



Techniques of isolating the soil solution for chemical characterization and analyses  
by Ahmed Diab Mubarak

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry  
Montana State University  
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**Abstract:**

A simple laboratory technique that combines the reliability of immiscible displacement principles with the convenience of centrifugation has been developed for isolating solutions from soils falling within the field moisture range. A measured excess of (CCl<sub>4</sub>) is added to a moist soil sample in a centrifuge tube and the contents are shaken and then centrifuged for a selected time interval. As a result of the (CCl<sub>4</sub>) being immiscible with water and of greater density, it displaces the soil solution upward where it can be removed for analyses. The technique is effective in removing enough solution volumes from naturally occurring soils to permit many analyses.

The immiscible displacement by centrifugation (ID) technique, described above, was used for measuring the naturally occurring pH and salinity of soils. Errors induced upon pH and salinity measurements when using low soil:water ratio and/or saturated pastes techniques were found to be minimized by using the (ID) technique.

An ultrasonic nebulization procedure has been devised for wetting soil samples with aqueous solutions to selected moisture contents.

The procedure is relatively simple and believed to cause a minimum of alteration in the chemical and physical properties of the soil sample.

Effect of the (CCl<sub>4</sub>) used for displacement in the (ID) technique on the equilibrium concentrations of trace metals in the soil solution was investigated. It was found that compositions of soil solutions obtained with the (ID) technique and with direct centrifugation, from identical and relatively wet soil samples, were approximately the same although substantial concentrations of some of the heavy metals were tested in the CCl<sub>4</sub> after it was used for displacement. When using the carbon rod atomizer, negative interfering effects on the absorbances of Mn, Fe, and Ni were found to occur in the presence of the chlorides of the major cations (Ca, Mg, Na) in the soil solution. These interferences were corrected either by precipitating the chlorides with silver nitrate or by incorporating 20 percent sulphuric or nitric acid into the sample volume. Magnesium ion, irrespective of the associated anion, was found to lower the cadmium signal on the carbon rod atomizer. High concentrations of magnesium sulfate caused lowering of the manganese signal when using air-acetylene flame. This lowering effect of magnesium sulfate was avoided upon using nitrous oxide-acetylene flame. No interferences were noticed when using the Woodriff furnace (WF) for Mn and Zn analyses.

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DEDICATION

TO

"My parents and the rest of the displaced Palestinians"

TECHNIQUES OF ISOLATING THE SOIL SOLUTION FOR CHEMICAL  
CHARACTERIZATION AND ANALYSES

by

AHMED DIAB MUBARAK

A thesis submitted in partial fulfillment  
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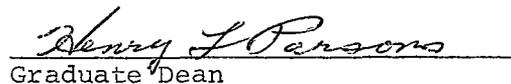
in

Chemistry

Approved:

  
Chairperson, Graduate Committee

  
Head, Major Department

  
Graduate Dean

MONTANA STATE UNIVERSITY  
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## ABSTRACT

A simple laboratory technique that combines the reliability of immiscible displacement principles with the convenience of centrifugation has been developed for isolating solutions from soils falling within the field moisture range. A measured excess of  $(\text{CCl}_4)$  is added to a moist soil sample in a centrifuge tube and the contents are shaken and then centrifuged for a selected time interval. As a result of the  $(\text{CCl}_4)$  being immiscible with water and of greater density, it displaces the soil solution upward where it can be removed for analyses. The technique is effective in removing enough solution volumes from naturally occurring soils to permit many analyses.

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## Chapter I

### GENERAL INTRODUCTION

The criteria for characterizing a soil system with regard to its suitability as a substrate for higher plants has been of much controversy that dates back to the emerging days of soil science. Prior to the Twentieth Century, and on the basis of the John Woodward experiment (1), the idea that earth was the principal nutritional medium for growing plants was common and soil scientists conclusively focused their attention to investigating the soil solid phase (soil particles). At the turn of the century, Frank Cameron (2) published a bulletin in which he postulated that the soil solution was the medium from which nutrient ions were obtained by plants. Although, at the time, there was little or no evidence to support his postulates, his ideas of intimate relationship between the ionic composition of the soil solution and plant growth had shifted research interests from the soil solid phase (soil particle) to its liquid phase (soil solution) and several procedures for isolating the soil solution were independently reported. A few years later, Parker (3) reviewed the procedures for obtaining soil solutions and the difficulties associated with them and subsequently the interest had shifted from examination of the soil solution to that of the soil particle. Since then, the controversy has taken on a rather more quantitative fashion. At Berkeley, California, Jenny and Overstreet (4), and others (5-7) using tracer

