cdot 10^{-5}$ M TMM in 2 M $CaCl_2$ from 0.851x0.488/0.519=0.800 to 0.900. The procedure for making this correction was published by Harris and Kratochvil(1981); the symbols used are:

P_o is the power of the incident light(=1)

P_T is the power of the transmitted light

P_s is the power of stray light

Abs is absorbance.

By definition

$Abs = \log(P_o/P_T)$;

and, using the condition that P_s is a fraction of P_o,

$$Abs=\log((P_o+P_s)/(P_T+P_s)).$$

At Abs=0.9, P_T=0.126; the measured absorbance of $5\cdot10^{-4}$ M TMM in 2 M $CaCl_2$ is 0.8, so P_s=0.039. Measured absorbance is then corrected using the relationship

$$\text{real absorbance}=\log(1/P_T)$$

where P_T=(1.039/antilog measured absorbance)-0.039.

The value of log $K_{f,CaTMM}$, using these corrections to measured absorbance, is 2.837±0.043. Again the uncertainty is expressed as the 95% confidence limits:

$$p(759 \geq K_{f,CaTMM}=688 \geq 623)=0.95.$$

This value for $K_{f,CaTMM}$ is slightly higher than the value calculated using uncorrected absorbance data. It is lower than the value(970) published by Ohnishi(1978), and is not much different from the value(617) published by Gysling and Schwarzenbach(1949). The large difference between the value determined here and that of Ohnishi might be because of an error in calculating the activity coefficient of Ca^{+2} (using the Davies equation) which was used to convert Ohnishi's conditional stability constant(K_f^*=360; determined at only one ionic strength, I=0.1) to a thermodynamic stability constant($\gamma_{Ca^{+2}}$ at I=0.1 using Davies equation is 0.37):

$$K_f=K_f^*/\gamma_{Ca^{+2}}=360/0.37=970.$$

To convert $K_{f,CaTMM}$ from 360 to 688 requires $\gamma_{Ca^{+2}}$=0.52. Such a large error in calculating $\gamma_{Ca^{+2}}$ is not likely and this explanation for the difference in values for $K_{f,CaTMM}$ can be dismissed.

b) H^+ interference

Absorbance measured in solutions of TMM, and which may or may not contain Ca, was observed to decrease rapidly when pH was less than about 4. The effect was first observed in solutions of TMM containing aluminum. The rate at which absorbance decreased was only slightly slower in solutions of $AlCl_3$ as in equivalent solutions which contained sufficient HCl to give the same pH as results from the hydrolysis of Al^{+3}. The cause of the decrease in absorbance is, therefore, thought to be the result of a reaction involving the protonation of TMM^- or decomposition catalyzed by H^+.

At pH 5, absorbance did not decrease significantly over a 15 minute time period. At pH 4, a 3 percent decrease in absorbance was observed after 15 minutes. At pH 3.5, absorbance decreased 5 percent after 15 minutes; the same change at pH 3 took 1.5 minutes.

Jeremy(1975) observed decreases in the absorbance of TMM solutions containing calcium. He related the decrease in absorbance to calcium concentration and did not observe a proton concentration effect. Observations made in this study did not show a decrease in absorbance because of the presence of calcium. The causes of the effect observed here and by Jeremy(1975) do not seem to be related.

c) comparison to species calculation method

The colourimetric and species calculation methods were used to determine (Ca^{+2}) in some synthetic solutions and the values were compared for agreement. First, the effects of Na^{+} and Mg^{+2} on the determination of (Ca^{+2}) were examined. The absorbances(differences between absorbances measured at 507 and 554 nm) of solutions containing $5 \cdot 10^{-5}$ M TMM and 0.05 M Na_2SO_4 or $MgSO_4$ were measured and found to be 0.045 and 0.002, respectively. These results suggest that the Mg^{+2} interference in this analytical method is small and can be ignored without introducing significant error because magnesium concentrations in soil solutions are expected to be less than 0.05 M. However, the effect of sodium in solution should be recognized and its presence accounted for.

Using Ohnishi's(1978) values for the formation constant and molar absorptivity coefficient of Na-TMM, the absorbance of a solution containing $5 \cdot 10^{-5}$ M TMM and 0.05 M Na_2SO_4(species calculation gives $[Na^{+}]$=0.094 M) is calculated to be 0.131. The difference between the calculated and measured absorbances for this solution can be the result of inaccurate species calculation of Na^{+}, SO_4^{-2}, and $NaSO_4^{-}$ in the Na_2SO_4 solution or inaccurate values for the formation constant and molar absorptivity coefficient for the Na-TMM complex in the colourimetric method. The magnitude of these errors is shown in Table 5.

Table 5. Relative error observed when using colourimetric method to determine (Ca^{+2}) when Na_2SO_4 solutions(1-6) or NaCl solutions(7-12) are used, and values of correlation coefficients(r) when relative error is regressed on $[Na]_T$.

Solution	$[Ca]_T$ me/L	$[Na]_t$ me/L	Relative Error(%)'	r	
1	5	29	46		
2	5	58	55	0.9211	
3	5	87	56		
					0.6422
4	10	29	54		
5	10	58	71	0.9981	
6	10	87	85		
7	5	25	44		
8	5	50	60	0.9999	
9	5	75	75		
					0.9724
10	10	25	46		
11	10	50	67	0.9976	
12	10	75	84		

'Relative Error $= \dfrac{(Ca^{+2})spec. - (Ca^{+2})colour.}{(Ca^{+2})spec.}$

Three indications of error are evident in the data presented in Table 5: the increase in relative error with increasing $[Na]_T$ (solutions 1 to 3, 4 to 6, 7 to 9, or 10 to 12), the increase in relative error with increasing $[Ca]_T$(solutions 1 vs 4, 2 vs 5, 3 vs 6, 7 vs 10, 8 vs 11, or 9 vs 12), and the difference in the rate of increase of relative error with increasing $[Na]_T$ in solutions of Na_2SO_4 and NaCl(solutions 1 to 3 vs 7 to 9 or 4 to 6 vs 10 to 12). The sources of these errors are in species calculation(estimates of activity coefficients and values of formation constants) and in accounting for aqueous Na^+(values of the formation constant and molar absorptivity coefficient for the Na-TMM complex). It is difficult to

account for the contributions of individual sources of error to the total error. For example, the high values of r for solutions 1 to 3 , 4 to 6, 7 to 9 and 10 to 12 suggest a significant relationship between total sodium concentration and % relative error between the two methods for estimating (Ca^{+2}). Decreases in the values of r are observed when linear regression analysis is used to analyze the data for solutions 1 to 6(Na_2SO_4) and 7 to 12 (NaCl). The small decrease in r for solutions containing NaCl(no ion pairing) indicates small errors in the colourimetric method. A larger decrease in r for solutions containing Na_2SO_4 includes these small errors in the colourimetric method and some apparently larger errors in the species calculation method, but the contribution of each error to the total error is not easily determined or extrapolated for use in soil solutions. It is not within the scope of this study to verify the values of the formation constants for the $NaSO_4^-$ ion pair and the Na-TMM complex or for the molar absorptivity of the Na-TMM complex, or to test the relative accuracies of various methods of estimating activity coefficients.

Differences in the values of predicted (Ca^{+2}) between the colourimetric and species calculation methods are accepted; most of these differences are accounted for by the presence of aqueous sodium. If similar differences are observed when analysing soil solutions, then more evidence is gained that aqueous sodium is the major cause. If differences greater than those observed in synthetic

solutions are observed in soil solutions, then other interferences and/or inaccuracies are indicated.

B. Soil Solutions

The ability of the potentiometric and colourimetric methods to measure (Ca^{+2}) was tested by comparing the predicted values of (Ca^{+2}) in soil solutions to the equivalent prediction using the species calculation method. Of the saturated paste extracts collected from the 51 soil samples studied, 14 extracts were excluded from the comparisons because of poor ion balance(the ratio of the sum of anions to the sum of cations;ion balance is used as a test of the internal consistency of a set of analytical data). Only those extracts for which the ion balance was greater than 0.90 and less than 1.10 were included in the comparisons of predicted (Ca^{+2}). More commonly, poor ion balances are less than 0.90 than they are greater than 1.10; this effect is thought to be because the concentration of soluble organic anions was not determined(Mattigod *et al*,1981). Another 6 extracts were excluded from the comparisons of predicted (Ca^{+2}) using the colourimetric and species calculation methods because low pH prevented accurate absorbance measurement. Absorbance was measured for all prepared soil extracts first at 554 nm, and about 1/2 hour lapsed between the time TMM was added to soil extacts and absorbance measurement at 554 nm was complete. A second measurement was made and, if absorbance was at least 95

percent of the first measurement, the data was used in the methods comparison. Thus, 37 soil extracts were included in the comparison of predicted (Ca^{+2}) using the potentiometric and species calculation methods, and 31 soil extracts in the comparison of results using the colourimetric and species calculation methods.

1) Potentiometric method vs species calculation method

Good agreement was observed between the values of (Ca^{+2}) predicted by the potentiometric and species calculation methods(Table 6). Percent relative error was within 5% for 54% of the soil extracts and within 10% for 81% of the (Ca^{+2}) predictions. There was no obvious relationship between soil properties and relative error. Correcting for the presence of Na^{+}, K^{+}, and Mg^{+2} reduced relative error so that 68% of (Ca^{+2}) agreed to within 5%, and 84% agreed to within 10%. The large differences for samples 21 and 31(Table 6) may have been related to errors in the species calculation method because of high ionic strength and consequent inaccurate estimates of activity coefficients. The large difference for sample 31 may also have been related to interference in the potentiometric method because of high hydronium ion concentration (the pH of the extract was 1.56). Any relationship between relative error and pH is difficult to describe because the solutions studied here were not uniformly distributed along the pH range represented(1.5 to 8.5). Three groups of solutions are

Table 6. Values of calcium ion activity($x10^3$) in soil solutions using a speciation method(method 1) and values of percent relative error(error relative to the speciation method) when potentiometric(method 2) and colourimetric methods(methods 3 to 6) are used to determine calcium ion activity in the same soil solutions.

