THE EFFECTS OF GREEN MANURE ON SOIL STRUCTURE IN CALCAREOUS SODIC AND NON-SODIC SOILS

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SUMMARY

Inappropriate soil management has resulted in structural degradation of red-brown earths in southern Australia. Decades of continuous cropping have caused some red brown earths of South Australia to have a weakly structured surface horizon that is prone to further deterioration under further cultivation and exposure. Further, accumulation of sodium in some sub-soil layers has exacerbated the structural problems due to damaging effects of sodicity. Dense subsoils have few macropores, restricting profile drainage and depth of wetting. A proper management system to improve and maintain soil structure while concurrently allowing opportunities for cropping is necessary to sustain the productivity in these soils.

It is well known that organic matter is essential for the improvement of soil structure. Addition of organic residues has been shown to improve the structure of non-sodic red brown earths. Clay swelling and dispersion are the major factors affecting structural degradation in sodic soils. Most of the sodic red brown earths in Australia are highly alkaline and also contain lime ($CaCO_3$) in an insoluble form. Dissolution of this lime will help in generating Ca ions in solution to provide electrolyte effect in flocculating the soil clays and exchanging Na from the clay surfaces. Decomposition of organic matter can produce CO_2 and organic acids which may help in dissolving the native lime. Therefore, the aim of the present study was to investigate the efficiency of green manuring to ameliorate the degraded soil structure both in non-sodic and calcareous sodic soils.

A non-sodic red-brown earth from Urrbrae (0 - 15 cm) and two calcareous sodic soils of the B-horizons (15 - 30 cm) from Strathalbyn and Two Wells were used in this study. All experiments were carried out in glasshouse conditions in pots containing 1 kg soil. The non-sodic soils from Urrbrae rotation plots (maintained over > 50 years duration) were taken from the treatments wheat/fallow, continuous wheat, and permanent pasture. In the sodic soils, the effect of green manure was examined with and without the addition of gypsum, while for the surface non-sodic soils, green manure only was added.

Because green manuring requires the addition of a considerable amount (mass) of plant material, plants to be used had to be selected largely on this basis. Pilot experiments were thus conducted to determine the production of biomass from the following green manure plants: common vetch *(Vicia sativa)*, alfalfa *(Medicago sativa)*, cowpea *(Vigna sinensis)* and white clover *(Trifolium repens)* as influenced by soils with different previous management histories. Without its breakdown by microorganisms, the incorporated organic matter is of little value to the soil. Because succulence is related to the efficiency of plant matter decomposition, estimates of the quality of green manure produced were carried out via a subjective index of succulence. Of the above mentioned plant species, the common vetch was found to be the most succulent, whilst achieving more biomass in these soils.

In the main experiments, common vetch was chosen as a green manure plant. For the sodic soils with gypsum treatment, gypsum (20 t/ha) was added initially to ameliorate sodicity, where four cycles of wetting and drying allowed exchange of Na^+ with subsequent leaching. Green manure crops were then planted in the sodic soils. After the growth and harvesting, soils, both sodic and non-sodic, were incubated with green manure (20 t/ha equivalent) by incorporating fresh plant material throughout the soil mass in the pots at 25° C in a sealed cabinet under the following water regimes: (1) alternate wet and dry, (2) field capacity (3) 80% field capacity.

Soil structural stability of non-sodic soils was assessed by wet sieving, water retention at -100 kPa potential and saturated hydraulic conductivity (K_S). These measurements were chosen for the following reasons: (1) Organic materials in general have been observed to maintain pore openings in soils by holding aggregates intact and thereby reducing dispersion which results in the filling of small pores with clay particles. (2)The stability of aggregates to wetting helps to determine the speed at which water flows through a column of soil. (3) The amount of water retained at various potentials depend on texture and structural characteristics of a soil, indicating that at the lower potentials a fine texture and good structure increases the amount of water retained by soils and available for plant use.

In sodic soils, spontaneous and mechanical dislocation of clay particles facilitate their mobility in the soil solution, thereby blocking pores and microchannels. Low permeability in clayey soils such as sodic subsoils, is the main problem. Additional measurements for sodic soils thus included clay dispersion, electrophoretic mobility of clays and particle size analysis.

In non-sodic Urrbrae soils, the improvements due to green manuring on water stable macroaggregation (WSMA), and water retention at -100 kPa potential were not statistically significant. However, these measurements showed a significant soil structural improvement in the Urrbrae soil which had previously been under permanent pasture. Further, green manure when incubated at 80% field capacity substantially improved the structural features in this soil. Saturated hydraulic conductivity values were improved by green manuring in all soils under all conditions due to the increasing trend in macroaggregation.

In sodic soils, generally, the improvements in soil structure was in the following order of treatments: gypsum + green manure > gypsum > green manure > control. The K_s increased in the same order. The soils incubated at 80% field capacity showed highest increases. The differences in water retention and water stable macroaggregation measurements were not statistically significant. In sodic soils, green manure increased the cations Ca^{++} and Mg^{++} in solution and the electrical conductivity, and pH was reduced. A marked decrease in pH was observed in Strathalbyn soil containing 15% $CaCO_3$, due to the dissolution of native $CaCO_3$ by the protons and CO_2 produced by green manure. The combination of these changes reduced the sodium absorption ratio (SAR) of these soils considerably.

Green manure did not improve macroaggregation in sodic soils, although in non-sodic soils, a slight improvement was observed. However, in sodic soils, stabilisation occurred at the microstructure level. The average size of dispersed materials in control soils were < 0.5μm, whereas after green manuring, the average particle size increased up to 30μm. The products of decomposition of green manure were both organic compounds and the release of Ca^{++}, which aggregated the clay particles and stabilized the domains. Thus, the effect of green manure on sodic soils containing $CaCO_3$ markedly differs from non-sodic soils. The results of this experiment promise the use of green manure as an economic ameliorant for sodic soils with $CaCO_3$ and high pH.

DECLARATION

This disssertation contains no material which has been accepted for the award of any other degree or diploma in any University. To the best of the author's knowledge and belief, this dissertation contains no material previously published or written by another person, except where due reference is made in the text.

I consent to this dissertation being made available for photocopying and loan.

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Chapter 1

Introduction

1. Introduction

1.1 The Problem

The red brown earths are important grain-producing soils on which South Australian agriculture depends. Structural decline and the formation of a surface crust have long been a feature of continuously cultivated red brown earths and also have been linked traditionally with an accompanying decline in the levels of organic matter in these soils (Emerson, 1954). As a result of clearing of the natural vegetation for crop cultivation, extensive damage has been done by exposure of the soil to the weather. In South Australia, the continuation of erosion in many cropped red brown earths, is exacerbated by the effects of overgrazing by rabbit, sheep, cow and goat in dry inland areas, in further exposing organic matter to atmospheric conditions. (Handreck, 1979).

Now largely depleted of macroaggregates, most of the continuously cultivated red brown earths of South Australia have a weakly structured surface horizon that is prone to further deterioration under frequent cultivation for crop growth (Hamblin, 1984). With each episode of cultivation microorganisms decompose the exposed organic matter, further resulting in a new flush of inorganic nitrogen (Boekel, 1985) which is then lost through leaching, and under waterlogged conditions, through denitrification. These losses lead to lower crop yields (Adams *et al.* 1987).

Traditional methods for the improvement of such soils through the addition of organic matter includes agroforestry, and permanent pasture rotation. In the former, nitrogen-fixing trees improve the growth of crops beside them through the addition of top-growth (Katchaka *et al.* 1993). However, In a semi-arid climate it is not possible to grow such forest trees. The structure of these soils would also improve under a pasture phase, because of the inputs of roots and other organic matter to the soil (Emerson, 1954). The effects of the introduction of pasture in rotations have corrected the problem in some areas, as indicated by several workers (Tisdall and Oades, 1979; Tisdall and Oades, 1980; Oades 1984; Smettem *et al.* 1992). In many areas however, crops must be grown continually for human needs, and it may be that the maintainance of pastures for periods of years may not be a sustainable option.

Calcareous, sodic soils of low fertility and inhospitable physical conditions, occupy large tracts of red brown earth in south eastern Australia (Rengasamy and Olsson, 1991). Though free lime in the soil does not appear to be harmful to plants (Hausenbuiller, 1978), high levels of lime (> 1.0 %) and pH (> 8.4) are associated with poor growth conditions. Lack of major nutrients in calcareous situations (where Ca by weight > 3.5 % of the whole soil), particularly of nitrogen (Willis, 1963; Lloyd and Pigott, 1967; Jeffrey, 1987;) are a constraint to the growth of vegetation on such soils (Jeffrey, 1987). The usually high pH in calcareous sodic soils is inimical to adequate growth of most plant species. The pH of such soils can be reduced through the introduction of organic acids into the soil (Yadvinder-Singh *et al.* 1992). When high CO_2 concentrations are thereby generated, hydrogen ion concentration and $CaCO_3$ dissolution rates are high (Bear, 1968). The Ca^{++} released inhibits the spontaneous breakdown of such soil aggregates by then replacing Na^+ on the clay colloids (Rengasamy and Olsson, 1991). This is of particular importance in the subsoil zones, where the higher clay content exacerbates the effects of sodic conditions, by restricting infiltration. After irrigation of these soils, surface waterlogging restricts oxygen availability to roots, whilst on drying, soil strength increases to levels at which root elongation is severely restricted (Loveday, 1984). It has also been found that decalcification of a low carbonate soil is associated with continued decomposition of organic matter (Jeffrey, 1987).

1.2 Green Manure

Green manuring has been defined as the practice of enriching the soil by turning under undecomposed plant material either in place or after transporting it from a distance (Pieters, 1927). In some instances, high levels of increases in crop yields following green manuring have been recorded. After green manuring Chen and Wang (1987), observed increases of 956 kg/ha, 805 kg/ha and 2474 t/ha for wheat, rice, and maize respectively in one extensive study. However it is still not clear as to whether or not these dramatic yield increases were accompanied by improvements in the physical properties of the soils, due to the green manure. For sodic soils in particular, regardless of the amounts of inorganic fertiliser added to the soil, the prevailing soil physical condition prevents, or severely restricts the facility of roots to imbibe the nutrients. Yet, incorporated green manure has been shown to increase crop yields in sodic soils (Paratchapreecha *et al.* 1993).

In combination with organic matter, calcium compounds have been reported to have reduced dispersion in sodic soils. This was observed by Muneer and Oades (1989), and Baldock *et al.* (1994). Sekhon and Bajwa (1993) observed that the enhancement of the release of Ca^{++} into the soil solution can be achieved through the incorporation of rapidly decomposing organic materials, such as green manure. The Ca^{++} reduces dispersion of clay particles from aggregates, by becoming cation bridges between negatively charged clay particles, and between organic anionic groups. The effectiveness of incorporation of green manures into the soil to ameliorate and restore the structural integrity of soils between rotations has not been fully investigated in South Australian soils, and could possibly be a method of improving degraded soils.

1.3 Aim

The aim of the present study was to investigate the efficiency of green manuring to ameliorate the degraded soil structure both in non-sodic and calcareous sodic soils.

1.4 Hypothesis

It is well known that organic matter is essential for the improvement of soil structure. Addition of organic residues has been shown to improve the structure of non-sodic red brown earths. Most of the sodic red brown earths in Australia are highly alkaline and also contain lime ($CaCO_3$), where green manure may help in dissolving the native lime. The hypothesis for the proposed study, therefore, is that structurally degraded red brown earths (alkaline sodic soils and non-sodic) will show significant physical improvement when treated with incorporated green manure.

1.5 Outline of Thesis

The outline of the thesis is as follows: A review of the literature on green manure and its effects on soils (chapter 2), is followed by a chapter on pilot experiments to determine a suitable green manure crop (experiments in this study are conducted in indoor conditons to reduce the number of uncontrollable variables) for the improvement of soil structure. In the main experiments which follow (chapter 4), the effects of green manure on soil structure for non-sodic soils are assessed. Soils are incubated with green manure under three water regimes (field capacity, 80% field capacity, and alternate wetting and drying), three soil types (i.e. management histories) which include continuous wheat, wheat fallow, and permanent pasture. Incubation periods are 4 weeks, 8 weeks, and 12 weeks.