techniques, found that uptake of a nutrient was higher when roots were submerged in a clay or resin suspension than when they were submerged in a solution at equilibrium with the suspension. The explanation therein made was that plant roots when placed in suspension effectively penetrate the electrical double layer of the colloidal surfaces where the activity of counter ions is higher than that in the equilibrium solution. These workers described the manner by which plants obtain their nutrients by a cation exchange process between the colloidal surfaces and the plant roots.



According to the exchange theory which has been known as the "contact exchange theory," cations held on soil colloids are in a state of oscillation and could transfer directly, that is, without the medium of the soil solution, to a plant root surface whenever the oscillation volumes of the cations adsorbed on the root and colloidal surfaces overlap. Since uptake from suspension was higher than from its equilibrium solution, in most of their experiments, it was concluded that the driving force for ion uptake is a gradient in the chemical potential of the ion. The chemical potential is defined by Eq. [1].

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad [1]$$

in which  $\mu_i$  is a constant at a given temperature and pressure,  $a_i$  is the activity of the ion,  $R$  the gas constant, and  $T$  the absolute temperature. Research emphasis accordingly was shifted towards measuring ion activities in colloidal suspensions. Marshall (8-10), for example, fabricated ion membrane electrodes from clays to determine ion activities in clay suspensions by potentiometric techniques. Marshall's ideas were championed by Peech (11) as he developed a method for simultaneous determination of the activities of co-existing cations in soil water systems. The method is based primarily on the Donnan membrane equilibrium in which the total, or electrochemical potential,  $\bar{\mu}_i$  of each diffusible ionic species will be the same in both phases (the clay and the aqueous phase). The electrochemical potential of an ion of species  $i$  within a given phase is defined as:

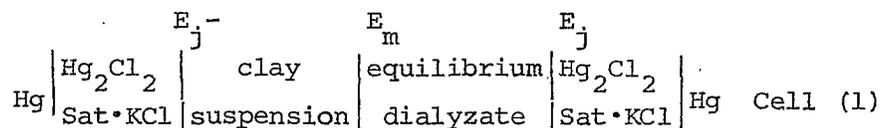
$$\bar{\mu}_i = \mu_o + RT \ln a_i + Z_i F \psi \quad [2]$$

in which  $\mu_o$  is a constant at a given temperature and pressure,  $a_i$  the activity of the ion,  $Z_i$  is its valence,  $\psi$  the electrical potential of the phase,  $R$  the gas constant,  $T$  the absolute temperature, and  $F$  the Faraday constant. From the condition for electrochemical equilibrium (the identity of electrochemical potentials of each diffusible ionic species in the two phases), it follows that

$$\psi'' - \psi' = \Delta E_{\text{cal}} = \frac{RT}{Z_i F} \ln \frac{a'_i}{a''_i} \quad [3]$$

in which the superscripts prime and double prime refer to the clay and the aqueous phase, respectively. The membrane or the phase boundary potential  $\Delta E_{\text{cal}}$ , is measured as the difference between the potentials of two identical calomel electrodes, one electrode placed in each phase.

The EMF of cell 1 was taken as a measure of  $\Delta E_{\text{cal}}$



The junction potential,  $E_j^-$  was erroneously assumed to be negligibly small. The membrane potential  $E_m$  was measured as  $\Delta E_{\text{cal}}$ . The aqueous phase is analyzed by conventional chemical methods, and the activity of the ion in the aqueous phase,  $a''_i$ , is calculated from its concentration and the ionic strength. The activity of the ion in the clay phase,  $a'_i$ , is then calculated by Eq. [3].