Sample Number	Sample Description			Method[1] 1	2	3	4	5	6
	A.High sulphate systems								
1	Hemaruka Ccasa			1.6515	9	20	97	69	39
2	salt spill + gypsum			5.6570	4	-26	41	5	-14
	Duagh-tillage,treatment,horizon								
3	Normal	Nil	Csk1	1.6722	2	-9	47	28	6
4			Csk2	1.7935	4	-8	50	29	7
5		$CaSO_4$	Csk1	1.7733	0	-4	57	36	12
6			Csk2	1.7413	5	0	62	40	16
7		$CaCO_3$	Csk1	1.8238	2	-5	55	34	10
8			Csk2	1.8403	4	-8	50	30	7
9	Deep Plow[2]	Nil	Ap	3.2158	2	-38	5	-13	-28
10			Bnt1	3.8810	-1	-39	4	-14	-30
11			Bnt2	2.2298	2	-23	27	9	-10
12			Csk	1.9473	2	-20	30	13	-7
13		$CaSO_4$	Ap	4.1790	-2	-40	4	-16	-31
14			Bnt1	3.1744	2	-30	19	-2	-19
15			Bnt2	2.1542	17	-16	38	18	-3
16			Csk	1.8442	6	-15	37	19	-2
17		$CaCO_3$	Ap	3.3835	0	-39	3	-14	-29
18			Bnt1	3.3764	2	-30	20	-1	-19
19			Bnt2	2.4881	3	-21	31	11	-9
20			Csk	1.7717	9	-9	48	28	6
	B.Highly soluble calcium salts								
21	salt spill + $Ca(NO_3)_2$			6.1824	51	146	458	247	186
	C.Low total salt content								
22	Malebisch			0.3568	-17	-40	-9	-16	-30
23	Culp Cca			0.7168	-12	-23	20	9	-11

	D.Low pH					
24	Boundary Cs	0.1486	-8	-56	-34	-38	-49
25	Josephine BCg	1.4367	-16	-34	6	-6	-23
	near sulphur blocks						
26	0 - 1 cm	3.7438	0	-61	-36	-45	-55
27	"	4.1042	0	-4	5	-15	-31
28	"	1.3356	10				
29	"	2.2825	10				
30	"	2.8160	1				
31	"	1.0351	87				
32	1 - 3 cm	2.6568	-6	-53	-25	-34	-46
33	"	2.5083	-6	-59	-34	-42	-52
34	"	4.2282	1	-42	0	-19	-33
35	"	3.4962	-6	-38	7	-12	-28
36	"	1.7817	0				
37	"	2.8435	10				

Method	$K_{\ell,CaTMM}$	a_{CaTMM}	$K_{\ell,NaTMM}$	a_{NaTMM}
3	970	18000	13.1	6300
4	681	17000	13.1	6300
5	688	18000	13.1	6300
6	835	18000	13.1	6300

[2] samples were collected at depths corresponding to the Ap, Bnt1, Bnt2, and Csk horizons

[3] blanks mean comparisons of (Ca^{+2}) estimates were not done because low pH caused unstable absorbance

evident(Appendix 3 and Table 6)- 1 solution at pH 1.5, (relative error is 87.8%), 11 solutions from pH 2 to 4(relative error ranges from 10.2% to -16.3%), and 25 solutions from pH 6.5 to 8.5(relative error ranges from 17.0% to -12.3%,except number 21 at 51.4%). The manufacturer of the calcium ion-selective electrode used in this study claims that errors in measuring calcium ion concentration at 2 me/L should be no more than 10% if pH is no less than 2.4 and ionic strength is similar for samples and standards(Orion,1979). The solutions with pH less than 4 showed up to 10% deviation - the relative error between the two methods used to estimate (Ca^{+2}) increased to about 10% when the pH was decreased to 2.5 and then relative error increased to 87.8% at pH 1.56. Solutions were not included between pH 2.5 and 1.5 so, although supporting evidence can not be presented , the electrode seems to fail significantly in estimating (Ca^{+2}) when the pH is less than about 2.5. Differences in (Ca^{+2}) predictions for three other solutions (samples 22,23,25) were between 10 and 20 percent. The calcium ion activities of these solutions, as predicted by the species calculation method, were among the lowest of the solutions studies. Errors in the species calculation method have the greatest effect on calculated relative error in solutions of low (Ca^{+2}). Occurrence of such errors is not unexpected - the total calcium concentration is reported to the nearest 0.1 me/L and, at low $[Ca]_T$, an error of 0.1 me/L is large enough to account for a 5 to 10 percent error in

calculating (Ca^{+2}) using the species calculation method(Table 7).

2) Colourimetric method vs species calculation method

Estimates of calcium ion activity in soil solutions using the colourimetric and species calculation methods agreed poorly. Less than 50% of the estimates agreed to within a relative error of 15%(Table 8).

As was observed in synthetic solutions, relative error correlates closely to total sodium concentration(Table 8). The presence of sodium in solution seems to be the largest contributor to differences in (Ca^{+2}) estimates. Another, smaller contributor to error could be inaccuracies in the values used for the formation constant and molar absorptivity coefficient of the Ca-TMM and Na-TMM complexes. Four combinations of these values were tested for their respective effects on the relative error in (Ca^{+2}) estimates using the species calculation and colourimetric methods.

Methods 3 to 6(Table 8) are the same except that different values for the formation constant and molar absorptivity coefficient of CaTMM were used to calculate calcium ion activity. Method 3 used the values published by Ohnishi(1978). Methods 4 and 5 used the values determined in this study. Method 6 used values which gave the same estimates of (Ca^{+2}) in a saturated gypsum solution using the colourimetric and species calculation methods. This method was included as an attempt to reduce the uncertainty in

Table 7. Effect on relative error between (Ca^{+2}) predictions using the potentiometric and species calculation methods when errors are made in determining low total calcium concentration.

Sample Number	1	% Relative Error 2	3	4
22	0.3568	-17	+13	-8
23	0.7168	-12	-8	-3
25	1.4367	-16	-12	-7

1 (Ca^{+2})x10^3 using the species calculation method
2 assume determination of (Ca^{+2}) is correct
3 assume $[Ca]_T$ should be 0.1 me/L lower
4 assume $[Ca]_T$ should be 0.2 me/L lower

deriving the formation constant for the Ca-TMM complex. The ion pairing properties of Ca^{+2} and SO_4^{-2} are well known and an estimate of (Ca^{+2}) in a saturated solution of gypsum, along with some colourimetric data, was used to derive $K_{f,CaTMM}$.

Estimates of (Ca^{+2}) in a saturated gypsum solution using methods 3 to 5 agree poorly with (Ca^{+2}) estimates using the species calculation method(Table 8). If the value used for either the formation constant or the molar absorptivity coefficient for the Ca-TMM complex is low, the estimate of (Ca^{+2}) is high. The relative magnitude of the relative error was the same regardless of which values for $K_{f,CaTMM}$ or a_{CaTMM} were used. In other words, of the 31 relative errors calculated from a comparison of predictions of (Ca^{+2}) in soil solutions using the colourimetric and species calculation methods, some soil solutions always showed the highest relative error and some other soil solutions always showed the lowest relative error(Table 6). Both positive and

Table 8. Effect on determination of (Ca^{+2}) in soil solutions of errors in estimating the formation constants and molar absorptivity coefficients of the Ca-TMM and Na-TMM complexes.

Method[1]	Fraction(%) of (Ca^{+2}) estimates within a relative error of: ±5%	±10%	±15%	±20%	Relative error (%) in estimates of (Ca^{+2}) in saturated gypsum solution[2]	r
3	7	23	23	37	-13.9	0.91[3]
5	7	20	40	60	21.4	0.74[3]
6	7	27	43	53	0.0	0.91[3]

[1]Method 3 used $K_{f,CaTMM}$=970 and a_{CaTMM}=18000(Ohnishi,1978)
5 used $K_{f,CaTMM}$=688 and a_{CaTMM}=18000(this study)[a]
6 used $K_{f,CaTMM}$=835 and a_{CaTMM}=18000(this study)[b]

[a]values calculated using corrected absorbance data

[b]values that give zero relative error for a saturated gypsum solution

[2]Calculation is of relative error in (Ca^{+2}) using a colourimetric method and assuming the species calculation method to be correct.