Chapter 5 evaluates the effect of green manure on the calcareous sodic subsoils. For the two calcareous sodic subsoils, the effect of gypsum on soil structure is compared with the effect of green manure alone, and with green manure in combination with the gypsum treatment. Treatments are similar to those previously adopted for the non-sodic soils, but with gypsum as the additional factor. Thus for the sodic soils the factors are soil type, water regime, time period of incubation, gypsum/no gypsum, green manure/no green manure. It has been widely established that in sodic soils the microaggregates are more unstable than those of non-sodic soils (Oster *et al.* 1980; Greene and Ford, 1983; Rengasamy *et al.* 1984). According to Warkentin (1982), for clayey soils, the flocculation of clay particles (< 30µm) is enhanced by both inorganic (e.g. via cation bridges) and organic binding agents. Therefore in addition to the measurements for structural change mentioned above for the non-sodic soils, the following additional techniques were used to assess structural stability and microstructural changes in the calcareous, sodic subsoils for the various treatments:

spontaneous dispersion
mechanical dispersion
sub-micron particle size analysis
electrophoretic mobility

In addition, the pH, electrical conductivity (EC), sodium absorption ratio (SAR) and total cations were also measured by standard methods (Rengasamy *et al.* 1984) as further evidence for structural changes. This is followed by a general conclusion.

Chapter 2

Literature Review

2.1. The Importance of Organic Matter in Soil Structure

Organic matter is that fraction of the soil which includes plant and animal residues at various stages of decomposition, including cells and tissues of soil organisms and the substances synthesized by them (Houghton and Charman, 1986). This material helps to stabilise soil structural units called aggregates, against wetting, by acting as an organic bonding agent linking the soil particles in an open network (Russell, 1973b), and reducing the wetting rates, through its inherent hydrophobicity (Low, 1955). It has also been observed that in many of the soils of South Australia, especially the loamy red-brown earths, organic matter is the chief structural stabilising factor (Oades *et al.* 1981). Grierson *et al.* (1972) found that decreases in water-stability of aggregates have been associated with reductions in total amount of carbon in the soil in semi-arid areas of South Australia. It is known that the contents of soil organic matter decline in soils used for continuous cropping (Gustafson, 1943; Low, 1972; Tisdall and Oades, 1982), because whenever soil is cultivated, aggregates are broken down (Oades, 1984). Organic matter becomes exposed and can then be rapidly decomposed by oxidation (Golchin *et al.* 1994) and broken down by micro-organisms (Rovira and Graecen, 1957; Oades, 1984). As indicated through simulation soil-crop models combined with field experiments, the above results have been verified (Van Lanen *et al.* 1992). In one particular field trial after eleven years of continuous maize cultivation, the proportion of water-stable aggregates in the > 2 mm range had decreased by 34% (Sparling *et al.* 1992). Agricultural activities over a 60 year period have been responsible for the breakdown of water-stable aggregates > 1000 µm in diameter on the Urrbrae fine sandy loam into microaggregates of < 250 µm (Grierson *et al.* 1972; Oades *et al.* 1984).

The importance of carbon content to soil stability applies to soils under various climates and geographical areas (Donahue, 1971; Tisdall and Oades 1979; Benito and Diaz-Fierras 1992; Van Lanen *et al.* 1992). Stability is increased as slaking is slowed or prevented by factors such as organic matter, which retard the wetting process and bind particles together.

Other studies have revealed that the losses of organic carbon are strongly correlated to amounts of water-stable aggregates in several Australian soils (Tisdall and Oades, 1980; Smettem *et al.* 1992). Data from a long-term rotation trial at Tarlee, Australia, indicate that the consistent burning of stubbles had reduced the stability of soil aggregates in comparison to the incorporation into the soil of organic matter (Hermann, 1990). Thus Tisdall and Oades (1980) estimated that for each 0.1 per cent increase in organic carbon, there is a 2 per cent increase in water stable aggregation and a one per cent increase in the soil moisture holding capacity. Tisdall and Oades (1982) found that for six separate soils, water stable particles > 2000, 1000-2000, 500-1000 and 250-500 μm in diameter were stabilized largely by organic matter. In order to have stable aggregates, the humus content must be at least 10% of the overall clay content of a soil (MacRae and Mehuys, 1987). The ameliorative needs for soils with low humus content are clear. Thus for structural amelioration of soils, a range of management systems which restores physical fertility and integrity to the soil fabric under different climatic conditions is required.

2.2 The Role of Green Manuring

2.2.1 Historical development

Historical records show that the Chinese grew and ploughed in green crops, mostly legumes, directly, or as compost for the purpose of manuring rice fields, and in Greece and Rome, even before the time of Christ, green manuring was a common practice. Later, in Germany, and a century later in England and France, green manure partially replaced animal manures. When the European colonisers arrived in America they found no need to follow these practices as they were confronted with (rich) virgin land. However as new soils lost their fertility a few American farmers began to adopt the green manuring system, and its use increased in subsequent years.

2.2.2 Effects of Green Manure on Soils

It has been reported that in many of the green manure studies done, one of the chief factors in the improvement of wheat yields has been the improvement of the physical condition of the soil (Pieters, 1927; Paratchapreecha *et al.* 1993). Lander *et al.* (1923)

using the legume guara *(Cyampoposis psoraloides)*, along with a non-legume for green manuring on wheat soils concluded that the main factor responsible for the increase in yield was the improvement in soil physical structure due to the addition of the green manure. The mechanism by which this occurs is believed to be linked with increased organic matter in soils (Allison, 1973). Connell and Hadfield (1961) asserted that green manures when ploughed in, could help to improve the soil physical properties. This is supported by field trials in the Netherlands, where Boekel (1985) found that the long-term effects of green manure were to improve soil physical properties by increasing humus content. Paratchapreecha *et al.* (1993), after soaking green manure under flood waters for three days, and then incorporating it into soil, found that in addition to increasing P and K in the soil, the green manure reduced the bulk density of the soil. This is largely because it has been observed that the association of humus with clays can profoundly influence the physical properties of the soil. For example, as soon as a fresh mass of plant material is turned under (under ideal conditions) all the activities normally going on in the soil are speeded up and new ones develop (Aber and Mellilo, 1980). As the biological activities increase, they produce organic compounds which react with the inorganic materials in the soil (Pieters, 1927; Swaby 1949; Warkentin, 1982), to form organo-mineral complexes (Theng, 1974).

Compared with non-leguminous plant material, the speed of decomposition of fresh leguminous plant material is, in favourable soil and temperature conditions, unsurpassed (Gustafson, 1943; Yadvinder-Singh, 1992). Under suitable conditions of warmth and moisture, decay of fresh plant matter takes place quickly (Swaby, 1949; Swift *et al.* 1979), with desirable effects on the soil (Allison, 1973) including aggregation (Geltser, 1943; Gustafson 1943; Connell and Hadfield, 1961). Furrow burial of chopped up plant matter achieves this aim, if time is allowed for decomposition prior to the next crop (Gustafson, 1943). Decomposition of *Croatalaria juncea* and *Sesbania aculeata*, after incorporation in hot wet conditions is rapid (Tamai *et al.* 1990); especially of the more readily decomposable parts such as leaves and young stems (Franzluebbers *et al.* 1994). It seems reasonable to postulate that soil physical properties such as infiltration rates and aggregate stability could be improved by leguminous green manures.

The response of soils to the addition of organic matter depends largely on the texture of the soil. MacRae and Mehuys (1985), found that improvements in physical properties of soil after green manuring were limited to those of clayey texture. In a comparison of vertisols of different texture, it has been found that certain fine-textured vertisols have shown greater soil structural stability as affected by organic matter levels than those vertisols with a coarser texture (Coughlan, 1984). The "century model" for organic matter decomposition in soils indicates that soil texture influences the turnover of the active soil organic matter (SOM) (Parton *et al.* 1992). A high rate of decomposition of organic matter is generally observed in sandy soils. In soils with high clay contents, especially in clays having high exchange capacities, it has been observed that the rate of decay of organic matter is slowed (Allison, 1973; Sorenson 1975), and therefore organic matter is retained in the soil. For example, McRae and Mehuys (1987), 3 years after incorporating green manure to a gravelly loamy sand and a clay, found that the green manure increased organic matter on the clay site. On the sandy site, no increase in organic matter levels was noted. This trend is not limited to aerobic soil conditions. For example, under anaerobic conditions, (Frankenberger and Abdelmagid, 1985), found that after 32 days of flooding, the N release from vetch green manure plus rice straw was 26% in heavy clay but only 15.6% in a clay loam soil. Because incorporated organic matter is not as quickly lost in fine textured soils, the physical properties of clayey soils are more greatly improved than those of the sandy soils. Thus the incorporation of red clover into a clay soil improved dry-aggregate distribution and reduced bulk density (MacRae and Mehuys, 1987).

On the sandy soils, the lack of response in soil physical properties to green manure can be attributed to the lack of total organic matter increase accrueing from green manure treatment of such soils. Without clay, the interactive surface areas in the soil are limited. For example, in experiments with polymers in soils, Schamp and Huleybroeck (1972) found that a 1% application of kaolinite was sufficient to cause a marked increase in the water stability of synthetic soils. The strength of the adhesive bond between organic and inorganic particles is dependent on their interfacial interaction and the cohesive strength of the polymer-inorganic surface interaction.

Organo-mineral complexes are therefore, in all soil types, of fundamental importance in the creation of water-stable aggregation. The production of such colloid complexes exert chemically and physically beneficial effects. In one green manure study, it was estimated that 51% of the organic matter applied went towards organo-mineral complexing (Chen and Wang, 1987). During green manure decomposition, large amounts of insoluble polymers are formed, some with relatively low molecular weights, and negatively charged (Yadvinder-Singh *et al.* 1992). These substances are able to form a complex with clays, via metal ions in the soil (Chen and Wang, 1987). As this process is accretive, it causes the increase in the size of the domains and flocculation of clay particles (Turchenek and Oades, 1978). As a result, the hydraulic conductivity and permeability of soils incubated with green manure are increased.

Other effects on the green manured soil relate to changes in the nutrient status. Because leguminous green manure plants increase the nitrogen status of soils, it seems reasonable to postulate that for the dual purpose of N increase and aggregate stability, the addition of organic N via leguminous green manure can be more beneficial to the soil. For example, water-stable particles >1000 μm in diameter have been positively correlated with the percentage of total nitrogen in red brown earths at $r^2 = 0.93$ (Tisdall *et al.* 1978). Leguminous green manures are thus better choices for the rehabilitation of physically degraded soils; furthermore, mineral N is needed by microorganisms, and therefore N is indirectly needed for decomposition in green manured soils. In addition, it has been found that under field conditions, more N is returned to soil which has been ameliorated with fresh plant material as compared with other organic amendments such as straw (Patterson, 1960). For example, in 60 - day pot trials, *Crotolaria juncea,* produced significant increases in dry matter yield and 160-250 kg/hectare of N were also accumulated (Fox *et al.* 1990). Nitrate accumulation ranged from 2 - 1995 kg/ha for tropical legumes, to 56 - 338 kg/ha for winter legumes, and 98 - 532 kg/ha for stem-nodulating legumes. The vetch, cowpeas, and clover have high yields (Williams, 1966). The hairy vetch, which is grown in semi-arid conditions, has been observed to have the lowest C:N ratio amongst annual legumes (Williams, 1966). Other species, such as the *Sesbania aculeata* have similarly low C:N ratios, but they grow better in wetter soil conditions (Singh, 1974)

2.2.3 The Rates and Methods of Application of Green Manure

Though the effectiveness of organic matter in soil structure stabilization has been documented, it has also been found that relatively high rates of organic materials (Allison 1973; Tisdall *et al.* 1978; Swift 1992) or green manure application (Pieters, 1927; Patrick *et al.* 1957; Williams and Doneen, 1960; Tamai *et al.* 1990) were needed to improve degraded soils. Ghai *et al.* (1988) added green manure from *Sesbania Aculeata* and *Croatalaria juncea,* at the rate of 24.7 and 20.8 t/ha respectively, to wheat soils, with a subsequent increase in yield equivalent to the addition of 122 and 78 kg/ha of N. Also, over a period of 5 years, in 22 soil types spanning 17 provinces in China, the amount of soil organic matter was increased in the range 7.3 - 33.6 % by green manure incorporated at a rate of 22.5 - 30 t/ha (Chen and Wang, 1987). Tamai *et al.* (1990) incorporated green manure at 1 % (by weight), with significant crop yield increases.