According to Guggenheim (12,13) the primary condition of equilibria is that for any infinitesimal process occurring in a system at constant temperature and pressure, the free energy change,  $dG$ , must be zero. Therefore, the partial molal free energy,  $G_x$ , which is defined as,

$$G_x = \partial G / \partial n_x \quad [4]$$

where  $n$  is the number of moles of ion  $x$ , in the system (which is a function of both the chemical composition and the electrical potential of that system) must be similar in both phases. This could be verified experimentally by placing two identical metal electrodes in the colloidal and the non-colloidal phases and connecting the electrodes to a potentiometer. The electromotive force of this galvanic cell may be evaluated in terms of the free energy change of the process as follows

$$E = \Delta G/nF \quad [5]$$

where  $E$  is the electromotive force,  $n$  is the number of equivalents transferred and  $F$  is the Faraday equivalent. Since, at equilibrium,  $\Delta G$  is zero,  $E$  must also be zero. According to Eq. [3], an electric potential difference may be registered between two such identical electrodes, pointing to the possibility that work might be gained from a system under thermodynamic equilibrium. Obviously, this is not correct and the method is misleading. Indeed, it has been shown by Olsen and Robbins (14) and others (15,16) that  $\Delta E_{cal}$  was caused by a liquid junction potential ( $E_j$  in Cell (1)) between the calomel electrode and the negatively charged colloidal particles in the suspension.

Shortly after the "contact exchange theory" ( $da_1/dx$  theory) was established, Olsen and Peech (17) at Cornell University in New York, reported contradictory experimental evidence showing that uptake of ions by plant roots was equal whether roots were immersed in

suspensions or in their equilibrium dialyzate. They accordingly concluded that, the driving force for ion uptake is a gradient in the electrochemical potential  $d\bar{\mu}_i/dx$ . The interpretation therein made is that, in a suspension of negatively charged ions, the activity of a cation is high and its electrical potential is low while in the equilibrium solution the activity is lower and the electrical potential is higher (less negative) which makes the total electrochemical potential of each diffusible ion in both phases of any system under equilibrium to be equal. Proponents of the  $d\bar{\mu}_i/dx$  hypothesis (17-22) concluded that under equilibrium conditions, the ionic environment of the plant root should be completely characterized by the chemical composition of the soil solution and called for the amendment of the "contact exchange theory."

In this author's opinion, and on the basis that the electrochemical potential of a diffusible ion (which is a function of its chemical and electrical potentials) in a suspension under equilibrium with a solution is the same in both phases and in the light of recent calculations (23) showing that the electrical potential of any diffusible ion at distances as close  $10\text{\AA}$  (approximately three water molecules thick) from the colloidal surface is zero, it is likely that the roots placed in the suspensions did not effectively penetrate the ion swarms (electrical force fields). The suspensions used were at fairly high water content. The equality observed in the rate of ion

uptake from both suspensions and their equilibrium dialyzates could therefore be attributed to an equality in their chemical potentials surrounding the plant roots in the two media. Accordingly, one may postulate that the driving force of an ion in suspensions and solutions under equilibrium is in fact a gradient in its chemical potential ( $da_i/dx$ ). This hypothesis, if sound, should not discredit, at least qualitatively, the  $d\bar{\mu}_i/dx$  hypothesis in that the rate of uptake of an ion from a suspension is equal to that from a solution provided that the two phases are under equilibrium. It certainly, of course, disqualifies the "contact exchange theory," on the basis of thermodynamic considerations, in that in a suspension under equilibrium with its solution, the activity of a diffusible ion is higher in the suspension than that in the solution. There are certainly more factors involved in the rate of ion uptake from soils such as the ionic strength of the soil solution and the soil buffering capacity, etc., however, it is not the intention of this author to go into more details in this subject, since this author has not been directly involved in ion uptake measurements.

On the basis of the  $d\bar{\mu}_i/dx$  hypothesis, attempts to characterize the soil have accordingly shifted from techniques aimed at extracting "available" ions from the soil solid phase to techniques aimed at assessing the composition of the soil solution. Unfortunately, however, actual investigations of the soil-solution have been seriously

hampered by two experimental factors, viz (a) the difficulties and tediousness involved in trying to conveniently obtain a representative sample of the soil solution within the field moisture range, and (b) the analytical problems encountered in measuring trace quantities of the many ions of interest in the small volume of extracted solution.