[3]Linear regression does not include sample number 21 because both relative error and $[Na]_T$ are very high and inclusion of this data pair forces a good correlation coefficient. Regression is of $[Na]_T$ on % relative error.

negative values for relative error were observed. Positive values indicate that the effects of sodium were undercorrected; the result was that (Ca^{+2}) was overestimated. Similarly, negative relative error suggests an overcorrection for Na^{+} effects; the estimate of (Ca^{+2}) would then be low. Figure 4 shows the magnitude of relative error using four methods of calculating (Ca^{+2}). In Figure 4, the numbers 3, 4, 5, and 6 represent the four methods used to calculate (Ca^{+2}). The numbers are placed above a range of relative error and to the right of the corresponding number of (Ca^{+2}) estimates falling within that range of relative error. For example, using method 5, six estimates of (Ca^{+2}) are within 10% of the same estimates using the species calculation method. Using method 3, seven estimates are within 10%; using method 6, eight estimates are within 10%; and, using method 4, nine estimates are within 10%. At six places in Figure 4, one or more numbers would fall on top of an already placed number (when two or more methods estimate (Ca^{+2}) equally well). For those six cases, the numbers representing the methods are clustered to the right of a dot which is properly placed. Because of generally lower relative error, methods 5 and 6 seem to be superior to methods 3 and 4. Values of the correlation coefficient for relative error and $[Na]_T$ (Table 8) indicate that about 80% of the differences in (Ca^{+2}) predictions can be explained on the basis of the presence of sodium in solution. Method 6 seems to be superior to method 5 because of a better

accounting for variation in the data as a result of sodium in solution(Table 8).

The results of this study suggest that accurate values for the formation constants and molar absorptivity coefficients for the Na-TMM and Ca-TMM complexes are required for the method to be successful. Until high quality values are available, this colourimetric method is of little value in determining (Ca^{+2}), especially when aqueous sodium is present.

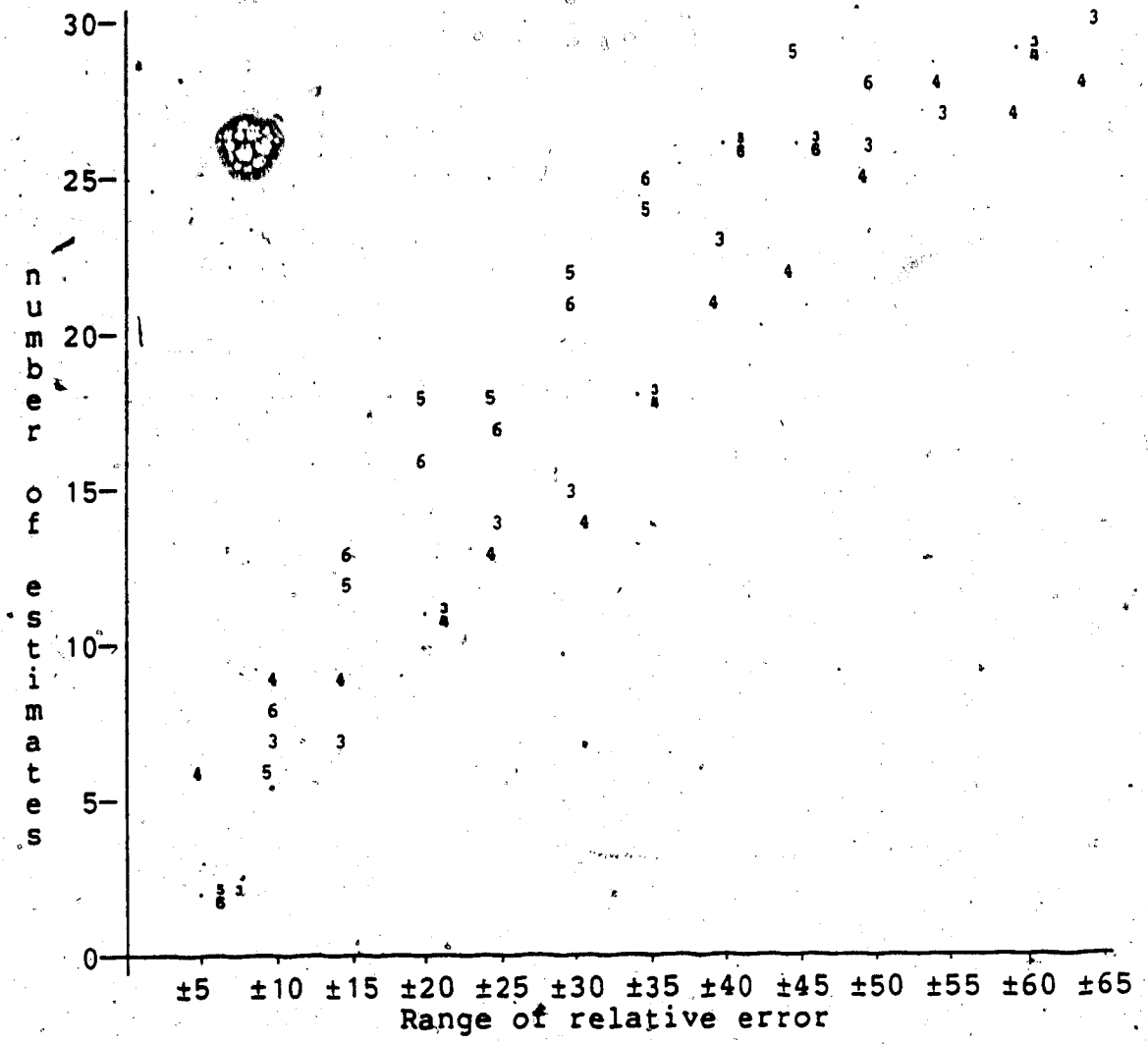

Figure 4. Distribution of relative error in terms of the number of (Ca^{+2}) estimates(maximum is 30 - sample #21 is omitted) within various ranges of relative error.

V. CONCLUSIONS

Three methods were used to determine calcium ion activity in soil solutions and the (Ca^{+2}) estimations obtained by them were compared for agreement. Good agreement was observed between the (Ca^{+2}) estimations using species calculation and ion-selective electrode methods. A colourimetric method using tetramethylmurexide agreed poorly with the other two methods and is considered to be an unreliable method of estimating (Ca^{+2}) under the present conditions of use.

The main sources of disagreement between the species calculation and potentiometric methods are thought to be inaccurate values for the formation constant of the $CaCl^{+}$ ion pair and for the potentiometric selectivity coefficients which describe Na^{+}, K^{+}, and Mg^{+} interference in the potentiometric determination of (Ca^{+2}). Despite these sources of error, only 19% of 37 soil extracts tested disagreed by more than 10% relative error. This disagreement is thought to be acceptably small.

Differences which are greater than estimated experimental error are seen in the comparison of (Ca^{+2}) estimations using the species calculation and colourimetric methods. Less than 50% of the estimates of (Ca^{+2}) in soil solutions agree to within 15% relative error. The greatest contributor to this difference is thought to be the interference caused by sodium in solution. Sodium forms a coloured complex which contributes to measured absorbance.

Attempts to correct for this added absorbance were only partly successful. The values available for the formation constant and molar absorptivity coefficient of the Na-TMM complex are thought to be insufficiently accurate. These inaccuracies seem to preclude reliable corrections for sodium interference in the colourimetric method for calcium ion activity.