High rates of application are necessary because of the low ratio of active to passive organic matter in plant materials. According to the *Century Model* for soil organic matter decomposition (Parton *et al.* 1992), it is the labile and active organic matter that improves soil carbon content in the short-term. For example, under both submerged and aerobic conditions, the decomposition kinetics of *Sesbania aculeata* was divided into two distinct components; the labile, and the recalcitrant (Sur *et al.* 1993). According to them, the proportion of labile organic matter, though relatively high in fresh plant matter (as compared to dried material), is still usually less than 20%. In several soil types, Chen and Wang (1987) found that green manure increased the amount of active organic matter content and total humus content by 17.4, and 6.1% respectively.

There are, however, advantages in applying dried plant material to soil. Transportation costs can be dramatically reduced by the drying of the plant material prior to transporting it. However, it has been found that as plant material becomes dry it is less effective as a green manure (Katchaka *et al.* 1993; Yadvinder-Singh *et al.* 1992). For instance, it has been observed that fresh plant matter from *Azolla pinnata* released up to 2.5 times more NH_4^+ - N than dried *Azolla pinnata* (Yadvinder-Singh *et al.* 1992). Joachim (1931) stated that such drying converts soluble hemicelluloses into less soluble forms. This is a possible explanation for the reduced mineralisation rate of green manure (by 20%) observed by Lohnis (1926) in upland soils. This effect does not seem to vary with soil water content, as Lohnis (1926) also found that the effect of drying sesbania and milk vetch for 24 hours at 60^o C prior to incoporation into soil at different water contents, had similar influences on N release.

There are several good reasons for growing plant material for green manure in the soils where it is needed. These include high costs of transport for undried material, and the added improvement to the soil physical and chemical properties due to *in situ* root growth (Oades, 1993). Yields of green manure plants in the range of less than 10 - 20 t/ha (dry matter) have been regarded as effective in the restoration of soils (Franzluebbers *et al.* 1994). Yet, it must be remembered that much lower yields of leguminous species are normally obtained from most semi-arid soils. For example, Mayfield *et al.* (1994) in field experiments in semi arid areas of South Australia, obtained yields of 6 - 11 t/ha of green manure tops, with the vetch species *Vicia sativa* achieving the highest mass (10.7 t/ha) (dry matter). In a Sub-Sahelian Alfisol, millet intercropped with cowpeas yielded shoots weighing 3 t/ha and 2 t/ha respectively for use as green manure (Franzluebbers *et al.* 1994). The technique they applied was that of shallow incorporation (6 - 10 cm) of green manure, where the tonnage required was consequently greatly reduced, compared with that required for traditionally deeper applications of 15 - 25 cm adopted by previous workers (Williams and Doneen, 1960; Williams, 1966). This is also in keeping with recent trends towards tillage reduction in soils, where an advantage is that under the shallower incorporation, a more thorough permeation of the soil with organic matter is achieved. Thus green manure crops grown at a dry matter yield of only 5 t/ha, when incorporated at the soil surface, caused improvement in crop yields (Franzluebbers *et al.* 1994).

2.3 Types of Green Manuring

The main methods of crop growth for green manuring have been described by Pieters (1927); and Allison (1973) and summarised here.

2.3.1 Main Crop

A main green manure crop occupies the ground during the summer, to the exclusion of any other crop and may be turned under in autumn or the following spring. This is an expensive procedure as the crop is not sold and the cost of seed and labour is not recouped by an immediate income from the occupied land. Due to the lack of immediate financial returns, such a crop is not usually grown except on very poor soils which must be greatly improved to be productive.

2.3.2 Companion Crop

As a companion crop, the green manure crop grows on, after the main crop has been harvested. Traditionally (in the U.S.A. especially), the choice has been clover; (1) it adds nitrogen and (2) at the same time does not compete with other main crops for light (due to its low height) and (3) it needs shade (provided by the main crop) to grow well. The main advantage of a companion crop is that though it sometimes occupies the ground for a longer time than the main crop it does not do so to the exclusion of the main crop. As a result, in monetary terms, this would be the most economical type of green manuring.

2.3.3 Winter Cover Crop

A cover crop seeded for the purpose of soil improvement becomes a green manure crop after it has served its function of protecting the exposed soil after harvest of a main crop. It also immobilises valuable N for the ensuing crop and acts as a winter cover which may be then turned under in the spring. However, especially in semi-desert climates, competition for water should be considered, as there is the danger of such a cover crop depleting the soil water resources to the point of endangering the soil productivity for the ensuing main crop. Winter ground cover crops include legumes such as alfalfa, peas, and lupins (Calegari 1990).

2.3.4 Catch Crop

Crops having a brief period of growth (e.g. cowpeas, mustard, soybeans) are worked into the soil during the short time interval between rotations. A crop may be grown for the purpose of ploughing it in to improve the soil (e.g. legumes) for a succeeding crop species which normally make heavy demands on soil nutrients.

2.4 Choice and Justification of Green Manure Crop Type

Several reasons exist for growing a main crop for incorporation into degraded soils, which relate to costs, amount of biomass required, level of soil degradation prevailing, and time required for alternative methods of amelioration, e.g. growth period of grasses. They are as follows:

(1) Of the growing systems described above, the *main crop* system, by excluding other crops, would produce the greatest amounts of plant material for incorporation. Such a programme may be applied where the soil is very degraded and first needs to be physically rejuvenated before becoming able to support growth of most crop plants. In such cases a high level of soil rehabilitation is not initially sought; instead the aim is to bring the soil fertility and structure up to a level to which the soil would be able to support vegetation leading to long term stabilisation.

(2) In some areas, such as densely populated rural zones and market gardens, there is not enough time between rotations for the growth of grasses for soil rehabilitation; There would therefore, be a need for rapid methods of soil structural restoration.

(3) Due to the logistics involved in transporting great quantities of fresh organic matter to a rehabilitation site, the source in any large-scale programme of amelioration must be from locally grown plants.

2.5 Soil Structure

Brewer (1964) has defined soil structure as "the physical constitution of a soil material as expressed by the shape, size and arrangement of the solid particles and voids, including both the primary particles to form compound particles and the compound particles themselves; fabric is the element of structure which deals with arrangement." Brady (1974) characterises structural elements as single grained, massive, or aggregated:

(1)*Single grained*	When particles are entirely unattached to each other, the structure is completely loose, as in the case of sands.
(2)*Massive*	Where soil is tightly packed in large cohesive blocks, the structure is massive when dry, as in sodic clays
(3)*Aggregated*	Between the two extremes are intermediate conditions where aggregates of soil particles exist.

Formation and maintenance of stable aggregates to a level of good tilth occurs when the soil is optimally loose, friable and porous, permitting rapid movement of air and soil-water, easy cultivation and planting, and germination and growth (Hillel, 1982).

Because it is in the pores that the fluxes of water, gases and nutrients occur, their size, shape, distribution and connections are important parameters (Warkentin, 1982). Desirable soil structure for plant growth thus occurs when there are adequate inter-linked networks of pore spaces existing in well-aggregated soil. Interped and interaggregate pores are useful for the movement of gases and water; intra-aggregate pores contain water available for plant growth, and interdomain pores contain water involved in interparticle and physico-chemical forces. The solid phase is also important. Oades' (1993) definition of structure as "the arrangement of particles and pores within a soil" indicates the significance of spatial heterogeneity of the different components of the solid phase of the soil and the mechanisms by which they are held together (Dexter, 1988).

The definition of structure includes the resistance of aggregates to deformation by applied stress. The integrity and stability of pores and peds in water are thus important. As the extent of an aggregate's resistance to physical deformation depends on the strength of the bonds within it, the internal particle-particle binding energies must supercede the strength of the external forces acting on the aggregates. Thus, for the maintainance of good soil structure, at least 40% of the soil should be comprised of water-stable macroaggregates (> 250μm < 5mm) (Reid and Goss, 1981).

Good aggregation is demonstrated when aggregate breakdown occurs in several steps, according to their size. This is a hierarchical order of aggregation. On the other hand the "powdering" of a macroaggregate with a single blow of a hammer signifies poor soil structure (Dexter, 1988). When climax vegetation has been on the soil for many years, the soil will have usually attained "good" structure; with significant amounts of clay, the structural arrangement in such soils is "hierarchical" (Taylor and Brar, 1991). This hierarchy of aggregate size in ascending order, ranges from clay platelets through to floccules (or domains), micro-aggregates and macro-aggregates with each aggregate size incorporating all smaller sizes (Dexter, 1988). However, each particular aggregate size responds differently to particular stresses (Oades, 1984). Edwards and Bremner (1967) postulated that the only stable compound soil particles were microaggregates. Tisdall and Oades (1980) found that particles of 50 - 250 μm in diameter in a red brown earth under various management systems over a period of 50 years, showed high levels of stability. In keeping with the porosity exclusion principle, where porosity is cumulatively greater in larger aggregates, smaller aggregates are more dense (Dexter, 1988). This leads to a greater number of physical connections within the smaller aggregates. Thus, binding strength is greatest in smaller aggregates, while larger aggregates are more easily disrupted. Ultrasonic and wetting treatments have demonstrated the existence of such a hierarchy, because break-up of an Alfisol and a Mollisol has been shown to occur in defined steps (Barzegar *et al.* 1996) as follows:

(1)	aggregates > 250 μm	(first step)
(2)	aggregates 20-250 μm	(second step)
(3)	aggregates < 20 μm	(third step)

2.6 Structure of Sodic Soils

Many soils used in agriculture in Australia, and also in many parts of the world are sodic and are difficult to manage due to their tendency to disperse. As a result they exhibit physical and nutritional problems due to poor soil-water and soil-air relations (Rengasamy and Olsson, 1991). Excess exchangeable sodium in soils is harmful to plants because it induces undesirable physical and chemical characteristics in the soil environment (Hausenbuiller, 1985). It is the ready disintegration of sodic soil aggregates, which often causes surface sealing and hard setting. When these soils are wetted rapidly or disturbed, the fine clay particles are dispersed into the solution, blocking pores, and thereby reducing infiltration (So and Alymore, 1993).

Clay minerals are layered phyllo-silicates of colloidal size (<2 μm), with the ability to shrink and swell. The effects of exchangeable cations and electrolytes in controlling swelling are largely dependent on the type of clay mineral present in the soil (Frenkel *et al.* 1978). Thus interactions between constituents of the clay fraction and the soil solution in the pores largely determine soil behaviour. Exchangeable Na^+ in smectites cause indeterminate swelling, while exchangeable Ca^{++} causes only limited swelling (Frenkel *et al.* 1978). This is because the sodium ion is the most highly hydrated ion in soils. In keeping with such effects, as related to the double layer theory, sodicity causes swelling in clays, thereby cutting off flow in interconnected channels and reducing hydraulic conductivity (Shainberg *et al.* 1981).

2.6.1 Main Effects of Sodicity on Plant Growth

Soils with a high pH (> 8) have little or no soluble aluminium present but calcium, magnesium and sodium are present in abundant amounts. When the soil pH is above 10, sodium is the dominant cation and few plants grow (Seatz and Peterson, 1968). More than strong alkalinity *per se,* the attendant physical restrictions are inimical to plant growth (Rengasamy and Olsson, 1993). Furthermore, the restrictions that strong alkalinity imposes on the availability of the other nutrients, such as Zn, Fe, Mn makes it even more detrimental to plant growth. In strongly alkaline soils, Al toxicity can also occur in soils (Corbett, 1969). At pH > 10, there is an overriding tendency for Al to form $Al(OH)_4^-$, leading to the formation of soluble Al in soils (Hausenbuiller, 1978). The high solubility of Al in such compounds could contribute to poor plant growth in soils of exceptionally high pH (Hausenbuiller, 1978).

2.6.2 Dispersion and Dispersive Factors in Sodic Soils

The dispersive nature of the soil can be classified into two groups, based on response to applied stresses:

(1) Spontaneous dispersion where clay is translocated on wetting, without the application of mechanical energy.

(2) Mechanical dispersion, where kinetic energy is necessary to dislocate and separate clay particles.