Early procedures for obtaining samples of the soil solution have been reviewed by Parker (3), Richards (24), and more recently by Fried and Broeshart (25). More methods, however, have been reported since then, and therefore, an overall review of these methods is appropriate to incorporate in this chapter. In summary, these methods could be grouped under:

1. Laboratory Methods For Obtaining The Soil-Solution

- a. Displacement by liquid. Displacement techniques were first introduced by Schloesing (26) and then modified by Burd and Martin (27) who used water for a displacing liquid and obtained data indicating that the displaced soil solution was the true soil-solution in an unaltered condition. Ischerekov (28) followed by Parker (3) used ethyl alcohol for displacement and obtained similar results. Displacement techniques have been conclusively regarded by soil scientists as the standard technique, for soil solution studies, against which other techniques are compared (29-33). In general, the method consists of packing the moist soil (about 2 kgm) uniformly in a column

provided with an outlet at the lower end fitted with filter paper. The displacing liquid is then poured on top of the soil column and as it penetrates the soil, it displaces some of the soil solution. Frequently, air pressure is applied to the system to speed up the displacement. The displaced soil solution is collected in aliquots of 5-25 cc. The electrical conductivity of each portion is determined and is constant so long as the soil-solution is not mixed with the displacing liquid. A considerable change in electrical conductivity provides evidence that the true soil-solution is no longer being obtained. Chemical indicators are also used to ascertain obtaining the true soil-solution. Under these conditions, dilute solutions of KSCN or NaCl are used for displacement and  $\text{FeCl}_3$  or  $\text{AgNO}_3$  solutions are used for indicators. When alcohol is used as the displacing liquid, the iodoform test is commonly performed to detect any contamination of the soil solution by the displacing liquid.

Although the displacement by water technique has been in common use, criticisms of this technique have been:

- I. Its applicability is limited to soils of high moisture content (34).
- II. The method is not suitable for obtaining solutions from heavy soils.

- III. A period of several weeks is sometimes necessary for displacement during which the sample composition could be seriously altered due to microbial activity (27,35).
- IV. The high probability of contamination of the soil solution by the displacing liquid (because of unavoidable mixing).
- V. The inconvenience associated with monitoring solution composition.
- VI. The large amount of the soil sample needed and the difficulties encountered with packing it uniformly to minimize solution channeling (36).

The technique, however, is potentially adaptable and has been of much value for soil-solution investigation. This technique will be discussed further in the next chapter.

b. Displacement by gas. This method involves the use of a pressure membrane apparatus (24). A desired amount of soil is wetted to a selected moisture content and then placed on a porous membrane in a closed container. Various pressures of an inert gas (usually  $N_2$ ) is applied to force out the soil-solution. Although Richards (24) obtained small volumes of soil solution of constant composition, McBain and Stuewer (37) and later Bower and Geortzen (38) observed differences in concentration of the successively obtained aliquots of soil solution. They attributed that to a salt sieving effect exerted by the membrane and concluded that the method is not suited for soils

with high phosphate concentration. The extracting procedure also suffers from being so slow (as long as several days) as to promote microbial activity (39).

c. Centrifugation. This technique, which implies movement of water through and out of soils by centrifugal force, has long been employed in soil physics labs for the determination of moisture equivalent of soils (40,41). More recently, Davis and Davis (42) have reported a centrifugation technique for obtaining samples of the soil solution. Their technique, however, failed to extract solutions from soils below 30 percent moisture as indicated by their data. It also requires a special centrifuge tube and has a common disadvantage of requiring a filter.

d. Compaction. This technique involves squeezing out the soil-solution from soils by reducing their pore space volume using mechanical pressure (43). Although Northrup (44) postulated that the method could alter solution composition, Burgess (34) experimentally demonstrated its applicability to soils of various textural classes. He applied pressures as high as 100,000 lbs per sq. inch to soils and obtained solution increments of identical composition. The moisture percentage of the soils during pressing was reduced almost to the point of "unfree water."

e. Suction. This method which involves use of vacuum extractors was first introduced by Briggs and McCall (45). A ceramic cup is

installed in the soil at the desired depth and the air is withdrawn by a vacuum pump. When the soil-water suction is less than the applied vacuum, water is drawn into the sampler. The solution sample is removed by further application of vacuum and drawing the sample into a collection flask. Although some improvement has been made on the technique (46,47), it has been subject to serious limitations due to adsorption of ions on the ceramic cell, contaminants in the ceramic cell plugging of samplers, and its limited applicability to soil-water suction below 0.8 bar (48).