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A listing of the computer program SALT, which calculates the distribution of aqueous species in soil solutions, follows:

```
      REAL MG,MGT,MGCO3,MGHCO3,MGSO4,MGOH,MGTOT
      REAL MN,MNSO4,MNHCO3,MNCL,MNOH,MNTOT,MNT
      REAL NA,NAT,NACO3,NAHCO3,NASO4,NATOT
      REAL K,KT,KCO3,KHCO3,KSO4,KTOT
      REAL NO3,NO3T,NO3TOT,NH4
      REAL I
      INTEGER SMPLNO,ITN,NDS
      READ(5,10)NDS
   10 FORMAT(I3)
C NDS = NUMBER OF DATA SETS
      DO 200 J=1,NDS
      READ(5,20)SMPLNO,CNA,CK,CCA,CMG,CNH4,CFE,CMN,CAL
      READ(5,25)CSO4,ALKTIT,CCL,CNO3,CPO4,EC,PH
   20 FORMAT(I3,8F7.2)
   25 FORMAT(F10.2,6F7.2)
C TOTAL ION CONCENTRATIONS(T) IN MOLES/L CALCULATED
C FROM INPUT DATA(C) IN MEQ/L ARE:
      NAT=CNA*.001
      KT=CK*.001
      CAT=CCA*.0005
      MGT=CMG*.0005
      NH4T=CNH4*.001
      FET=CFE*.001/3.
      MNT=CMN*.0005
      ALT=CAL*.001/3.
C HYDRONIUM ION ACTIVITY IS DENOTED 'AH'
      AH=1./10.**PH
      SO4T=CSO4*.0005
      CLT=CCL*.001
      NO3T=CNO3*.001
      PO4T=CPO4*.001/3.
C AN INITIAL ESTIMATE OF TOTAL ALKALINITY(ALKTOT)
C CORRECTS FOR THE CARBONATE TITRATION BEING ACCOUNTED
C FOR TWICE IN THE TITRATED ALKINITY(ALKTIT):
      F1=10.**(-10.33)/AH
      F2=1000.*(1./(1.+F1)+2./(1.+1./F1))
      ALKTOT=ALKTIT/F2
C AN INITIAL ESTIMATE OF IONIC STRENGTH USES THE METHOD
C OF GRIFFIN AND JURINAK(1973):
      I=EC*0.013
C ACTIVITY COEFFICIENTS(G) ARE CALCULATED USING DAVIES
C EQUATION EXCEPT THAT CALCULATION OF G FOR NEUTRAL
C ION PAIRS USES THE SETCHENOW EQUATION(A SIMPLIFICATION
C OF THE DAVIES EQUATION USED WHEN THE CHARGE ON AN ION
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C PAIR IS ZERO) WHICH IS EXPRESSED AS LOG G=KI WHERE K
C IS A SALTING COEFFICIENT SET AT 0.1 (SPOSITO,1981).
C INITIAL ESTIMATES OF MAJOR CATION ACTIVITY COEFFICIENTS(G)
C ARE:
      Z=(I**.5/(1.+I**.5))-.3*I
      GAL=10.**(-4.6044*Z)
      GFE=GAL
      GCA=10.**(-2.0464*Z)
      GMG=GCA
      GMN=GCA
      GNA=10.**(-.5116*Z)
      GK=GNA
      GNH4=GNA
C INITIAL ESTIMATES OF MAJOR CATION ACTIVITIES ARE:
      ANA=NAT*GNA
      AK=KT*GK
      ANH4=NH4T*GNH4
      ACA=CAT*GCA
      AMG=MGT*GMG
      AMN=MNT*GMN
      AAL=ALT*GAL
      AFE=FET*GFE
C CALCULATION OF THE DISTRIBUTION OF AQUEOUS SPECIES USES A
C METHOD OF SUCCESSIVE APPROXIMATION; ITERATION STOPS WHEN
C THE CHANGE IN CALCIUM AND PHOSPHATE CONCENTRATIONS IS LESS
C THAN 0.01% OR AFTER A MAXIMUM OF 10 ITERATIONS(ITN)
      CA1=0.
      PTOT1=0.
      DO 30 ITN=1,25
      GCO3=GCA
      GSO4=GCA
      GHPO4=GCA
      GHCO3=GNA
      GNO3=GNA
      GCL=GNA
      GNACO3=GNA
      GNASO4=GNA
      GKCO3=GNA
      GKSO4=GNA
      GH2PO4=GNA
      GCAHCO=GNA
      GCAOH=GNA
      GCANO3=GNA
      GCACL=GNA
      GCAH2P=GNA
      GMGHCO=GNA
      GMGOH=GNA
      GALOH2=GNA
      GALSO4=GNA
      GMNOH=GNA
      GMNCL=GNA
      GMNHCO=GNA
      GFEOH2=GNA
      GFESO4=GNA
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      GFEHPO=GNA
      GALOH=GCA
      GFEOH=GCA
      GFECL=GCA
      GFENO3=GCA
      GFEH2P=GCA
      GCACO3=10.**(0.1*I)
      GCASO4=GCACO3
      GMGCO3=GCACO3
      GMGSO4=GCACO3
      GNAHCO=GCACO3
      GKHCO3=GCACO3
      GMNSO4=GCACO3
      GH3PO4=GCACO3
      GCAHPO=GCACO3
C THE SULFATE MASS BALANCE CONSIDERS 8 AQUEOUS SPECIES:
C SO4, NASO4, KSO4, CASO4, MGSO4, ALSO4, FESO4, MNSO4
C SULFATE ION ACTIVITY IS DENOTED 'ASO4'
      QS1=1.0/GSO4
      QS2=(10.**0.65)*ANA/GNASO4
      QS3=(10.**0.85)*AK/GKSO4
      QS4=(10.**2.31)*ACA/GCASO4
      QS5=(10.**2.23)*AMG/GMGSO4
      QS6=(10.**3.2)*AAL/GALSO4
      QS7=(10.**4.15)*AFE/GFESO4
      QS8=(10.**2.26)*AMN/GMNSO4
      ASO4=SO4T/(QS1+QS2+QS3+QS4+QS5+QS6+QS7+QS8)
C THE ALKALINITY MASS BALANCE CONSIDERS 11 AQUEOUS SPECIES:
C CO3, NACO3, KCO3, CACO3, MGCO3,
C HCO3, NAHCO3, KHCO3, CAHCO3, MGHCO3, MNHCO3
C BICARBONATE ION ACTIVITY IS DENOTED 'AHCO3'
C CARBONATE ION ACTIVITY IS DENOTED 'ACO3'
      QHC1=(10.**(-10.33))/(AH*GCO3)
      QHC2=(10.**(-9.78))*ANA/(AH*GNACO3)
      QHC3=(10.**(-9.03))*AK/(AH*GKCO3)
      QHC4=(10.**(-7.18))*ACA/(AH*GCACO3)
      QHC5=(10.**(-7.45))*AMG/(AH*GMGCO3)
      QHC6=1./GHCO3
      QHC7=(10.**0.16)*ANA/GNAHCO
      QHC8=(10.**(-0.25))*AK/GKHCO3
      QHC9=(10.**1.02)*ACA/GCAHCO
      QHC10=(10.**0.95)*AMG/GMGHCO
      QHC11=(10.**1.8)*AMN/GMNHCO
      AHCO3=ALKTOT/(QHC1+QHC2+QHC3+QHC4+QHC5+QHC6+QHC7+
     +QHC8+QHC9+QHC10+QHC11)
      ACO3=(10.**(-10.33))*AHCO3/AH
C THE NITRATE MASS BALANCE CONSIDERS 3 AQUEOUS SPECIES:
C NO3, CANO3, FENO3
C NITRATE ION ACTIVITY IS DENOTED 'ANO3'
      QNO1=1.0/GNO3
      QNO2=(10.**0.68)*ACA/GCANO3
      QNO3=10.*AFE/GFENO3
      ANO3=NO3T/(QNO1+QNO2+QNO3)
C THE CHLORIDE MASS BALANCE CONSIDERS 4 AQUEOUS SPECIES:
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C CL, CACL, FECL, MNCL
C CHLORIDE ION ACTIVITY IS DENOTED 'ACL'
      QCL1=1.0/GCL
      QCL2=(10.**0.6)*ACA/GCACL
      QCL3=(10.**1.48)*AFE/GFECL
      QCL4=(10.**0.61)*AMN/GMNCL
      ACL=CLT/(QCL1+QCL2+QCL3+QCL4)
C THE PHOSPHATE MASS BALANCE CONSIDERS 7 AQUEOUS SPECIES:
C HPO4,H2PO4,H3PO4,FEH2PO4,FEHPO4,CAH2PO4,CAHPO4
C H2PO4 ACTIVITY IS DENOTED 'AH2PO4'
      QPO1=1./GH2PO4
      QPO2=(10.**(-7.2))/(AH*GHPO4)