It has been established that the internal cohesiveness between clay particles is the primary force responsible for microaggregate stability (Kay and Dexter, 1990; Ekwue, 1991). It has also been shown that clay dispersion is positively correlated with soil loss and negatively with infiltration (Miller and Baharuddin, 1986). Some of the chief factors affecting soil dispersion include:

(1) Clay mineralogy
(2) Electrolyte concentration of Soil Solution

2.6.2.3. Effects of Clay Mineralogy on Dispersion

The kinds and proportions of clay minerals in a soil system greatly influence dispersion. For example, even at low ESP, montmorillonitic soils disperse (Frenkel *et al.* 1978). Stern *et al.* (1991) noted also that soils with montmorillonites were more erodable than the kaolinitic soils even at low ESP (< 2.6). Goldberg and Glaubig (1987) found significant positive relationships between hydraulic conductivity and proportions of kaolinite; the converse was observed with montmorillonite.

Illites have been shown to be extremely dispersive, even more so than montmorillonite (Oster *et al.* 1980), and are well represented in Australian red-brown earth soils. A great susceptibility of illitic red brown earths to disperse even under low SAR and weak mechanical forces was detected by Rengasamy *et al.* (1984). On the other hand, it has been observed that the swelling effect of illites on kaolinites is less than that of montmorillonites on kaolinites, due probably to the intermediate shape of the illite particles (Stern *et al.* 1991). Thus the irregular surface of illites (Quirk, 1977) results in poor, irregular contact between particle surfaces. Poor contact between illite surfaces and edges (hence increasing the distance between opposite charges) is responsible for its high level of dispersiveness in water. But though the flat surfaces of montmorillonites afford a large area of good contact between particles (Van Olphen, 1977), high charge enhances imbibation of water in the interlayer region of montmorillonites and thus promotes swelling.

Rengasamy *et al.* (1984) have indicated that surface illitic soils with Sodium Adsorption Ratios (SAR) > 3 will disperse spontaneously, whilst those with an SAR < 3 disperse only after mechanical shaking. The illite component of a soil clay in one study played the dominant role in determining the dispersive behaviour as a function of solution pH and the SAR value, even when present in small amounts (Suarez *et al.* 1984). Alperovitch *et al.* (1985) observed that illites were even more dispersive than montmorillonites, as they are made of small, poorly defined flakes commonly grouped together in irregular aggregates, but then he also observed in one study that illitic clays moved down easily in hydraulic conductivity columns without blocking pores, due to the effect of minimal swelling (in contrast to montmorillonites). Because all clay-sized mineral particles disperse in varying degrees, it is the proportion of each present and their associations that determine stability of the soil aggregates under mechanical or osmotic stress. But Sumner (1993), cautions that the dispersion and flocculation of clays in a soil aggregate usually differ from the corresponding phenomena in simple clay-water suspensions. The additive effect of several minerals normally occuring together in soil systems, with other materials, are always more complex than that for pure clays. Flocculation and dispersion of clay particles within a clay matrix have been found to occur at different electrolyte concentrations to that required for clay suspensions (Quirk, 1977). Thus, though low dispersion of kaolinites have been most often reported, compared with those for the other clay minerals (Goldberg and Glaubig, 1987), this is not always the case. This is primarily because soil systems are not simply composites of clay minerals, but of materials covered with a variety of organic and inorganic films and coatings often bonded together into aggregates by various cementing agents. As such coatings can dictate the behaviour of clay in field soils, and are difficult to characterize, extrapolation from pure clay to soil systems is dangerous (Sumner, 1993). For example, based on Emerson's (1959) postulation that organic matter that has been mechanically detached from organo-mineral complexes in certain conditions leads to dispersion, such organic matter would seem to be a possible dispersant even for kaolinites, especially at high pH. Oades (1984) found that deflocculation of kaolinitic clay can be brought about by anions from decomposing organic matter. On the other hand it is well known that organic matter can increase soil cohesiveness (Ekwue, 1991). Thus organic matter can cause either dispersion or flocculation of clay particles; the nature of the organic polymers used can therefore help to determine the effectiveness of any organic soil amendment.

2.6.2.4 Effects of Electrolyte concentration of Soil Solution

After determining the amount of mechanically dispersible clay in a red-brown earth, Baldock *et al.* (1994) found that Ca^{++} and Mg^{++} were equally effective at reducing the amount of clay dispersed, with concentrations of the order of 2.0 meq/l being required to minimize dispersion, compared with 3.0 meq/l and 5.0 meq/l for K^{+} and Na^{+} respectively. Thus, even though K^{+}, and particularly Na^{+} may be more numerous in a soil, the relative effectiveness of the four cations in decreasing dispersibility was ranked in the following order:

$$Ca^{++} = Mg^{++} > K^{+} > Na^{+}$$ (Hausenbuiller, 1985).

2.6.3.. Green Manure and Dispersion

2.6.3.1. pH

Green manure amelioration of dispersive sodic soils may indirectly occur mainly by reducing the pH of alkaline soil (Bear, 1968). The effect of incorporation of green manure into soil is also greater, the greater the rate of application (Singh, 1974). For example, the pH of alkaline soils is inversely proportionate to the pCO_2 because CO_2 dissolves in water to produce carbonic acid. In the equation :

$$2\,CO_2(gas) + H_20 = H_2CO_3 + CO_2(aq) = 2HCO_3^- + 2H^+ ,$$

the greater the input of organic matter the greater the production of CO_2 (Bear, 1968). As the pCO_2 increases with the decomposition of organic matter, under moist conditions more CO_2 dissolves in water to produce carbonic acid. But the negative effects on soil quality with extremely low pH values is also reduced with green manure, for as pH decreases, gaseous CO_2 is liberated, lowering the concentration of the carbonic acid, thereby preventing the pH from falling below 5 (Russell, 1977). It thus seems that in sodic soils high in native soluble $CaCO_3$, protons released via the action of H_2CO_3 and organic acids could reduce the pH below 8, but not to highly acidic levels.

2.6.3.2. Green Manure Effects on Electrical Conductivity

There are two mechanisms whereby cations in soil solution may increase with green manure:

(1) their addition in legumes,

(2) their dissolution from soil minerals by decomposing plant matter .

The decomposition of green manure increases the solubility of minerals in soils. Leguminous plants in particular, possess a strong ability to absorb certain cations from the soil (Yadvinder-Singh *et al.* 1992). Thus soils in which leguminous green manures have been incorporated have shown a greater availability of K for plants (Katyal, 1977; Swarup, 1987). Groffman *et al.* (1987) found that ploughing in of red clover resulted in greater levels of K, Ca, and Mg in the soil. As green manure adds cations to the soil, the accompanying increase in the electrolyte concentration of the soil solution tends to decrease clay dispersion. This should increase the saturated hydraulic conductivity of such soils.

Under green manure, the accumulation of CO_2 (i.e. from respiration of microorganisms) would help to increase ions in the soil (section 2.6.3.1), thereby increasing EC (Yadvinder-Singh *et al.* 1992). Wen and Yu (1988) reasoned that because green manure contained large amounts of easily decomposable material, reducing conditions are promoted. Such conditions, they claim, lead to changes in the ion exchange and complexing properties of the soil.

2.6.4 Effects of Subsoil Sodicity

Subsoil sodicity can be deleterious to successful plant growth. Extended periods of wetting at near saturation of both topsoil and subsoils also cause a low concentration of oxygen (Olsson *et al.* 1995). Due to sodicity, clay is released from microaggregates, followed by its translocation downwards, creating dense impermeable sub-soils which cause impeded drainage (Shainberg *et al.* 1981). There is diminished water storage, and reduced water and oxygen transport (Gupta and Abrol 1990), which reduce root development and elongation (Cockroft and Bakker, 1966). Infiltration rates have been observed to have slowed from 7.5 mm/hr in aggregated soils to less than 0.2 mm/hr in dispersed sub-soils (Hausenbuiller, 1985). Heavy losses of peach trees in northern Victoria have occurred as a result of low permeability in the B-horizon of soils (Cockroft and Bakker, 1966). Low sub-soil permeability further predisposes the crops to the effects waterlogging, leaves become stressed with reductions in leaf initiation and expansion and the plants are exposed to soil—borne pathogens (Rengasamy *et al.* 1992).

In dense subsoils, storage pores commonly comprise less than 10% of the soil or 10 mm /dm depth of soil , whereas for well-structured soil that value is 20% (20mm/dm depth) (Williams, 1983). Low storage and rates of water movement through subsoils lead to a restricted volume of soil for root proliferation and exploration. Currently, sodicity is treated with gypsum ameliorants, where sodium is replaced by exchangeable calcium. Van Beekom *et al.* (1953) noted that a high humus content made soil less susceptible to the unfavourable influence of sodium. Subsequently, organic matter had been found to bind (such) clay particles together in soil aggregates so strongly that aggregates did not disperse in water, even if most of the exchangeable cations had been first replaced by sodium (Emerson, 1983).

Soil strength is controlled by a number of factors, and is an indicator of other soil physical conditions (Dexter and Chan, 1991). These include water content, the amount of clay (Kemper and Rosenau, 1984), and amount of dispersible clay (Shanmuganathan and Oades, 1983; Kay and Dexter, 1990). In sodic subsoils, the effect of dispersion is recognised as a major cause of pore blockage and the restriction of saturated water flow (Rengasamy and Olsson, 1992).

The problem of high soil strength is widespread in sodic soils in Australia, where 86 % of them have dense subsoils with an alkaline (8.0 - 9.5) pH trend (Rengasamy and Olsson, 1991). According to Rengasamy *et al.* (1992), a penetrometer resistance of < 1 MPa and an air-filled porosity of > 15% may be considered to be non-limiting for root growth. The range of soil strength and water content which are non-limiting to plant growth on modified and unmodified sub-soils are depicted in Figure 1.1 (Rengasamy *et al.* 1992): Here, aeration porosity begins at "0" in saturated sub-soils (Figure 1.1). It is seen that the unmodified sub-soil then has to dry over a much longer period than does the modified sub-soil of high macroporosity, in order to attain the lower limit for aeration porosity. Yet, after a short drying period, the unmodified subsoil would have become too strong for root proliferation, regardless of its aeration porosity. Thus at position "A" the increasing soil strength is limiting for roots, at a much higher water content than that of the modified sub-soil. For the unmodified soil a restricted opportunity therefore exists between A and B for root growth. Thus the chief physical problem of such subsoils is that of simultaneously acquiring and maintaining adequate water and aeration for plants, while not exceeding the threshold of mechanical resistance for root growth.

Figure 1.1

Ranges of water content (volumetric) in subsoils where aeration and strength are non-limiting for root growth (after Rengasamy *et al.*, 1992)

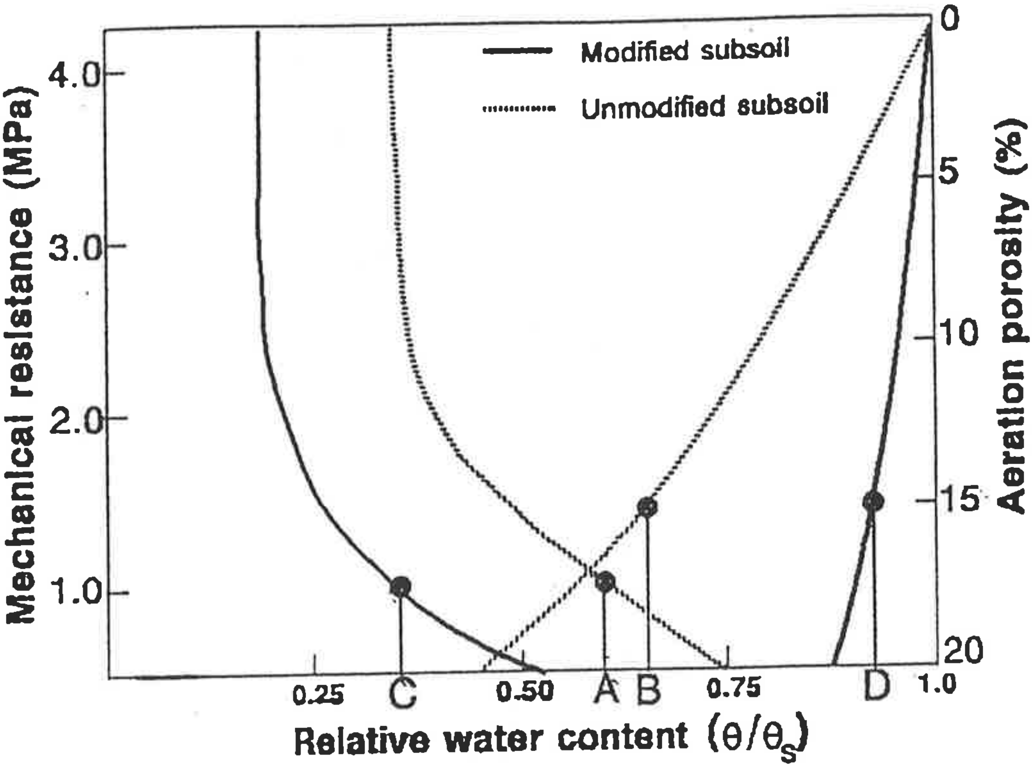


Table 1.1: Yield of Irrigated Pastures, Crops and Trees on Structurally Modified (Gypsum-treated) Red-brown Earths (After Cockroft and Martin, 1981).