2. Methods Involved in Measuring Concentrations of  
in situ Soil Solutions

A variety of such methods have been proposed for measuring the concentration of in situ soil solutions. The use of electrical sensors for measuring electrical conductance was first suggested by Davis and Bryan (49). More recently, salinity sensors have been used for determinations of salts in saline and alkali soils (50,51). The readings obtained, however, are subject to effects of soil texture, organic matter content, and soil-water content.

3. Soil-water Extraction Techniques

Due to the inherent difficulties in obtaining true soil-solutions, filtration of soil-water pastes has been commonly employed in soil testing laboratories. Unfortunately, however, these filtrates

are not water extracts representative of the in situ soil solution due primarily to the solvent effect of water, ion exchange reactions, dissolution, precipitation, and hydrolytic reactions induced by dilution. Burgess (34), for example, reported an increase from 2 to 30 times in the concentration of K, S, and P in the 1:5 extract over the comparable values in displaced soil solution. Kelly and Brown (52) similarly found increasing amounts of carbonates dissolved when alkali-soils were extracted with increasing proportions of water. Hibbard (53), Reitemeier (54), and more recently Khasawneh (55) compared composition of displaced solutions with that of water extracts of a variety of alkali and saline soils and concluded that dilution considerably alters the composition of the in situ soil-solution. They concluded that the displaced soil solutions are decidedly superior for sampling the in situ solution of soil.

It is seen that dependable characterization of a soil system with reference to concentration of nutrient elements has been made difficult due primarily to the large volumes of solutions needed for the classical analytical techniques. The recent developments of more sensitive analytical techniques (56-61) has made possible the determination of many analyses on relatively small solution samples. Interest has therefore been stimulated in again trying to isolate the true soil-solution in the light of its increasing value for both soil and plant research.

In this thesis, a new laboratory technique for isolating the soil solution within the field moisture range of soils is presented. Utilizing this technique, more reliable assessments of chemical parameters of the soil solution such as pH, electrical conductivity (EC) and ionic composition (macro and micronutrients) have been obtained. Attention has also been devoted to optimizing analytical conditions for the micronutrients (trace elements). Also a new methodology for uniformly wetting soil samples to moisture levels within the field moisture range is reported and utilized.

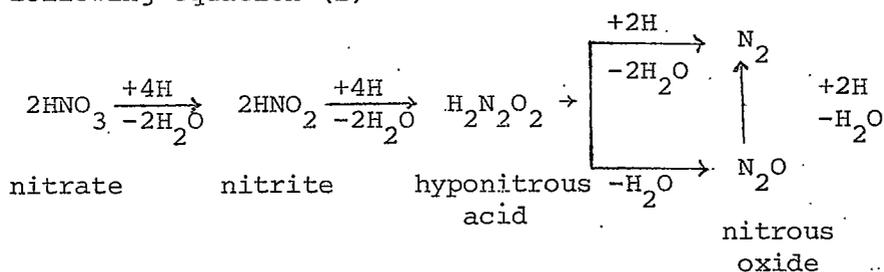
## Chapter II

### IMMISCIBLE DISPLACEMENT OF THE SOIL SOLUTION BY CENTRIFUGATION

As noted by Pearson (29), "... of the procedures used for obtaining samples of the soil solution, the displacement techniques offer the least chance for change in solution composition during extraction since no invading ions are introduced into the system and the solution does not have to pass through a membrane or plate with the attendant hazard of ion sieving or adsorption." The limitations of the traditional displacement technique and other proposed techniques have been discussed in the previous chapter. In this chapter, a new laboratory method for obtaining soil solutions which combines the reliability of displacement with the convenience of centrifugation is presented. It simply involves adding a measured excess of carbon tetrachloride to a moist soil sample in a centrifuge tube. The tube and contents are then shaken and centrifuged for selected time intervals. As a result of the carbon tetrachloride being immiscible with water and of higher density ( $d = 1.6 \text{ gm/ml}$ ), the soil solution is displaced. It rises to the surface where it can be removed for analyses.