      QPO3=(10.**2.15)*AH/GH3PO4
      QPO4=(10.**5.43)*AFE/GFEH2P
      QPO5=(10.**3.71)*AFE/(GFEHPO*AH)
      QPO6=(10.**1.4)*ACA/GCAH2P
      QPO7=(10.**(-4.46))*ACA/(AH*GCAHPO)
      AH2PO4=PO4T/(QPO1+QPO2+QPO3+QPO4+QPO5+QPO6+QPO7)
C THE SODIUM MASS BALANCE CONSIDERS 4 AQUEOUS SPECIES:
C NA, NAHCO3, NACO3, NASO4
      QNA1=1./GNA
      QNA2=(10.**0.16)*AHCO3/GNAHCO
      QNA3=(10.**0.55)*ACO3/GNACO3
      QNA4=(10.**0.65)*ASO4/GNASO4
      ANA=NAT/(QNA1+QNA2+QNA3+QNA4)
C THE POTASSIUM MASS BALANCE CONSIDERS 4 AQUEOUS SPECIES:
C K, KHCO3, KCO3, KSO4
      QK1=1./GK
      QK2=(10.**(-0.25))*AHCO3/GKHCO3
      QK3=(10.**1.3)*ACO3/GKCO3
      QK4=(10.**0.85)*ASO4/GKSO4
      AK=KT/(QK1+QK2+QK3+QK4)
C THE CALCIUM MASS BALANCE CONSIDERS 9 AQUEOUS SPECES:
C CA, CAHCO3, CACO3, CASO4, CAOH, CANO3, CACL, CAH2PO4
      QCA1=1./GCA
      QCA2=(10.**1.02)*AHCO3/GCAHCO
      QCA3=(10.**3.15)*ACO3/GCACO3
      QCA4=(10.**2.31)*ASO4/GCASO4
      QCA5=(10.**(-12.7))/(AH*GCAOH)
      QCA6=(10.**0.68)*ANO3/GCANO3
      QCA7=(10.**0.6)*ACL/GCACL
      QCA8=(10.**1.4)*AH2PO4/GCAH2P
      QCA9=(10.**(-4.46))*AH2PO4/(AH*GCAHPO)
      ACA=CAT/(QCA1+QCA2+QCA3+QCA4+QCA5+QCA6+QCA7+QCA8+QCA9)
C THE MAGNESIUM MASS BALANCE CONSIDERS 5 AQUEOUS SPECIES:
C MG, MGHCO3, MGCO3, MGSO4, MGOH
      QMG1=1./GMG
      QMG2=(10.**0.95)*AHCO3/GMGHCO
      QMG3=(10.**2.88)*ACO3/GMGCO3
      QMG4=(10.**2.23)*ASO4/GMGSO4
      QMG5=(10.**(-11.42))/(AH*GMGOH)
      AMG=MGT/(QMG1+QMG2+QMG3+QMG4+QMG5)
C THE IRON MASS BALANCE CONSIDERS 8 AQUEOUS SPECIES:
C FE, FEOH, FE(OH)2, FECL, FENO3, FESO4, FEH2PO4, FEHPO4
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C FE ACTIVITY IS DENOTED 'AFE'
      QFE1=1./GFE
      QFE2=(10.**(-2.19))/(AH*GFEOH)
      QFE3=(10.**(-5.69))/((AH**2.)*GFEOH2)
      QFE4=(10.**1.48)*ACL/GFECL
      QFE5=10.*ANO3/GFENO3
      QFE6=(10.**4.15)*ASO4/GFESO4
      QFE7=(10.**5.43)*AH2PO4/GFEH2P
      QFE8=(10.**3.71)*AH2PO4/(GFEHPO*AH)
      AFE=FET/(QFE1+QFE2+QFE3+QFE4+QFE5+QFE6+QFE7+QFE8)
C THE MANGANESE MASS BALANCE CONSIDERS 5 AQUEOUS SPECIES:
C MN, MNOH, MNCL, MNHCO3, MNSO4
C MN ACTIVITY IS DENOTED AMN
      QMN1=1./GMN
      QMN2=(10.**(-10.95))/(AH*GMNOH)
      QMN3=(10.**0.61)*ACL/GMNCL
      QMN4=(10.**1.8)*AHCO3/GMNHCO
      QMN5=(10.**2.26)*ASO4/GMNSO4
      AMN=MNT/(QMN1+QMN2+QMN3+QMN4+QMN5)
C THE ALUMINUM MASS BALANCE CONSIDERS 4 AQUEOUS SPECIES:
C AL, ALOH, AL(OH)2, ALSO4
C AL ACTIVITY IS DENOTED 'AAL'
      QAL1=1./GAL
      QAL2=(10.**(-5.02))/(AH*GALOH)
      QAL3=(10.**(-9.3))/((AH**2.)*GALOH2)
      QAL4=(10.**3.2)*ASO4/GALSO4
      AAL=ALT/(QAL1+QAL2+QAL3+QAL4)
C AQUEOUS SPECIES CONCENTRATIONS IN MOLES/L:
      NA=ANA*QNA1
      NAHCO3=ANA*QNA2
      NACO3=ANA*QNA3
      NASO4=ANA*QNA4
      K=AK*QK1
      KHCO3=AK*QK2
      KCO3=AK*QK3
      KSO4=AK*QK4
      CA=ACA*QCA1
      CAHCO3=ACA*QCA2
      CACO3=ACA*QCA3
      CASO4=ACA*QCA4
      CAOH=ACA*QCA5
      CANO3=ACA*QCA6
      CACL=ACA*QCA7
      CAH2PO=ACA*QCA8
      CAHPO4=ACA*QCA9
      MG=AMG*QMG1
      MGHCO3=AMG*QMG2
      MGCO3=AMG*QMG3
      MGSO4=AMG*QMG4
      MGOH=AMG*QMG5
      FE=AFE*QFE1
      FEOH=AFE*QFE2
      FEOH2=AFE*QFE3
      FECL=AFE*QFE4
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```
      FENO3=AFE*QFE5
      FESO4=AFE*QFE6
      FEH2PO=AFE*QFE7
      FEHPO4=AFE*QFE8
      MN=AMN*QMN1
      MNOH=AMN*QMN2
      MNCL=AMN*QMN3
      MNHCO3=AMN*QMN4
      MNSO4=AMN*QMN5
      AL=AAL*QAL1
      ALOH=AAL*QAL2
      ALOH2=AAL*QAL3
      ALSO4=AAL*QAL4
      H2PO4=AH2PO4*QPO1
      HPO4=AH2PO4*QPO2
      H3PO4=AH2PO4*QPO3
      SO4=ASO4*QS1
      CO3=AHCO3*QHC1
      HCO3=AHCO3*QHC6
      NO3=ANO3*QNO1
      CL=ACL*QCL1
      CO3T=CO3+NACO3+KCO3+CACO3+MGCO3
      HCO3T=HCO3+NAHCO3+KHCO3+CAHCO3+MGHCO3+MNHCO3
      ALKTOT=(ALKTIT-1000.*CO3T)/1000.
      CHECK=ABS((CA-CA1)*100./CA)
      IF(CHECK .LE. 0.01)GO TO 35
      CA1=
      GO T
   35 PTOT=HPO4+H2PO4+H3PO4+FEH2PO+FEHPO4+CAH2PO+CAHPO4
      CHECK2=ABS((PTOT-PTOT1)*100./PTOT)
      IF(CHECK2 .LE. 0.01)GO TO 40
      PTOT1=PTOT
C THIS SECTION CALCULATES IONIC STRENGTH(I)
C AND THE NEXT ESTIMATE OF THE ACTIVITY
C COEFFICIENTS OF THE CATIONS
   45 R=9.*(FE+AL)
      S=4.*(SO4+CO3+HPO4+CA+MG+MN+FENO3+FECL+FEH2PO+
     +FEOH+ALOH)
      T=HCO3+NO3+CL+H2PO4+NA+K+NH4T+NASO4+KSO4+FESO4+ALSO4
      U=NACO3+KCO3+CAHCO3+MGHCO3+MNHCO3+CANO3+FEHPO
      V=CACL+MNCL+CAOH+MGOH+MNOH+FEOH2+ALOH2+CAH2PO
      I=0.5*(R+S+T+U+V)
      Z=(I**.5/(1.+I**.5))-.3*I
      GAL=10.**(-4.6044*Z)
      GFE=GAL
      GCA=10.**(-2.0464*Z)
      GMG=GCA
      GMN=GCA
      GNA=10.**(-.5116*Z)
      GK=GNA
      GNH4=GNA
   30 CONTINUE
C THIS SECTION, FOR THE PURPOSE OF PROVIDING A HARD
C COPY OUTPUT, CONVERTS THE CONCENTRATIONS AND
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C ACTIVITIES OF AQUEOUS SPECIES TO MMOLES/L
  40 NA=NA*1000.
     ANA=ANA*1000.
     NAHCO3=NAHCO3*1000.
     ANAHCO=NAHCO3*GNAHCO
     NACO3=NACO3*1000.
     ANACO3=NACO3*GNACO3
     NASO4=NASO4*1000.
     ANASO4=NASO4*GNASO4
     K=K*1000.
     AK=AK*1000.
     KHCO3=KHCO3*1000.
     AKHCO3=KHCO3*GKHCO3
     KCO3=KCO3*1000.
     AKCO3=KCO3*GKCO3
     KSO4=KSO4*1000.
     AKSO4=KSO4*GKSO4
     CA=CA*1000.
     ACA=ACA*1000.