Crop	Yield (t/ha)	
	District average	Modified profile
White clover/rye grass pasture	3	10
Forage sorghum	12	30
Lucerne	10	22
Peach	20	75

In addition to the physical problems, the resulting low biological activity and high sodium are not conducive to the accumulation and mineralization of organic matter. Very low saturated hydraulic conductivities also restrict leaching, leading to the accumulation of toxic elements (Corbett, 1969; Hausenbuiller, 1985). Where the subsoils have been structurally modified, yields have increased (Table 1.1).

The creation of optimum conditions for increasing organic matter and biological activity in such subsoils, in addition to finding economic ways of maintaining a developed structure have therefore been seen as strategies for alleviating sub-soil constraints to plant growth in sodic soils (Rengasamy *et al.* 1992).

2.7 Green manure and soil structure

Because the aim of green manuring in this study is to increase aggregate stability, the appropriate targeted size range of aggregates to be treated needs to be ascertained before its application. Thus the factors affecting the breakdown and building up of macro and microaggregates are reviewed below.

2.7.1 Microaggregation

Ideally, most of the clay fraction present in the solid phase should be flocculated into micro-aggregates (< 250 µm). Aggregates of this size are highly stable (Oades, 1984). However, all natural organics are potentially degradable, to CO_2 (Schnitzer and Khan, 1978); therefore even microaggregates will eventually disintegrate under a consistent depletion of organic materials through physical disruption. This causes exposure and volatilisation (Golchin *et al.* 1994), leading to dislocation and dispersion of clay particles under intense mechanical stress such as the impact of rainfall and rapid wetting (Oades, 1993).

The organic matter inside the microaggregates may be replenished by colonies of gel-secreting bacteria (Foster, 1981). These microbial glues help to hold together the aggregates from within. Removal of crop residues leads to the acquiescence of the bacteria which the crop had been supporting mainly through the nutrients from root exudates and dead roots (Mason, 1977). However, under permanent pasture, where plants remain alive throughout the year, gel production maintains aggregate stability (Molope *et al.* 1987; Oades, 1993). However, the effects of management practices on microaggregate stability is not immediate, and microaggregates are normally in the "resilient" category, regardless of soil management practices (Tisdall and Oades, 1982). The usually high level of stability of microaggregates prevents the complete disaggregation of soils, thereby allowing good management systems to maintain soil structure (Oades, 1984).

2.7.2 Macroaggregation

The effects of soil management practices are more quickly reflected on macroaggregates compared to those on microaggregates. Stable macroaggregates (250µm - 5mm) are necessary for a seed bed. This is facilitated by large, stable inter-connected pores. Ideally, microaggregates in well-structured soil should be bound to each other to constitute macro-aggregates > 250µm in diameter. (Edwards and Bremner 1967; Oades, 1984) showed that macroaggregates under field conditions, readily break down when rapidly wetted at an air-dry water content. It has been shown that slaking (breakdown of macroaggregates) precedes, and occurs to a far greater degree than clay dispersion (Tisdall and Oades, 1980). But highly aggregated soils are generally less susceptible to breakdown by raindrop and erosion (Stern *et al.* 1991). Because of lack of vegetative cover under cropped rotations, aggregates are exposed to oxidation and the weather, and therefore weakened (Low 1972; Warkentin, 1982). Hence, they are more easily compacted under physical action during tillage. Conversely, virgin soils remain well aggregated at the macro - scale (Haynes *et al.* 1991; Sparling *et al.* 1992; Smettem *et al.* 1992; Van Lanen *et al.* 1992). The characteristics of stable macroaggregates are developed and maintained through interactions of the following factors (Warkentin, 1982):

(a) Biological activity
(b) Chemical action
(c) Physical forces

Because in this study the impact of green manure is being investigated, the biological inputs from plants, which promote structural stability are to be considered here.

2.7.2.1 Biological Activity

During the initial stages of aggregation, particles and smaller aggregates are brought together by physical and biological agents. Based on the level of persistence in the soil, Tisdall and Oades (1982) postulated the following three levels of organic stabilization:

(a) Transient materials, which include mainly polysaccharides (important in aggregates at the macro level) of both plant and animal origin

(b) Temporary binding agents which include living roots and fungal mycelia binding the soil through entrapment and entanglement, likened to a "sticky string bag" and also useful in macro-aggregate stabilization

(c) Persistent binding agents, which include all stable organic compounds such as humic acids and root exudates which combine and become fixed with inorganic compounds on the surfaces of clay minerals. These above-mentioned processes enhance microaggregation, through organo-mineral interactions.

2.7.3 Green Manure as a Source of Plant and Microbially-derived Polysaccharides

The creation and maintenance of stable aggregates requires the addition of organic matter which provides energy for the survival of heterotrophic microorganisms. However, when changes to land use result in a change in organic matter levels, the stability of macroaggregates changes more rapidly than the overall organic matter contents (Chaney and Swift, 1984; Haynes and Swift, 1990). Swift (1992), found that for a previous pasture soil, though organic matter content of the regrassed soil had not yet risen significantly, the aggregate stability had shown a substantial increase. Baldock and Kay (1987) also observed changes in aggregate stability relating to crop management without significant changes in the total organic matter. Haynes *et al.* (1991) also found that aggregate stability was more closely related to cropping rotations than organic C. This was attributed by the author to the presence of an "active" component which was changing more rapidly than the overall organic matter levels.

Soil carbohydrates are examples of transient organic constituents known to be very much involved in soil aggregation (Mehta *et al.* 1960; Oades, 1967; Oades, 1984;). It has been shown that stable aggregation increases with the addition of plant or microbially derived polysaccharide polymers to the soil (Greenland, 1965; Swincer *et al.* 1968., Theng, 1974; Tisdall *et al.* 1978; Swift 1992), and that polysaccharides are one of the most effective organic agents promoting soil aggregate stablity (Oades, 1971; Oades, 1984; Swift, 1992). They probably are of largely microbial origin, utilising root exudates as a substrate (Swincer *et al.* 1968; Russell, 1973;). But Oades (1967) found that though loss in aggregate stability accompanied a decrease in carbohydrates following cultivation of old pasture soils, a similar decrease was observed for other organic materials. It thus seemed that the stability of macroaggregates, rather than varying directly with total organic matter, was determined by particular organic components that could be readily destroyed.

Electron-micographs of soil in thin sections of the rhizosphere have shown colonies of bacteria encapsulated by polysaccharides to which were attached clay particles (Foster and Rovira, 1976). However, though they are produced rapidly, polysaccharides do not last for long periods in soils (Swincer *et al.* 1968; Oades, 1971; Oades, 1984; Oades 1993).

The above-mentioned materials are naturally replenished in (highly stabilized) pasture soils (Oades, 1984). Comparing the carbohydrates from soils under old permanent pasture and those of wheat-fallow rotation, polysaccharides in the pasture soil were found to contain the larger amount of high molecular weight materials. This is largely due to their being continually renewed. They thus showed that the old pasture soils contained more easily extractable recently synthesized microbial polysaccharides, and also four times as much polysaccharide material as the soil under wheat-fallow (Oades and Swincer, 1968; Swincer *et al.*, 1968). Thus Griffiths (1965) found that substrates containing polysaccharides must be frequently added to cultivated soils to maintain macro-aggregate stability, or otherwise applied at high rates to maintain such results. They are naturally renewed often under pasture, and are associated with large (> 250 µm) stable aggregates. Thus, it appears that fresh green manure, by promoting microbial activity can lead to the production of polysaccharides to stabilize aggregates.

The importance to soil aggregation of microbial release of digested plant material, as compared with plant derived gums (e.g. root exudates) has long been argued (Oades, 1967). Hayes (1980) states that it is likely that microbial intervention is necessary to catalyze the organic contribution from the humic substances. Even though a close correlaton was found between the amount of light fraction in the soil and aggregate stability, it has been suggested that this might simply be an indication, not that that light fraction promoted stability, but that the materials active as aggregate stabilizers were those actually produced by the micro-organisms decomposing that light fraction (Oades, 1967). This view is supported by the fact that in HCl extracts of soils, the materials of high molecular weight were microbially derived polysaccharides (Oades and Swincer, 1968). There are, therefore, indications that much of this polysaccharide material may not have been directly plant derived, but that when such substrates are attacked by microorganisms, the soil-binding gums are released. Thus plant substrates, such as easily decomposable green manure, which fuel microbal respiration, can be expected to release such gums.

2.8 Factors Influencing the Rapid Decomposition of Green Manure

As rapid rates of decomposition of organic matter in soil improve permeability (Pieters, 1927; Pillsbury and Huberty, 1941; Geltser, 1943;) and tilth (Swift, 1992), plant species which rapidly acquire biomass, and which decompose rapidly would be the most effective in soil structural stabilization. In this regard Yadvinder-Singh *et al.* (1992) indicated that the top growth of legumes is among the most rapidly degradable of plant materials, possibly because it is high in protein and low in lignin and other inhibitory polyphenolic compounds. Therefore in order to maximise improvements in soil structure by green manure, all the factors affecting the rapidity of decomposition of plant matter in releasing transient binding agents must be optimised. For organic matter degradation, these have been summarised by Oades (1993) and Parton *et al.* (1992) as follows:

Moisture, aeration, temperature, soil texture, age, condition, and nature of material turned under. Factors of rapid decomposition more specific to green manure in soils have been described by Yadvinder-Singh *et al.* (1992). They are listed as follows:

Lignin content and C:N ratio, polyphenol content, concentration of other organic compounds, soil texture, plant age, plant parts, moisture conditions, temperature, amount of biomass. The main points for the above-mentioned factors are discussed below.

2.8.1 Lignin Content and C:N Ratio

All plant residues are chemically complex organic substances which enter the soil annually, the substrate chemistry and soil properties influencing the rates of decomposition (Jenkinson, 1981). It has also been found that the decomposition of plant residues is largely mediated by extracellular enzymes whose activities are influenced by the physical and chemical nature, and complexity of the substrates and of the enzymes themselves (Molope *et al.* 1987) along with environmental factors (Oades, 1993). Simulation models of the cycling of substrate carbon through the soil biota have suggested a strong influence of substrate chemical complexity on decomposition rates (Ladd *et al.* 1996), wherein the highest values for decay rates and efficiencies of utilization have been assigned for the decomposition of water-soluble constituents. Fresh plant and animal residues are composed of varying proportions of particulate and soluble components. Lignins are large, structurally complex phenolic macromolecules unique to vascular plants, imposing rigidity and minimising water permeation between xylem cells and comprising up to 30% of woody tissue mass (Sarkanen and Ludwig, 1971). Their very great stability is the main factor in making lignin polymers abundant in the natural environment and the most resistant to microbial degradation (Alexander, 1977; Obatolu and Agboola, 1993). Thus for complete decomposition to occur, more mature plant residues high in lignin need longer periods than young succulent parts low in lignin and higher in N (Mellilo *et al.* 1982).