Carbon tetrachloride was chosen as the displacing liquid for the following reasons:

a. It is immiscible with water (the soil solution); b. has a density of about 1.6 gm/ml which makes it less dense than the soil particle and more dense than the water, thus enabling it to separate the solution phase (soil-solution) from the solid phase (soil-particle,  $d \approx 2.5$ ); c. solubility of the predominant electrolytes in carbon tetrachloride is negligibly small; d. it serves as a sterilizing agent when added to the soil thus prohibiting microbial activity (e.g., denitrification) during storage and/or displacement. Complete denitrification of soil samples by soil micro-organisms has been reported (35) when using traditional water displacement techniques. The probable pathways for loss of nitrates are indicated in the following equation (1)



e. it serves as a flocculant to soil colloidal particles thus increasing the hydraulic conductivity of soils which could speed up the displacement process.

### Experimental

Two types of soils were used in this investigation, a clay and a fine sandy loam. The clay soil (denoted clay) was comprised of

43 percent clay, 30 percent silt, and 27 percent sand. The fine sandy loam (denoted sand) was comprised of 17 percent clay, 18 percent silt, and 65 percent sand. A Beckman J-21 model centrifuge fitted with JA-20 rotor was used. Displacement of soil solutions involved these steps: (i) A sample of dry soil (10 gm was used in this case) was weighed into a 50-ml polypropylene centrifuge tube fitted with a polypropylene lid, (ii) 2.5 ml of water were added to each tube containing the 10 gm soil sample. The tube was closed and stored for 24 hours for equilibration, (iii) an excess of  $\text{CCl}_4$  was then added (10 ml was used), (iv) the tube was tightly stoppered and shaken for 1 min. to cause mixing. Although the 1 min. was an arbitrary chosen time for shaking, it is the impression of the author that it wouldn't have a significant effect on the percent displacement since the  $\text{CCl}_4$  tends to penetrate the soil column readily, (v) the tube and contents were centrifuged at 48,300xg. This centrifugal force was the highest allowed force for that particular centrifuge. Lower centrifugal forces were tested first that yielded less displaced solution volumes. However, data pertaining to this was not recorded. Ten gram duplicates of each of the clay and fine sandy loam soils were wetted to 25 percent by the addition of 2.5 ml of distilled water from a graduated pipet directly onto the soil sample in the tube. The systems were stoppered and left in a refrigerator for 24 hours to allow equilibration. Duplicate tubes were then centrifuged for several

intervals of time at 48,300xg and volumes of displaced solutions were measured. Data are recorded in Figure 1. In another experiment, the 10 gm soil samples were wetted to selected moisture contents and centrifuged for two hrs. at 48,300xg, and again volumes of displaced solutions were measured. Data are recorded in Figure 2. Also as a preliminary check of the reliability of the technique for removing representative samples of the soil solution,  $\text{BaSO}_4$  was thoroughly washed with distilled water. After drying at 50°C, eight samples were wetted in centrifuge tubes to the following moisture contents: 30, 50, 70, 150 percent. Then 10 ml of the  $\text{CCl}_4$  was added to each tube for displacement. The tubes and contents were left to equilibrate for 24 hours and then centrifuged for two hours at 48,300xg. The solutions removed were analyzed for  $\text{Ba}^{2+}$  using the Carbon Rod Atomizer, Varian Atomic Absorption Spectrometer AA-5. The data are shown in Table 1.