     CAHCO3=CAHCO3*1000.
     ACAHCO=CAHCO3*GCAHCO
     CACO3=CACO3*1000.
     ACACO3=CACO3*GCACO3
     CASO4=CASO4*1000.
     ACASO4=CASO4*GCASO4
     CAOH=CAOH*1000.
     ACAOH=CAOH*GCAOH
     CANO3=CANO3*1000.
     ACANO3=CANO3*GCANO3
     CACL=CACL*1000.
     ACACL=CACL*GCACL
     CAH2PO=CAH2PO*1000.
     ACAH2P=CAH2PO*GCAH2P
     CAHPO4=CAHPO4*1000.
     ACAHPO=CAHPO4*GCAHPO
     MG=MG*1000.
     AMG=AMG*1000.
     MGHCO3=MGHCO3*1000.
     AMGHCO=MGHCO3*GMGHCO
     MGCO3 =MGCO3*1000.
     AMGCO3=MGCO3*GMGCO3
     MGSO4=MGSO4*1000.
     AMGSO4=MGSO4*GMGSO4
     MGOH=MGOH*1000.
     AMGOH=MGOH*GMGOH
     FE=FE*1000.
     AFE=AFE*1000.
     FEOH=FEOH*1000.
     AFEOH=FEOH*GFEOH
     FEOH2=FEOH2*1000.
     AFEOH2=FEOH2*GFEOH2
     FECL=FECL*1000.
     AFECL=FECL*GFECL
     FENO3=FENO3*1000.
```

```
      AFENO3=FENO3*GFENO3
      FESO4=FESO4*1000.
      AFESO4=FESO4*GFESO4
      FEH2PO=FEH2PO*1000.
      AFEH2P=FEH2PO*GFEH2P
      FEHPO4=FEHPO4*1000.
      AFEHPO=FEHPO4*GFEHPO
      MN=MN*1000.
      AMN=AMN*1000.
      MNOH=MNOH*1000.
      AMNOH=MNOH*GMNOH
      MNCL=MNCL*1000.
      AMNCL=MNCL*GMNCL
      MNHCO3=MNHCO3*1000.
      AMNHCO=MNHCO3*GMNHCO
      MNSO4=MNSO4*1000.
      AMNSO4=MNSO4*GMNSO4
      AL=AL*1000.
      AAL=AAL*1000.
      ALOH=ALOH*1000.
      AALOH=ALOH*GALOH
      ALOH2=ALOH2*1000.
      AALOH2=ALOH2*GALOH2
      ALSO4=ALSO4*1000.
      AALSO4=ALSO4*GALSO4
      HCO3=HCO3*1000.
      AHCO3=AHCO3*1000.
      CHCO3=HCO3T*1000.
      CO3=CO3*1000.
      ACO3=ACO3*1000.
      CCO3=CO3T*1000.
      SO4=SO4*1000.
      ASO4=ASO4*1000.
      NO3=NO3*1000.
      ANO3=ANO3*1000.
      CL=CL*1000.
      ACL=ACL*1000.
      HPO4=HPO4*1000.
      AHPO4=HPO4*GHPO4
      H2PO4=H2PO4*1000.
      AH2PO4=AH2PO4*1000.
      H3PO4=H3PO4*1000.
C THE ANION/CATION BALANCE(BAL) IS:
      ANIONS=CSO4+CHCO3+CCO3+CCL+CNO3+CPO4
      CATION=CNA+CK+CCA+CMG+CFE+CMN+CAL+CNH4
      BAL=ANIONS/CATION
      NATOT=NA+NASO4+NACO3+NAHCO3
      KTOT=K+KSO4+KCO3+KHCO3
      CATOT=2.*(CA+CASO4+CACO3+CAHCO3+CANO3+CACL+
     +CAOH+CAH2PO+CAHPO)
      MGTOT=2.*(MG+MGSO4+MGCO3+MGHCO3+MGOH)
      FETOT=3.*(FE+FESO4+FENO3+FECL+FEH2PO+FEOH+
     +FEOH2+FEHPO4)
      MNTOT=2.*(MN+MNSO4+MNHCO3+MNCL+MNOH)
```

```
      ALTOT=3.*(AL+ALSO4+ALOH+ALOH2)
      SO4TOT=2.*(SO4+NASO4+KSO4+CASO4+MGSO4+FESO4+
     +MNSO4+ALSO4)
      CO3TOT=2.*(CO3+NACO3+KCO3+CACO3+MGCO3)
      HCOTOT=HCO3+NAHCO3+KHCO3+CAHCO3+MGHCO3+MNHCO3+CO3TOT
      NO3TOT=NO3+CANO3+FENO3
      CLTOT=CL+CACL+FECL+MNCL
      PO4TOT=3.*(HPO4+H2PO4+H3PO4+FEH2PO+FEHPO4+
     +CAH2PO+CAHPO4)
      WRITE(6,50)SMPLNO,I,BAL,PH,EC,ITN
   50 FORMAT('1',5X,'SMPLNO=',I2,2X,'I=',F6.4,2X,'BAL=',
     +F4.2,2X,'PH=',F5.2,2X,'EC=',F5.2,2X,'ITN=',I2)
      WRITE(6,55)
   55 FORMAT('0',10X,'I/D',7X,'FREE',5X,'SO4',6X,'CO3',6X,
     +'HCO3',5X,'NO3',7X,'CL',5X,'H2PO4',5X,'HPO4',6X,
     +'OH',5X,'[OH]2',4X,'TOTAL')
      WRITE(6,60)'I/D',CSO4,ALKTIT,CNO3,CCL,CPO4,'(MEQ/L)'
   60 FORMAT(A,F32.4,F18.4,3F9.4,28X,A)
      WRITE(6,65)'FREE [ ]',SO4,CO3,HCO3,NO3,CL,H2PO4,HPO4
   65 FORMAT(A,F27.4,6F9.4)
      WRITE(6,65)'      A/C',GSO4,GCO3,GHCO3,GNO3,
     +GCL,GH2PO4,GHPO4
      WRITE(6,65)'      ( )',ASO4,ACO3,AHCO3,ANO3,
     +ACL,AH2PO4,AHPO4
      WRITE(6,70)'NA    [ ]',CNA,NA,NASO4,[illegible]NAHCO3,NATOT
   70 FORMAT('0',A,5F9.4,F63.4)
      WRITE(6,75)'A/C',GNA,GNASO4,GNACO3,GNAHCO
   75 FORMAT(6X,A,F18.4,3F9.4)
      WRITE(6,75)'( )',ANA,ANASO4,ANACO3,ANAHCO
      WRITE(6,70)'K     [ ]',CK,K,KSO4,KCO3,KHCO3,KTOT
      WRITE(6,75)'A/C',GK,GKSO4,GKCO3,GKHCO3
      WRITE(6,75)'( )',AK,AKSO4,AKCO3,AKHCO3
      WRITE(6,80)'CA    [ ]',CCA,CA,CASO4,CACO3,CAHCO3,CANO3,
     +CACL,CAH2PO,CAHPO4,CAOH,CATOT
   80 FORMAT('0',A,10F9.4,F18.4)
      WRITE(6,85)'A/C',GCA,GCASO4,GCACO3,GCAHCO,GCANO3,
     +GCACL,GCAH2P,GCAHPO,GCAOH
   85 FORMAT(6X,A,F18.4,8F9.4)
      WRITE(6,85)'( )',ACA,ACASO4,ACACO3,ACAHCO,ACANO3,
     +ACACL,ACAH2P,ACAHPO,ACAOH
      WRITE(6,90)'MG    [ ]',CMG,MG,MGSO4,MGCO3,MGHCO3,
     +MGOH,MGTOT
   90 FORMAT('0',A,5F9.4,F45.4,F18.4)
      WRITE(6,95)'A/C',GMG,GMGSO4,GMGCO3,GMGHCO,GMGOH
   95 FORMAT(6X,A,F18.4,3F9.4,F45.4,F18.4)
      WRITE(6,95)'( )',AMG,AMGSO4,AMGCO3,AMGHCO,AMGOH
      WRITE(6,100)'FE    [ ]',CFE,FE,FESO4,FENO3,FECL,FEH2PO,
     +FEHPO4,FEOH,FEOH2,FETOT
  100 FORMAT('0',A,3F9.4,F27.4,6F9.4)
      WRITE(6,105)'A/C',GFE,GFESO4,GFENO3,GFECL,GFEH2P,
     +GFEHPO,GFEOH,GFEOH2
  105 FORMAT(6X,A,F18.4,F9.4,F27.4,5F9.4)
      WRITE(6,105)'( )',AFE,AFESO4,AFENO3,AFECL,AFEH2P,
     +AFEHPO,AFEOH,AFEOH2
```

```
      WRITE(6,110)'MN    [ ]',CMN,MN,MNSO4,MNHCO3,MNCL,
     +MNOH,MNTOT
  110 FORMAT('0',A,3F9.4,2F18.4,F27.4,F18.4)
      WRITE(6,115)'A/C',GMN,GMNSO4,GMNHCO,GMNCL,GMNOH
  115 FORMAT(6X,A,F18.4,F9.4,2F18.4,F27.4,F18.4)
      WRITE(6,115)'( )',AMN,AMNSO4,AMNHCO,AMNCL,AMNOH
      WRITE(6,120)'AL    [ ]',CAL,AL,ALSO4,ALOH,ALOH2,ALTOT
  120 FORMAT('0',A,3F9.4,F63.4,2F9.4)
      WRITE(6,125)'A/C',GAL,GALSO4,GALOH,GALOH2
  125 FORMAT(6X,A,F18.4,F9.4,F63.4,F9.4)
      WRITE(6,125)'( )',AAL,AALSO4,AALOH,AALOH2
      WRITE(6,130)'TOTAL [ ] (MEQ/L)',SO4TOT,HCOTOT,NO3TOT,
     +CLTOT,PO4TOT
  130 FORMAT('0',A,2F18.4,3F9.4)
  200 CONTINUE
      STOP
      END
```