When added to soils, the water-soluble organic components are the first to dissolve, followed by the celluloses and hemicelluloses (Jenkinson, 1981; Amato *et al.* 1987). However, for a given C:N ratio of the organic matter, an increase in lignin has been known to retard its speed of decomposition and release of N (Alexander, 1977) as the lignin content exerts more influence over decomposition than the N content (Mellilo *et al.* 1982; Katchaka *et al.* 1993., Obatolu and Agboola, 1993;). An interaction between lignin content and C:N ratio in controlling the decomposition rate of plant material has been described in a decomposability index (Katchaka *et al.* 1993) as,

$$[\ (C;\ N)\ x\ (\%\ lignin)\ ]\ x\ (\%\ carbohydrate^{-0.5})$$

This was correlated inversely with CO_2 evolution from decomposing roots during a 47 week incubation of three grass species. The higher the decomposability index, the lower is the rate of decomposition of the material due to a higher lignin content and a lower C:N ratio. This observation was further confirmed by work involving the legumes *Sesbania siamea, Lathyrus leucocephala, Datura Barteri and Fragarus macrophylla* (Katchaka *et al.,* 1993) each having different amounts of lignin and lignin/N ratios. The resulting decomposition rate was observed to be in the following decreasing order: *L. leucocephalia* > *S. siamea* > *F. macrophylla* > *D. barteri* which roughly coincided with increasing lignin/N ratios for the different species. After 140 days of aerobic incubation, 65% of the applied C was mineralized for *L. leucophala*, 55.8% for *S. siamea*, 44.7% for *F. macrophylla*, and 26% for *D. barteri* . The decomposition rates of N and C in the legumes after 140 days of aerobic incubation also exhibited a strong, significant linear relationship (r^2 =0.996, 0.954 respectively), between net N and C mineralized, and the lignin/N ratio. From these results the authors concluded that the lignin/N and lignin + polyphenol/N ratios are predominant factors in determining decomposition and nutrient release. Katchaka *et al.* (1993) found that this even overruled the effect of a large fraction of readily soluble components in the fresh plant materials. There is therefore strong evidence to suggest that, regardless of the composition, age or proportion of water-soluble components of the legume material, a high lignin content is unfavourable to rapid decomposition of incorporated plant material in soils.

2.8.2 Effect of Plant Age

The tissues of immature plants decompose much more rapidly than those of mature plant materials, because plants acquire compositional changes antagonistic to rapid decomposition as they get older (Mellilo *et al.* 1982). For example, in soils treated with freshly buried 60 and 75 - day - old *Sesbania aculeata* plant matter, it was observed that maxima of NH_4 -N were achieved at 15 and 30 days of incubation respectively (Yadvinder-Singh *et al.* 1992). Plant matter consisting of fresh, growing leaves are expected to contain significant amounts of metabolically active, readily soluble compounds such as sugars, and amino acids and proteins (Katchaka *et al.* 1993). As maturity sets in, the content of N, protein, and water soluble constituents decrease. For example, Aber and Mellilo (1980) found that a 2 week delay in the desiccation date of red clover and hairy vetch increased their C:N ratio and cellulose, hemicellulose and lignin contents, but caused reduced N contents. When large amounts of highly carbonaceous material are made available to plant microorganisms without a corresponding increase in N, the microorganisms must draw on the indigenous soil N for nitrogen. Crops planted after that will consequently be poorly supplied with N if artificial supplies are not then applied. Green manure incorrectly applied can therefore exacerbate the impoverishment of soils. Thus ideally, for rapid decomposition to occur, a green manure crop should be turned under when young, i.e. before flowering (Yadvinder-Singh *et al.* 1992).

2.8.3 Effect of Plant Parts

Different plant parts differ widely in their chemical makeup and thus in their rates of chemical decomposition. The stems and roots of green manure plants, for example, are generally lower in N with greater C:N ratios than their foliage parts (Frankenberger and Abdelmagid 1985; Palm *et al.* 1988). As these parts decompose more slowly, immobilisation of N occurs. The young shoot material from legumes is high in protein (Allison, 1973), the fine structure of the leaves being conducive to fast degradation (Pieters 1927). Yadvinder-Singh *et al.* (1992) reported that such plant parts are low in lignin and the inhibitory polyphenols. However, roots which are rich in N sometimes undergo relatively rapid decomposition. This has also been reported for the root of the cowpea (Frankenberger and Abdelmagid, 1985). However, Franzluebbers *et al.* (1994) found that this proportion was true only when the cowpea roots nodulated prolifically, at a percentage nodule dry matter weight of over 2% of the whole plant (Franzluebbers *et al.* 1994). It thus seems that if there is no root nodulation, very little N is trapped in the roots and C:N ratios become higher than those of foliage. For example, Amato *et al.* (1987) observed that after one year, residual N accounted for 56 per cent in the shoots and 63 per cent in the roots, but those plant roots had nodulated. Thus it seems that roots, at least in certain species, may decompose rapidly only when they nodulate. This observation implies that wherever a buildup of N occurs (whether it be roots or other plant parts) decomposition is speeded up. Thus for four different legumes, Frankenberger and Abdelmagid (1985) have shown that greater N release occurs from the leaves (which contained more N) than from the stems and roots. According to Bouldin (1988), green manure thus has two fractions, one that decomposes within days or weeks of incorporation, and the other more slowly over several months or years. With most green manure crops, the first fraction (fast decomposition) contains 50%-80% of the total N in the crop (Bouldin, 1988). Palm *et al.* (1988) found that stems and roots released marginal amounts of N compared with leaves, which released 73 per cent of N for the whole plant in 4 days under submerged conditions and 88 per cent after 14 days. Besides generally having higher C:N ratios and lower N contents, stems and roots are more lignified than leaves (Yadvinder-Singh *et al.* 1992). Thus it would seem that stems and roots with possibly few exceptions, could characteristically be categorised within the "slow fraction", while younger leaves are normally within the relatively "rapidly decomposing" category.

2.8.4 Moisture Conditions

The results of green manuring have been unsatisfactory in regions of low rain, due to two main factors:

(1) Green manure plants remove large amounts of water during growth (Pieters, 1927)

(2) Large quantities of water are needed for the growth (Townley-Smith *et al.* 1993) and decay process (Allison, 1973; Franzluebbers *et al.* 1994) of green manure. Townley-Smith *et al.* (1993), after investigating the water use of peas, faba beans and alfalfa, observed that these green manures used similar amounts of water to wheat grown to maturity. They thus stated that improved methods of water conservation must be found to replace the water used to grow green manures. Shortage of water, especially in summer months has been more effective in slowing down decomposition of green manure in upland fields than was submergence in paddy fields (Lin and Wen, 1990). This point was demonstrated by Ladd *et al.* (1981), who, working in four soils under semi-arid conditions of South Australia found that at 32 weeks, legume residues had not decomposed.

An oversupply of water can also retard decomposition in soils. Hutchinson and Milligan (1914) observed that after plant residues were incorporated for 8 weeks in a soil at different water contents, the following amounts of decomposition had been observed (Table 2.1):

Table 2.1: Effect of Soil Water Content on Amount of Decomposition of Fresh Incorporated Clover

Moisture Content	Amount Decomposed (%)
Air-dry	10.8
12%	59.4
18%	67.8
24%	52.2
48% (saturation)	0.0

It is seen therefore, that no decomposition occurred at a saturation moisture content (Table 2.1); in spite of the need for great amounts of water for the decomposition of green manure, increase in decomposition proceeds with increasing soil moisture content only up to a certain maximum soil water content. This level is substantially less than the saturation point of soils (Allison, 1973; Linn and Doran, 1984; Tamai *et al.*, 1990; Franzluebbers *et al.* 1994). For example, to ensure aerobic conditions of decomposition, Tamai *et al.* (1990) incubated the green manure plant *Crotalaria juncea* at 50% of the water holding capacity of soil; this resulted in high levels of mineralization. This was probably due to good aeration under moist soil conditions. Franzluebbers *et al.,* (1994) observed that in soils at or above 90 per cent of their water holding capacity, a lack of oxygen seriously hindered biological activity and hence also decomposition rates. The range for optimum decomposition in soils thus seems to be somewhere between 50 and 80 per cent of the water holding capacity of a soil (Hutchinson and Milligan, 1914; Yadvinder - Singh *et al.* 1992; Franzluebbers *et al.,* 1993). These results also suggest that at 90% water-holding capacity, there is an indirect, negative effect on soil structure. It would thus seem that partially aerobic conditions provide a better environment during green manure decomposition than anaerobic conditions (Bajpai *et al.* 1980), for the development of soil structure. Thus

Connell and Hadfield (1961), and Donahue *et al.* (1971) have stressed several advantages of aerobic conditions in soils, with each factor either directly or indirectly promoting soil structural improvement. These advantages are summarised as follows:

(1) Good drainage decreases losses of N from the soil from denitrification, thereby promoting aggregate water-stability, healthier plant growth and hence quicker acquisition of plant biomass for green manure. The subsequent decomposition of these increased amounts of plant material lead to improved soil structure.
(2) Good drainage hastens decomposition of organic matter and the subsequent nitrification whereby N is made available for plants. This increases the proportion of protein in plants and hence N percentage which in turn accelerates the decompositon process. The percentage of K, Ca and Mg is also increased as a result. This increase of cations in the soil solution helps to reduce clay dispersion.
(3) Soil structure is improved, as the increased wetting and drying, due to drainage, accompanied by aerobic conditions creates greater aggregation. But soil water at zero suction in the soil tends to destroy its aggregated structure.
(4) Deeper penetration by plant roots is induced by drainage, thereby (a) extending the depth of soil structural improvement via roots and (b) increasing the amounts of nutrients availiable for plants, resulting in the production of greater amounts of above-ground photosynthate produced. This subsequently increases inputs of carbon into the soil. Longer roots also make plants more drought resistant (and thereby create sturdier green manure crops in areas of limited water supplies, as is the case in semi-arid localities of South Australia)
(5) Greater root growth, earthworm activity and intensified growth of microorganisms and fungi resulting from better drainage and aerobic conditions all help to create desirable soil structure.
(6) An oxygen deficiency under anaerobic conditions can result in a chemical reduction of manganese, which may be toxic to plant growth.

On the other hand, waterlogged conditions, though utilized in green manuring in rice culture (Singh *et al.* 1981; Yadvinder -Singh *et al.* 1992; Sekhon and Bajwa, 1993;), cause fast mineralisation and losses of N to the air. In addition, other deleterious effects such as the buildup of toxic substances in the root zone occurs, thereby reducing the roots' supply of exudates amongst soil particles. For example, faster rates of mineralisation have been observed after the first two months under waterlogged conditions than for the same period under conditions of optimum moisture (for root growth) (Katyal, 1977). In an alfalfa incubation after 30 days under aerobic conditions, the amount of N mineralised was the equivalent of only 7 days under anaerobic conditions (Yadvinder-Singh *et al.* 1992). The increased rates of mineralisation of N under anaerobic conditions could lead to large losses via leaching and volatisation, as the rate of uptake by microorganisms is exceeded.

2.8.5 Decomposition of Green Manure Under Alternate Wetting and Drying

Because a lack of moisture reduces microbial activity, it would seem that decomposition of plant material would also be concurrently curtailed; yet it has been observed that alternating wetting and drying also stimulates decomposition (Birch, 1958; Connell and Hadfield, 1961; Tisdall *et al.* 1978; Amato *et al.* 1987). Birch (1964) reported that the release of N from five grass species was enhanced by intermittent drying, with an increasing effect as drying became more advanced. Amato *et al.* (1987), in laboratory studies involving 20 weeks decomposition of *Medicago littoralis* plant parts, found that drying and wetting promoted the decomposition of plant parts, but the longer the time moist after drying, and the longer the wetting cycles, the greater the decomposition. Birch (1964), suggested that the physical disintegration of the organic matter occurred through the physical stresses imposed by contraction and expansion. This could have increased the surface area of the organic matter exposed to microbial attack and hence promoted its biodegradation, thereby leading to increases in aggregation of such soils.

It is also possible for the wetting/drying process to increase the stability of aggregates in other ways, for example through the indirect supply of nutrients to microbes. Dexter (1988) has shown that as the soil dries, clay particles, and other colloidal matter, become concentrated towards the periphery of soil aggregates. Such conditions would provide substrate material for organisms, and possibly lead indirectly to stabilisation of the soil (McCalla, 1946). However, such conditions cannot be created without adequate moisture, which is needed for the prior decomposition of plant material. Thus by speeding the rate of green manure decomposition, wetting and drying cycles can therefore cause the generation and stabilization of soil structure. This occurs by increasing the stresses within the organic fabric (Dexter, 1988) thereby indirectly increasing the level of aggregation generated.