### Discussion

The data of Figure 1 indicate that about half of the moisture, even from these relatively dry soils, was displaced by the technique, the percentage removed in two hours being 50 and 52 percent from the clay soil and from the fine sandy loam, respectively. Soil samples were at 25 percent moisture content. Owing to the leveling off of the curves, it is seen that two hours centrifuging time was nearly as effective as three hours. For reasons not completely understood, not

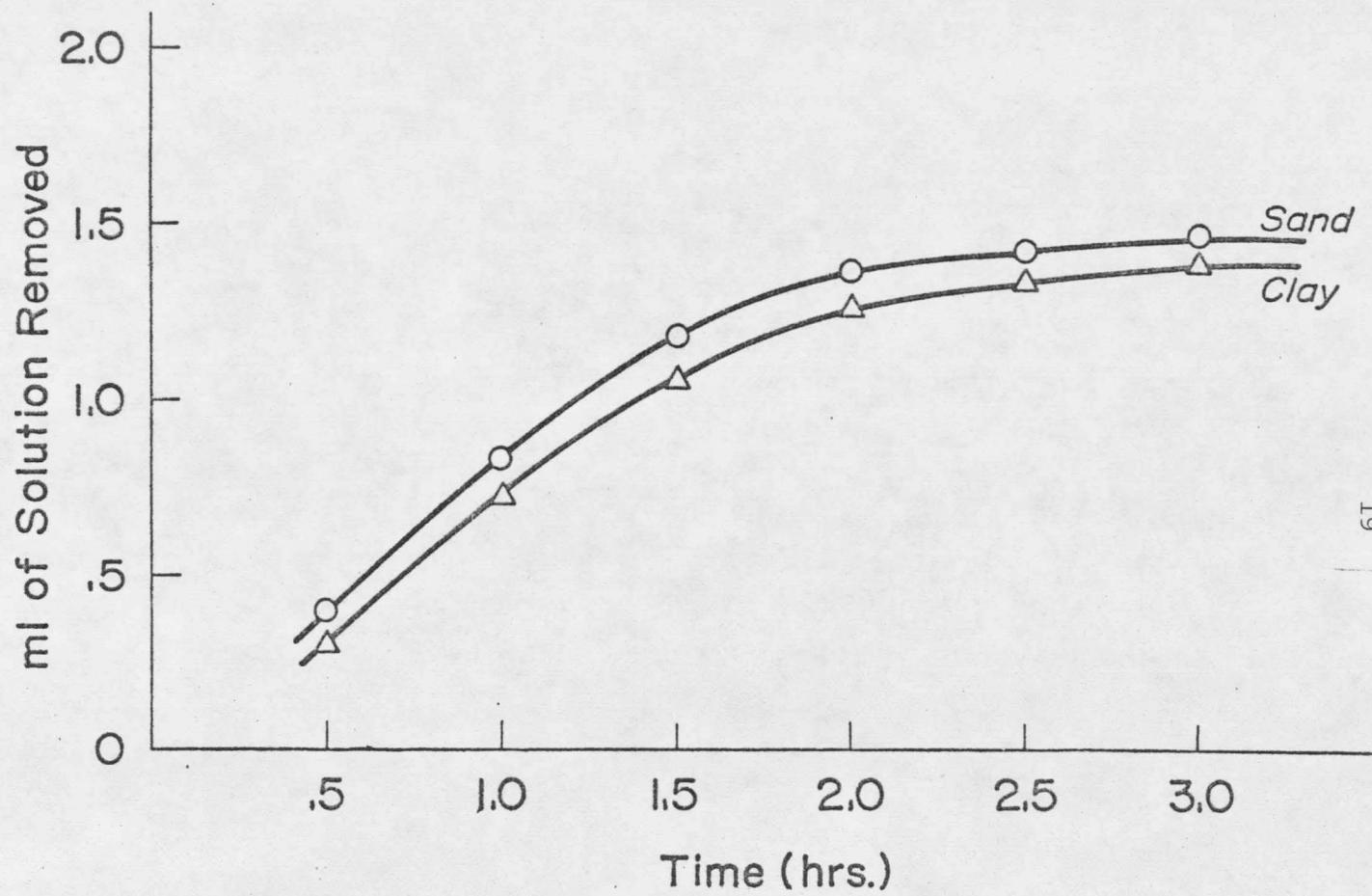


Figure 1. Amount of soil solutions removed as a function of time of centrifugation.

































































































































































































