VIII. APPENDIX 2

A listing of the computer program SALTIN, which arranges total ionic composition data in the format for SALT, follows:

```
C THIS INTERACTIVE PROGRAM ENTERS DATA FROM CHEMICAL
C ANALYSIS INTO A FILE WHICH THE PROGRAM "SALT" USES
C TO CALCULATE THE DISTRIBUTION OF AQUEOUS SPECIES.
C DATA ARE ENTERED AS THE TOTAL CONCENTRATION OF
C THE ANALYSED SPECIES(EXPRESSED IN MEQ/L).
C FIRST, SODIUM IS ENTERED FOR ALL SAMPLES, THEN K,
C CA, MG, NH4, FE, MN, AL, ALKALINITY, SO4, CL, NO3,
C PO4, E.C.(dS/m), AND pH.
C PROVISION IS MADE FOR CALCULATING THE DISTRIBUTION OF
C AQUEOUS SPECIES IN STANDARD CALCIUM CHLORIDE SOLUTIONS
C (CA AND CL TOTAL CONCENTRATIONS CAN BE ENTERED WITHOUT
C ENTERING ANY OTHER PARAMETERS - E.C. IS CALCULATED AS
C CA CONCENTRATION DIVIDED BY 10, pH IS AUTOMATICALLY
C ENTERED AS 7).
      INTEGER I,J,STD,SMPL,N,Z,Q,R,S,T,U,DSN,CN,GV,
     +SMPLNO(99)
      REAL DATA(99,15)
      PRINT*,'THE MAXIMUM NUMBER OF DATA SETS THAT CAN BE'
      PRINT*,'ENTERED IS 99(STANDARDS PLUS SAMPLES).'
      PRINT*,'ENTER THE NUMBER OF STANDARD SOLUTIONS'
      PRINT*,'(IF NONE ENTER 0)'
      READ*,STD
      PRINT*,'ENTER THE NUMBER OF SAMPLES(IF NONE ENTER 0)'
      READ*,SMPL
      N=STD+SMPL
      DO 10 I=1,N
      SMPLNO(I)=I
   10 CONTINUE
      IF(STD .EQ. 0.) GO TO 40
      DO 20 I=1,STD
      WRITE(6,290)'ENTER CALCIUM(MEQ/L) FOR STANDARD ',I
      READ*,DATA(I,3)
      DATA(I,11)=DATA(I,3)
      DATA(I,14)=DATA(I,3)/10.
   20 CONTINUE
      DO 30 I=1,STD
      DATA(I,1)=0
      DATA(I,2)=0
      DATA(I,4)=0
      DATA(I,5)=0
      DATA(I,6)=0
      DATA(I,7)=0
      DATA(I,8)=0
      DATA(I,9)=0
```

```
      DATA(I,10)=0
      DATA(I,12)=0
      DATA(I,13)=0
      DATA(I,15)=7
   30 CONTINUE
   40 IF(SMPL .EQ. 0.) GO TO 190
      Z=STD+1.
      DO 50 I=1,SMPL
      WRITE(6,290)'ENTER SODIUM(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,1)
      Z=Z+1.
   50 CONTINUE
      Z=STD+1.
      DO 60 I=1,SMPL
      WRITE(6,290)'ENTER POTASSIUM(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,2)
      Z=Z+1.
   60 CONTINUE
      Z=STD+1.
      DO 70 I=1,SMPL
      WRITE(6,290)'ENTER CALCIUM(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,3)
      IF(DATA(Z,3) .EQ. 0.)THEN
      DATA(Z,3)=0.01
      ENDIF
      Z=Z+1.
   70 CONTINUE
      Z=STD+1.
      DO 80 I=1,SMPL
      WRITE(6,290)'ENTER MAGNESIUM(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,4)
      Z=Z+1.
   80 CONTINUE
      Z=STD+1.
      DO 90 I=1,SMPL
      WRITE(6,290)'ENTER AMMONIUM(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,5)
      Z=Z+1.
   90 CONTINUE
      Z=STD+1.
      DO 100 I=1,SMPL
      WRITE(6,290)'ENTER IRON(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,6)
      Z=Z+1.
  100 CONTINUE
      Z=STD+1.
      DO 110 I=1,SMPL
      WRITE(6,290)'ENTER MANGANESE(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,7)
      Z=Z+1.
  110 CONTINUE
      Z=STD+1.
      DO 120 I=1,SMPL
      WRITE(6,290)'ENTER ALUMINUM(MEQ/L) FOR SAMPLE ',I
```

```
      READ*,DATA(Z,8)
      Z=Z+1.
  120 CONTINUE
      Z=STD+1.
      DO 130 I=1,SMPL
      WRITE(6,290)'ENTER SULPHATE(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,9)
      Z=Z+1.
  130 CONTINUE
      Z=STD+1.
      DO 140 I=1,SMPL
      WRITE(6,290)'ENTER ALKALINITY(MEQ/L ACID TO PH 4.5)
     +FOR SAMPLE ',I
      READ*,DATA(Z,10)
      Z=Z+1.
  140 CONTINUE
      Z=STD+1.
      DO 150 I=1,SMPL
      WRITE(6,290)'ENTER CHLORIDE(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,11)
      Z=Z+1.
  150 CONTINUE
      Z=STD+1.
      DO 160 I=1,SMPL
      WRITE(6,290)'ENTER NITRATE(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,12)
      Z=Z+1.
  160 CONTINUE
      Z=STD+1.
      DO 170 I=1,SMPL
      WRITE(6,290)'ENTER PHOSPHATE(MEQ/L) FOR SAMPLE ',I
      READ*,DATA(Z,13)
      IF(DATA(Z,13) .EQ. 0.)THEN
      DATA(Z,13)=0.01
      ENDIF
      Z=Z+1.
  170 CONTINUE
      Z=STD+1.
      DO 180 I=1,SMPL
      WRITE(6,290)'ENTER E.C.(mS/cm) FOR SAMPLE ',I
      READ*,DATA(Z,14)
      Z=Z+1.
  180 CONTINUE
      Z=STD+1.
      DO 190 I=1,SMPL
      WRITE(6,290)'ENTER pH FOR SAMPLE ',I
      READ*,DATA(Z,15)
      Z=Z+1.
  190 CONTINUE
      Z=INT(N/15.)
      DO 200 Q=1,Z
      R=Q*15.
      S=R-14.
      IF(N .LE. 14.) THEN
```

```
      S=1.
      T=N
      ENDIF
      U=0.
  210 WRITE(6,300)'NA','K','CA','MG','NH4','FE','MN','AL'
      DO 220 I=S,R
      WRITE(6,310)SMPLNO(I),(DATA(I,J),J=1,8)
  220 CONTINUE
      PRINT*,'IF A DATA VALUE IS TO BE CHANGED,'
      PRINT*,'ENTER DATA SET NUMBER(FAR LEFT COLUMN)'
      PRINT*,'IF NO CHANGES, ENTER 0'
      READ*,DSN
      IF(DSN .EQ. 0.) GO TO 230
      PRINT*,'THERE ARE 8 COLUMNS OF DATA'
      PRINT*,'NA=1,.....,AL=8'
      PRINT*,'ENTER COLUMN NUMBER OF VALUE TO BE CHANGED'
      READ*,CN
      PRINT*,'ENTER CORRECT VALUE'
      READ*,DATA(DSN,CN)
      GO TO 210
  230 WRITE(6,320)'SO4','ALK','CL','NO3','PO4','E.C.','PH'
      DO 240 I=S,R
      WRITE(6,330)SMPLNO(I),(DATA(I,J),J=9,15)
  240 CONTINUE
      PRINT*,'IF A DATA VALUE IS TO BE CHANGED,'
      PRINT*,'ENTER DATA SET NUMBER(FAR LEFT COLUMN)'
      PRINT*,'IF NO CHANGES, ENTER 0'
      READ*,DSN
      IF(DSN .EQ. 0.) GO TO 250
      PRINT*,'THERE ARE 7 COLUMNS OF DATA'
      PRINT*,'SO4=9,.....,PH=15'
      PRINT*,'ENTER COLUMN NUMBER OF VALUE TO BE CHANGED'
      READ*,CN
      PRINT*,'ENTER CORRECT VALUE'
      READ*,DATA(DSN,CN)
      GO TO 230
  250 IF(U .EQ. 1.) GO TO 270
  200 CONTINUE
      IF(INT(N/15.) .EQ. N/15.) GO TO 270
      U=1.
      S=Z*15.+1.
      R=N
      GO TO 210
  270 WRITE(7,340)N
      DO 280 I=1,N
      WRITE(7,310)SMPLNO(I),(DATA(I,J),J=1,8)
      WRITE(7,350)(DATA(I,J),J=9,15)
  280 CONTINUE
  290 FORMAT(A,I2)
  300 FORMAT(7X,A,6X,A,5X,A,5X,A,5X,A,4X,A,5X,A,5X,A,5X,A)
  310 FORMAT(I3,8F7.2)
  320 FORMAT(5X,A,4X,A,5X,A,4X,A,4X,A,4X,A,4X,A)
  330 FORMAT(I3,7F7.2)
  340 FORMAT(I3)
```

```
350 FORMAT(F10.2,6F7.2)
    STOP
    END
```

IX. APPENDIX 3

The results of analysis of the study soil solutions for major ions follow:

SMPL	Na	K	Ca	Mg	NH_4	Fe	Mn	Al	SO_4	TAlk	Cl	NO_3	PO_4	EC	pH
1	114	0.2	21.1	15.8	0.0	0.0	0.0	0.0	134	0.8	16.8	0.4	0.01	11.3	7.84
2	33.0	1.9	44.7	14.7	0.0	0.0	0.0	0.0	39.9	6.5	38.4	7.5	0.01	7.74	8.04
3	74.4	0.2	18.8	15.4	0.0	0.0	0.0	0.0	102	2.1	0.2	0.1	0.01	8.20	8.23
4	68.0	0.3	19.8	13.0	0.0	0.0	0.0	0.0	98.3	1.5	0.1	0.1	0.01	7.71	8.34
5	80.2	0.2	20.5	14.7	0.0	0.0	0.0	0.0	110	1.4	0.2	0.1	0.01	8.69	8.08
6	73.6	0.3	19.8	13.0	0.0	0.0	0.0	0.0	105	1.3	0.2	0.1	0.01	8.12	8.26
7	76.8	0.2	20.8	14.7	0.0	0.0	0.0	0.0	107	1.5	0.1	0.1	0.01	8.40	8.14
8	67.3	0.3	20.2	12.8	0.0	0.0	0.0	0.0	97.4	1.4	0.1	0.1	0.01	7.66	8.26
9	5.6	0.4	19.0	7.0	0.0	0.0	0.0	0.0	21.8	6.6	1.9	0.2	0.01	2.46	8.26
10	10.8	0.3	28.0	9.4	0.0	0.0	0.0	0.0	39.9	5.1	1.1	0.8	0.01	3.54	8.23
11	53.6	0.2	22.9	12.8	0.0	0.0	0.0	0.0	84.0	4.1	0.5	0.1	0.01	6.74	8.38
12	72.0	0.2	21.6	13.3	0.0	0.0	0.0	0.0	98.0	4.6	0.3	0.1	0.01	7.98	8.43
13	6.8	0.4	28.4	8.4	0.0	0.0	0.0	0.0	34.3	6.0	1.1	0.4	0.01	3.14	8.19
14	21.0	0.2	25.8	13.3	0.0	0.0	0.0	0.0	52.2	5.3	0.6	0.3	0.01	4.39	8.22
15	41.0	0.3	20.7	14.5	0.0	0.0	0.0	0.0	72.4	5.0	0.3	0.1	0.01	5.90	8.36
16	76.0	0.3	21.0	14.9	0.0	0.0	0.0	0.0	104	4.4	0.2	0.1	0.01	8.30	8.42
17	7.0	0.3	21.7	7.4	0.0	0.0	0.0	0.0	28.4	5.8	1.4	0.2	0.01	2.74	8.29
18	15.5	0.2	26.0	10.7	0.0	0.0	0.0	0.0	46.7	4.2	0.6	0.3	0.01	3.84	8.21
19	38.4	0.2	23.4	15.2	0.0	0.0	0.0	0.0	69.8	5.9	0.5	0.1	0.01	5.69	8.36
20	63.7	0.2	19.1	12.4	0.0	0.0	0.0	0.0	91.6	3.5	0.2	0.1	0.01	7.30	8.40
21	367	3.2	66.4	28.6	0.0	0.0	0.0	0.0	6.5	0.5	463	0.1	0.01	43.0	6.95
22	3.8	0.2	1.2	1.6	0.0	0.0	0.0	0.0	1.1	4.5	0.6	0.1	0.01	0.57	8.64
23	0.4	0.1	2.0	0.6	0.0	0.0	0.0	0.0	0.2	2.6	0.2	0.1	0.01	0.21	8.16
24	0.8	0.2	0.4	0.2	0.0	0.0	0.0	0.0	1.3	0.0	0.1	0.1	0.01	0.14	4.00
25	1.2	0.3	6.0	1.8	0.0	0.0	0.0	0.0	9.1	0.0	0.2	0.1	0.01	0.82	4.08
26	0.8	0.8	30.6	15.6	4.7	2.0	0.8	6.7	61.0	0.0	0.4	2.8	0.01	4.18	3.35
27	0.4	0.4	30.6	18.0	0.1	0.0	0.0	0.0	48.0	2.0	0.6	0.3	0.01	3.30	7.19
28	10.6	2.4	24.2	287	30.0	6.9	11.9	46.6	422	0.0	1.0	9.3	0.01	18.4	2.92
29	0.5	2.1	22.3	14.8	8.8	6.5	2.4	45.0	100	0.0	0.2	0.0	0.10	6.64	2.26
30	0.4	1.4	19.4	4.0	4.6	0.5	1.5	7.5	39.8	0.0	0.2	0.0	0.10	3.16	2.72
31	3.2	3.6	23.6	109	11.5	133	4.3	334	670	0.0	1.7	0.0	3.20	26.7	1.56