With regard to the mineral fabric of soils, the physical stresses occuring can also generate soil aggregation (Dexter, 1976) with the auxillary action of organic matter, such as green manure. The stresses generated by wetting and drying cycles can be classified as shrinkage on drying and swelling on wetting. In the former process, during shrinkage, soil particles are pulled together by the increasing tension exerted by a decreasing water film between particle surfaces. Desiccation cracks are then produced if the clay content is medium to high, the pattern, and spacing of such cracks depending on the drying rate (Utomo and Dexter, 1981a). During the drying process, binding agents, including organic molecules become concentrated in the soil solution (Utomo and Dexter, 1981b). Between soil aggregates, or particles, as the water menisci shrink, soil colloids, organic acids and mineral salts eventually become deposited between contact points of such soil particles (Semmel *et al.* 1990), thereby initiating and/or increasing bonding strengths of aggregates.

2.8.6 Temperature

Though soil microorganisms are active throughout a wide range of temperature, the optimum temperature for the evolution of CO_2 from green manure in soils has been observed as being between 30 and 40° C (Pieters, 1927). It was also found that an increase in soil water, without a decrease in temperature caused an increase in decomposition of plant residues. Tisdall *et al.* (1978) found, in incubation studies of plant residues into soil that the ideal temperature for microbial degradation was between 25 and 35° C. Chen and Wang (1987) found that 25° C was optimum for the efficiency of green manure decomposition. It thus seems that for an optimum decomposition rate, temperatures during decomposition should be in the range of 25 - 40° C.

2.8.7 pH and Green Manure Decomposition

It has been observed that decomposition of organic matter proceeds faster in neutral soils than in acid or alkaline soils. For instance, Bajpai *et al.* (1980) reported that N mineralisation from sesbania green manure was faster in neutral soils (pH 7.2) than in a saline-sodic soil (pH 9.9). However, though a neutral pH environment increases the rapidity of green manure decomposition, under alkaline conditions, the high soil pH can be reduced by green manure incorporation. A decrease in soil pH of a sodic soil by 0.2 unit after harvesting a rice crop green manured with *Sesbania aculeata* was observed by Swarup (1987). Soil pH change through green manuring is effected in two ways:

(1) By supplying protons through the actions of organic acids and CO_2 during plant matter decomposition, causing decreases in pH, and

(2) As organic anions are mineralised to CO_2 and H_2O, H^+ ions are removed causing an increase in pH (Yadvinder-Singh *et al.* 1992)

In highly alkaline soils a reduction in pH becomes necessary from the edaphic standpoint. However, though Pierre and Banwart (1973) found that the average ash alkalinity of legume crops (110 c mol Kg^{-1}) is markedly greater than that of non-legumes (69 c mol Kg^{-1}); a similar reduction usually occurs when either material is added to alkaline soils (Yadvinder-Singh *et al.* 1992). Cang *et al.* (1985) found that the greater the amount of such readily decomposed organic matter added to the soil, the greater is the fall in pH in alkaline soils.

The decrease in pH also occurs even while the green manure crop plants grow in the soil. As dissociation of organic acids occurs within the plant in response to the cation/anion imbalance caused by N fixation or NH_4 uptake, the plants secrete H^+ ions into the rhizosphere (Russell, 1977; Palm *et al.* 1988;). During green manuring such

H^+ ions (which were separated from anions) are returned to the surface layers rather than to the subsoil where most of them initially were released by the roots (Yadvinder-Singh *et al.* 1992); thus a lowering of pH in the surface layers is effected under such conditions. Katyal (1977) also reported that under alkaline conditions, green manures decreased the pH of a wide range of soils, and that pH had dropped by 1 or 2 units within 7 days of flooding. Nevertheless, it must be remembered that pH will decrease under anaerobic conditions even without green manure, towards a value of 6.5 (Russell, 1977).

Conversely, acidic soil conditions can be ameliorated also by the application of leguminous green manures. Working in waterlogged acid soil conditions, Singh *et al.* (1981) showed that green manure (*Sesbania aculeata*) raised the pH to significantly higher levels than were observed in controls; similar but well-marked increases in soil pH were observed by Debnath and Hajra (1972) under aerobic conditions. However, a longer time was needed under aerobic conditions, to achieve such results. Under waterlogged conditions, application of sesbania to acid non-calcareous gypsum amended soil resulted in a rise in pH (Yadvinder-Singh *et al.* 1992). Katyal (1977), also reported an increase in pH (from acidic conditions) in widely ranging textural and pedogenetic environments due to the decomposition of buried plant residues.

2.9 Strategies for the Amelioration of Sodic Soils

2.9.1 Gypsum Addition

Cohesiveness between clay particles can be significantly increased by inorganic cementing agents such as $CaCO_3$, and Fe and Al oxides (Bear, 1968). It has been stated that granulation is "flocculation plus" because flocculation alone cannot cause water-stable aggregation in soils; in other words, after the flocculation of clay domains at the soil surface (where there is greater soil forming activity than in the subsoil), cementing agents around in the soil must bind these floccules into stable micropeds (Quirk, 1978). In a study of African Ultisols and Oxisols, Ahn (1979) observed highly stable microaggregates not dependent upon organic matter. Therefore, such binding agents need not be from organic sources. Nevertheless, it has been found that organic matter was correlated with micro-aggregate stability of clayey soils low in organic matter (Warkentin, 1982). Though many studies have revealed statistically significant correlation coefficients with organic matter, clay content and iron oxides, properties such as infiltration rates are determined by the stability of microaggregates (Warkentin, 1982). But to achieve increases in infiltration rates in sodic soils, the Na must first be removed from the surfaces of clay colloids. This can be accomplished through cation exchange reactions facilitated by the addition of soluble substances containing suitable di-valent cations such as gypsum, $CaSO_4$ ($2H_2O$). This leads to the reduction in the dispersive potential of the soil (Rengasamy, 1983). This ameliorative practice has been widely adopted (Keren and Shainberg, 1981; Shanmuganathan and Oades, 1983; Baldock *et al.* 1994). Gypsum reduces surface crusting, decreases bulk density, and increases permeability (Sumner, 1993). Application of gypsum to a sodic soil increased the removal of Na in the drainage water, decreased soil Na saturation and improved crop yields (Sekhon and Bajwa, 1993). Cochrane and Aylmore (1991) detected significant improvements in wheat yields from the application of 5 t/ha of gypsum in Western Australia. After adding gypsum to two different red-brown earths, Shanmuganathan and Oades (1983) noted a reduction in the amount of dispersible clay, an increase in the proportion of water-stable aggregates of`size 50 - 250 μm diameter, and an increase in soil friability. Mechanical strength was reduced by gypsum addition (Aylmore and Sills, 1982).

2.9.2 The Choice of Gypsum Above other Multivalent Compounds

The reasons gypsum is so widely used are that it is very efficient in removing exchangeable sodium, improves the hydraulic properties by the electrolyte effect, and also is a cheaper resource compared to other inorganic amendments. It is not readily lost from the soil via leaching. In addition to being able to form highly stable complexes with organic matter, trivalent cations have greater replacing power than divalent ones such as Ca^{++}. However, Al^{+++} can be toxic (Hausenbuiller, 1978). In addition, due to their great stability, Al^{+++} or Fe^{+++} - organic complexes block off exchange sites and a reduction in CEC results. On the other hand, though the Ca^{++} promotes aggregation, the soil's CEC is not reduced, thereby promoting availability of nutrient ions.

In addition, Ca^{++} is non-toxic. Rengasamy (1983) reported that dialysed Ca-clays did not disperse in water even after a week and it has been found that dry aggregates of montmorillonite or illite saturated with Ca^{++} did not disperse when immersed in water (Rengasamy, 1983). Thus, replacement of the sodium on the clay colloids, with a non-toxic cation which produces better structure is achieved, as the Ca^{++} replaces the leached Na^+ cations (Goldberg and Glaubig, 1987).

2.9.3 Rationale for the Use of Gypsum as Compared with other Calcium Compounds

The use of highly soluble (i.e. with multivalent cations) amendments such as $CaCl_2$ have been advocated to speed up reclamation of alkali soils (Gupta and Abrol, 1990). This is because even in highly sodic soils, only a relatively small amount of such substances is needed to substantially decrease ESP levels. These are therefore high efficiency amendments. However they have disadvantages with $CaCl_2$. Its effectiveness declines to about 20 to 40%, below ESP values of 15 (Gupta and Abrol, 1990). In addition, Shainberg *et al.* (1981) stated that while $CaCl_2$ dissolves faster than gypsum (on application), the latter caused a higher saturated hydraulic conductivity in soil columns. $CaCl_2$ is costly and the Cl ion can be toxic to plants. Furthermore, $CaCl_2$ dissolves so quickly that it is usually leached out of the soil layers in a shorter period. Because the sparingly soluble gypsum remains in soil for a longer time, and opportunities are thereby provided for solvation to occur over many more effective exchange steps, it is both efficient and economical (Oster, 1982). Thus, Keren and Shainberg (1981) noted a reclamation efficiency of 81% for gypsum at a soil water flow velocity of 1.16 cm /hr.

The choice of gypsum over lime by many workers is due to the comparitively low activity of $CaCO_3$. The solubility of gypsum is less sensitive to pH than that of lime. At a pH of 10 and higher, lime, in contrast to gypsum, is insoluble (Corbett, 1969). Gypsum is chosen rather than lime because alkaline sodic soils containing sodium carbonate often have a pH of 10 in saturated solution. When gypsum is added in the soil, the adsorbed sodium on the clay colloids is still replaced by calcium. This is because during gypsum applications, sodium sulphate, a neutral salt is formed, rather than sodium carbonate, as would have been the case with lime applications (Corbett, 1969), according to the following equation :

$$2\ \text{Na-clay} + CaSO_4 \dashrightarrow \text{Ca-clay} + Na_2SO_4$$

The sodium sulfate maintains the pH close to 7 until the replacement reaction has proceeded enough to allow time for the calcium to dominate the colloid, with a marked soil structural improvement (Seatz and Peterson, 1968). The excess free sodium salts (such as Na_2SO_4) then have to be leached by repeated irrigations.

2.9.4 Calcium Compounds in Combination with Green Manure

In combination with organic matter, calcium compounds have been found to further reduce dispersion in sodic soils. Baldock *et al.* (1994) observed that the addition of a combination of gypsum or lime and wheatstraw over a two-year period induced a greater level of macroaggregation than caused by either treatment acting alone on a sodic soil. Similarly, Muneer and Oades (1989) found that the simultaneous incorporation of a source of calcium cations and organic material (glucose) into a red-brown earth increased the proportion of water-stable macroaggregates and also reduced the dispersion of clay particles. Without adding calcium, Sekhon and Bajwa (1993) observed that the enhancement of the release of Ca^{++} into the soil solution can be achieved through the incorporation of rapidly decomposing organic materials, such as green manure to a calcareous soil. This was caused by the action of organic acids produced by microorganisms decomposing the green manure in the calcareous soil.

It is necessary for clay minerals to remain in a flocculated state as microaggregates to maintain aggregate stability in a soil (Warkentin, 1982). Flocculation is enhanced by the presence of polyvalent cations, high electrolyte concentrations, organic matter and minimum disturbance (Muneer and Oades, 1989). It has also been postulated that the addition of readily decomposable plant material, rather than older decomposed plant or animal material is more efficient at enhancing the formation of CO_2 during incubation

(Swift, 1992). The addition of green manure from the plant *Sesbania aculeata* reduced the ESP of a non-calcareous soil more than by the addition of $CaCO_3$, but when added with $CaCO_3$, the effect on the decrease in dispersion was more substantial than that of either treatment (Singh, 1974). Evidence for the additive effects of calcium with organic matter led Muneer and Oades (1989), to suggest that there is a synergistic effect of calcium with organic matter on aggregation of soil. Most of the alkaline sodic soils contain $CaCO_3$ ranging from 2 to 2000 t/ha, but no soluble Ca^{++}. Dissolution of the native lime by *in situ* acid production by green manure biomass is highly efficient and economical (Rengasamy, 1995 pers. comm.). The improvement in soil physical properties could be at least partly attributed to an increase in the EC of the soil solution by green manure. For example, the addition of green manure with gypsum caused a greater increase in the EC in soil than the addition of gypsum alone (Sadana and Bajwa, 1985); this effect should also be reflected in increased soil permeability via reduced clay dispersion in the soil.