32	1.8	0.8	24.8	39.2	5.2	0.2	1.5	7.8	83.0	0.0	0.2	1.1	0.01	5.17	3.48
33	0.4	0.3	13.4	2.8	1.3	0.3	0.2	2.7	20.2	0.0	0.2	0.5	0.01	1.66	3.58
34	0.4	0.3	28.0	7.0	0.0	0.0	0.0	0.0	35.5	1.4	0.2	0.1	0.01	2.54	6.58
35	0.4	1.3	21.1	3.2	0.2	0.0	1.6	0.6	28.0	0.0	0.2	0.0	0.01	2.12	4.10
36	0.4	1.5	11.2	3.9	2.8	0.1	1.9	11.0	32.2	0.0	0.2	0.0	0.01	2.36	3.08
37	0.7	0.8	27.2	13.0	2.5	11.0	0.6	32.7	95.5	0.0	0.2	0.0	0.01	6.18	2.16

Notes: 1)Results are expressed in me/L except E.C.(in dS/m) and pH(in pH units)
2)TAlk is total alkalinity as me acid/litre sample to titrate to pH 4.5
3)Results below the detection limit are set at 0.0 me/L except PO_4 which is set at 0.01 me/L(PO_4 is used as a convergence check in the speciation method and 0.01 instead of 0.0 precludes division by 0). Detection limits for species other than PO_4 are usually 0.05 to 0.1 me/L.

X. APPENDIX 4

Profile descriptions of some of the study soils follow:

A. Series: Hemaruka

Subgroup: Brown Solodized Solonetz
Location: SW12-14-18-W4
Parent Material: till
Topography: level
Vegetation: short-grass prairie
Drainage: imperfect.

Ah	0-10	Dark brown(10YR 3/3m); SL; weak, fine, granular: friable; abundant,very fine and fine,random exped roots; clear, wavy boundary.
Ahe	10-13	Yellowish-brown(10YR 5/4d); SL; compound,weak, fine, platy and moderate, fine, subangular blocky; friable; plentiful, very fine and fine, random, inped and exped roots; clear, wavy boundary
Bnt	13-27	Brown(10YR 5/3d); SCL; compound, strong, coarse, columnar and strong, fine and medium, subangular blocky; firm; few, fine, vertical, inped and exped roots; abrupt, wavy boundary
Cca	27-78	Dark yellowish brown(10YR 4/4m); SCL; amorphous; friable; few, fine, vertical roots; gradual, wavy boundary (rooting depth 62cm).
Ccasa	78-115	Dark brown(10YR 3/3m); SCL; amorphous; friable.

Sample collected was from the Ccasa horizon.

B. Series: Maleb

Subgroup: Orthic Brown
Location: NW25-12-7-W4
Parent material: morainal
Topography: level to rolling
Aspect: north, midslope position
Vegetation: short-grass prairie
Drainage: well drained

Ah	0-12	Brown to dark brown(10YR 4/3); SL; strong, fine, granular; soft; plentiful, very fine, random, exped roots; clear, wavy boundary.
Bt	12-22	Dark grayish brown(10YR 4/2d); SL; strong, fine, prismatic and strong, medium, subangular blocky; hard; plentiful, very fine, random, inped and exped roots; abrupt, wavy boundary.
Cca1	22-48	Grayish brown(10YR 5/2d); L; weak, fine, subangular blocky; slightly hard; plentiful, very fine, random, inped and exped roots; gradual, wavy boundary.
Cca2	48-75	Dark grayish brown(10YR 4/2d); L; weak, fine, subangular blocky; slightly hard; few, very fine, random, inped and exped roots; gradual, wavy boundary.
Ck	75+	Dark grayish brown(10YR 4/2d); L to SiL; amorphous; soft to slightly hard; few, very fine, vertical roots.

Sample collected was from the Cca horizon.

C. Series: Culp

Subgroup: Orthic Gray Luvisol
Location: SE16-70-9-W6
Parent material: aeolian
Topography: rol[illegible]
Aspect: south, midslope
Vegetation: poplar, grasses, shrubs
Drainage: rapidly drained

Ap	0-35	Strong brown(7.5YR 5/6m); single grain; loose; few, coarse, medium and fine, random, exped roots; clear, smooth boundary.
Bt	35-64	Brown to dark brown(10YR 4/3m); SL; weak, fine, granular; very friable; few, coarse, medium and fine, vertical, exped roots; clear, wavy boundary.
Cca	64+	Brown to dark brown(10YR 4/3m); S; weak, fine, granular; friable; few, medium and fine, vertical, exped roots.

Sample collected was from the Cca horizon

D. Series: Boundary

Subgroup: Podzolic Gray Luvisol or Luvisolic Humo-Ferric Podzol
Location: SE8-82-8-W6
Parent material: shale
Topography: rolling
Aspect: southwest, mid-slope
Vegetation: poplar
Drainage: well

LFH	1-0	
Ah	0-2	Yellowish red(5YR 4/8m); SiCL; strong, medium, granular; friable; plentiful, fine and medium, rancom, inped and exped roots; clear, wavy boundary.
Ahe	2-7	Yellowish red(5YR 4/8m); SiCL; compound, weak, medium, platy and moderate, fine granular; friable; plentiful, fine and medium, random, inped and expecd roots; clear, wavy boundary.
AB	7-12	Yellowish red(5YR 4/6m); SiC; moderate, fine and medium, subangular blocky; friable; plentiful, fine and medium, random, inped and expedc roots; clear, wavy boundary.
Bt	12-27	Yellowish red(5YR 4/8m); SiC; strong, medium, subangular blocky; friable; many, fine and medium, oblique, inped and exped roots, clear, wavy boundary.
Btf1	27-37	Dark red(2.5YR 3/6m); SiC; strong, medium, subangular blocky; friable; few, medium, oblique, inped and exped roots; clear, wavy boundary.
Btf2	37-51	Dark red(2.5YR 3/6m); SiC; many, fine, prominent, brownish yellow(10YR 6/6m) salt deposits and veinlets; strong, medium, subangular blocky; friable; few, small, vertical, inped and exped roots; clear,wavy boundary.
Cs	51+	Gray(10YR 5/1m); SiC; common, medium, prominent, yebrownish yellow(10YR 6/6m) salt deposits and veinlets; amorphous; friable; very few, small, vertical, inped and expewd roots; .

Sample collected was from the Cs horizon.

E. Series: Josephine
Subgroup: Fera Luvic Gleysol
Location: NE23-81-9-W6
Parent material: acid shale
Topography: level
Vegetation: poplar, spruce, alder
Drainage: poor

L	3-2	
FH	2-0	
Ahe	0-8	Dark brown(7.5YR 3/2m); CL; moderate, fine, platy, to moderate, fine and medium, granular; friable; abundant, fine and medium, random, inped and exped roots; clear, wavy boundary.
AB	8-12	Dark brown(7.5YR 3/2w); CL; moderate, fine and medium, subangular blocky; slightly sticky; abundant, fine and medium, random, inped and exped roots; clear, wavy boundary.
Btg	12-18	Dark grayish brown(10YR 4/2w); SiC; common, fine, faint, yellowish brown(10YR 5/6w) mottles; moderate, fine and medium, subangular blocky; slightly sticky; plentiful, fine and medium, random, inped and exped roots; clear, wavy boundary.
Btgf	18-30	Gray(10YR 5/1w); SiC; many, medium, prominent(2.5YR 5/4w) mottles; moderate, fine and medium, subangular blocky; slightly sticky; plentiful, fine and medium, random, inped and exped roots; clear, wavy roots ; clear, wavy boundary.
BCg	30-50	Gray(10YR 5/1w); SiC; many, fine and medium, prominent yellowish brown(10YR 5/6w) mottles; weak, medium, subangular blocky; sticky; few, medium, oblique, inped and exped roots; clear, wavy boundary.
Cg	50+	Dark gray(10YR 4/1w); SiC; common, fine and medium, prominent, yellowish brown(10YR 5/6w) mottles; amorphous; sticky; few, medium, oblique roots.

Sample collected was from the BCg horizon.