2.9.5 Effects of Nature of Organic Material

In some instances when organic residues are incorporated into a sodic soil, simple organic anions can increase its dispersive potential (Rengasamy *et al.* 1984). Thus the composition of organic material applied is important in resisting dispersion. Colloidal anionic materials, which range in size from a few hundred molecules to a diameter in the order of microns (unlike long chain polysaccharide anionic materials), are mobile and move below the zone of organic matter inputs (Susanto, 1992). These negatively charged bodies could lead to increases in dispersion. Old farmyard manure also was found to cause increased dispersion in certain sodic soils (Gupta *et al.* 1984). Loveday (1984), for example found that straw (i.e. not fresh plant matter) did not improve the water entry into a sodic red-brown clay loam. Emerson (1954), also suggested that when organic bonds become broken, the mutually repulsive negative charges increases dispersion. The production of larger organic molecules in the initial stages of decomposition of fresh organic matter compared with later stages is a logical order of events. Thus at an early stage of decomposition of fresh plant material, these anions could be larger than the negatively charged inorganic silicate mineral colloids in a soil

(Greenland, 1965). Emerson *et al.* (1986) found that grassland, and to an even greater extent forest organic matter in soil aggregates, helped to counteract dispersion. Thus Rengasamy and Olsson (1991), after saturating a forest soil with solutions having an SAR value of 100 at 500 me/L^{-1}, and then leaching it with distilled water, found that the soil did not disperse. It also is possible that in the forest soil, organic matter, by blocking exchange sites on the colloids, may have thereby resisted the influence of sodicity. This is an indication that the fresh organic matter, as that of the root exudates, for example, mixed in with soil may help to reduce dispersion. Therefore, depending on its nature, organic material can act as either a bonding or dispersing agent in a soil.

2.10 The Effect of Soil management Systems on the Decomposition of Organic Matter

The structural response of a soil to incubations with organic matter depends to some extent on prior land use. The ability of microorganisms to form aggregates vary greatly, depending both on the nature of the organism and the nature of the substrates available (Griffiths, 1965), both of which in turn depends largely on the period of time under a particular land use system (Oades, 1988; Swift, 1992). This is because under different management systems, substantial changes in organic matter will occur in a soil and the rate of decomposition of fresh plant matter affects the extent of further soil aggregation (Swift, 1992). It has been postulated that even in some soils of high stability, further increases in aggregate stability can occur when incubated with easily decomposed organic matter (Lohnis, 1926; Swift, 1992). This has been attributed to an 'awakening' of 'dormant' organic material already in the soil, by the 'priming' action of latent microorganisms thriving on fresh additions of easily decomposed organic matter (Swift, 1992). It has been postulated that the organic material left in soils under permanent grassland is almost 20% per year of top growth (Allison, 1973). Due to the buildup of these energy rich substrates in such soils, the microfloral population would become far greater, both numerically and in species, in soils with a history of permanent pasture, than for soils with histories of continuous cropping. The initial 'flush' of decomposition due to the immediate utilisation of easily composed nitrogenous material suddenly added (Rovira and Greacen, 1957; Aber and Mellilo, 1980) is thereby sustained. A broad range of latent indigenous organic compounds already in soils under old pastures (due to a constant renewal of such fractions through the action of living roots) (Golchin *et al.* 1994) are then probably attacked by the extra number of micro-organisms.

Such microbial activity also accounts for at least one-third of the total aggregation in soils (Acton *et al.* 1963). Restrictions on microbial activity occur through the decrease of available native substrate, as results from several decades of continuous cultivation under the same crop (Golchin *et al.* 1994). At this stage, subsequent addition of easily decomposed material is incapable of rejuvinating and sustaining the decompositional process of the latent indigenous organic material (Swift, 1992).

Varadachari and Ghosh (1983) postulated that the more complex the carbohydrate, the more restricted the range and the more specialised the bacteria needed to solubilise and break it down. This is because prior to becoming assimilable as a source of C, highly refractory (complex) materials must undergo a vast number of biochemical transformations within the microbial cell (Evans, 1963). In the recently cultivated soil the easily decomposed indigenous organic fraction becomes quickly exposed and availaible to microorganisms and volatilisation. Should such a management system continue over many years until the soil becomes organically depleted, it is left with only resistant organic compounds largely comprising merely remnants of the broader original range typical of virgin soils (Golchin *et al.* 1994; Oades, 1984). In such soils, the organic carbon remaining largely consists, at this stage, of resistant compounds such as O-Alkyls and aromatic compounds (Golchin *et al.* 1994). It is difficult for the microorganisms to continue to degrade these resistant materials. They cannot be attacked by a large proportion of microorganisms for long periods, due to their "unpalatability" (Oades, 1993, pers. comm.). Macrae and Mehuys (1987), found that on a cultivated clay soil, infiltration was not increased, even after green manuring. Similar results were obtained on a cultivated sandy soil (Macrae and Mehuys, 1987). Thus even though some decomposition may have occurred in the above-mentioned soils, the degradative process seems to be not self- sustainable in impoverished soils, due to inherently low levels of degradative organisms. On the other hand, an increase in the rate of decompositional activities after green manure incorporation would normally be expected in the permanent pasture soils, compared with the cultivated ones, which contain a lower level of organic matter owing to the dried out and resistant nature of the organic fraction. This could lead to a greater amount of binding agents released in the permanent pasture soils and therefore greater stability of aggregates there.

2.11 Conclusions

(1) Good soil management should aim to improve soil physical properties, thereby creating optimum physical conditions for plant growth, including

- (a) adequate aeration for roots and microorganisms
- (b) adequate available water
- (c) ease of root penetraton, permitting thorough exploraton by roots of the soil for water and nutrients
- (d) rapid and even seed germination in surface layers
- (e) resistance of the soil to aggregate breakdown and consequently to erosion by wind and water .

Most of the characteristics are not to be found in poorly structured soils.

(2) The release of biological binding agents from decomposing freshly incorporated plant matter such as green manure can lead to increases in soil porosity, permeability and soil aggregation.

(3) For the production of stable aggregates, alternate wetting drying, good drainage, favourable conditions for root growth, and microbial action are necessary. Even though many studies have been done under waterlogged conditions in rice culture, with reported increases in rice yields, there has been little in the way of conclusive studies showing that green manuring under waterlogged conditions can lead to improvement in the physical structure of degraded soils.

4) Water regime is an important factor in the efficiency of green manure in improving soil structure. Linn and Doran (1984) observed that 60% of the water-filled soil porosity has been estimated to be the optimum water content for microbial activity. However, the subsequent effect on soil structure is not as well known. Nevertheless, the ideal moisture condition for increasing aggregate stability seems to be that of a continuous moisture regime at a water content that is less than the field capacity of the soil.

(5) The effect of green manure in calcareous, sodic soils can result in the lowering of soil pH. The release of protons and solubilization of the native $CaCO_3$ by the organic acids released lead to an increase of Ca^{++} in such soils. As a result of these extra protons and divalent cations in the soil, dispersion is decreased and flocculation of the clay particles increased.

Chapter 3

Pilot Experiments

3.1 Introduction

It is mainly because of the high rates of application of fresh plant material entailed in green manuring, and the consequently high cost of transportating such material (section 2.2.3), that green manure is normally applied *in situ* after its harvest. Although no "field experiments" were to be conducted in this study, the *in situ* method of green manuring in soils were simulated as far as possible in the pot experiments of this study. The above-mentioned criteria regarding rate of application, and plant matter characteristics, such as plant parts, age, and succulence (section 2.8, for the "nature" of green manure) were applied with regard to finding a "most suitable" green manure crop for the soils in this study. Pilot experiments were thus conducted in order to evaluate (1) the capability of the soils of this study to supply the amount of biomass suitable for green manuring, and (2) the suitability of certain plant species for green manuring, with respect to their degree of succulence (as a subjective indication of their decomposition rates) in soils.

The specific objectives were to determine:

(1) the amount of shoot mass produced,
(2) the ratio of root/shoot mass produced,
(3) the approximate level of succulence (i.e. water content, as taken as the ratio of fresh weight to dry weight) attained before flowering.

The properties sought in the green manure plants were:
(1) A high degree of root & shoot biomass
(2) Rapid acquisition of biomass
(3) Healthy growth of plants in the particular soil
(4) High level of nodulation on roots

3.2 Materials and methods

The red brown earth soil collected from the Waite Institute and used in the pot trial was non-sodic.

3.2.1 Soil Preparation

Samples of red brown earth were collected with a spade to a depth of 15 cm (A horizon) on a random basis from the wheat/fallow, continuous wheat, and permanent pasture plots of the Long Term Rotation Experiment (C1 paddock) at the Waite Agricultural Research Institute. After air - drying , the clods were broken and passed through a 5 mm sieve, thereafter being stored in air - tight containers until needed.

3.2.2 Plant Species, Management and Harvesting

Four leguminous plant species were selected and grown in a glasshouse in pots containing 1 kg soil from the wheat/fallow, continuous wheat, and permanent pasture plots. All seedlings were innoculated during germination and then grown for 5 weeks, which was to coincide with one week prior to the flowering of the earliest maturing species. The plant species chosen for the pilot experiment were: common vetch *(Vicia sativa)*, alfalfa *(Medicago sativa)*, cowpea *(Vigna sinensis)* and white clover *(Trifolium repens)* , mainly because they were leguminous (for N addition) and because they were known to have the capacity to grow well on impoverished soils (Pieters, 1927), whilst supplying adequate yields of biomass (section 2.2.2; section 2.2.3). Ten plants were grown in each pot, with four replicate pots per plant species arranged in a completely randomized design.

During growth, the plants were watered via a timed dropper system up to the predetermined field capacity of each of the three soils. Determination of the quantity of water needed at any time of watering for each pot was accomplished by the calculation of the weight difference between the mass of soil at field capacity and that of the current soil mass in the pot at the time of watering.

At 35 days all pots were harvested after the soils were air-dried. Top growth was removed, weighed and dried at 40°C until there was no further weight loss during successive weighings. Soil was washed from the roots, then the roots were weighed, dried at 40°C, and re-weighed. As "degree of succulence" has been implicated as a determining factor in the speed of decomposition of green manure (Pieters 1927; Franzluebbers *et al.* 1994), a crude 'index of succulence,' "I_S", was devised and applied as an indicator, to each species. Thus immediately after harvest the shoot weights were recorded and compared with the same material, after drying;

$$I_S = \left[\frac{\text{Wt fresh shoot - Wt dried shoot}}{\text{Wt. fresh}}\right] \times 100 \quad \left[\frac{\text{1 - Wt dried}}{\text{Wt. fresh}}\right] \times 100$$

Therefore in this simple subjective comparison, the larger the figure, the greater the degree of succulence. As an example, Alfalfa, at five weeks, with a relatively low dried/fresh wt. ratio had the lowest index of succulence (I_S = 3.8) while the other three species were roughly comparable, ranging from 5.9 to 7.1 (Table 3.1).

Table 3.1. Index of Succulence at 35 Days

Species	Wt dried/Wt fresh	I_S
Cowpeas	0.84	6.3^a
Vetch	0.86	7.1^a
Clover	0.83	5.9^{ab}
Alfalfa	0.74	3.8^c

($P < 0.05$) as determined by Tukey's H.S.D.

3.3 Results and discussion

3.3.1 Cowpeas

Nodulation on all plant roots except the cowpeas was abundant. The reason for this was not readily apparent. The greatest top weight acquisition was exhibited by the vetch, alfalfa and cowpea plants, although this was not paralleled in the root weights, especially for the cowpeas (Table 3.2):

Table 3.2 . Dry Weights of Roots and Tops (grams per pot) for Four Legumes

Species	Shoot/Root	Roots	%	Tops	%
Cowpeas	6.2	29^{c}	13.8	170^{b}	85.4
Vetch	4.5	42^{b}	18.1	190^{a}	81.9
Clover	3.0	33^{c}	24.8	100^{d}	75.2
Alfalfa	2.3	56^{a}	30.1	130^{c}	69.9

For differences within a column ($P < 0.05$) as determined by Tukey's H.S.D.

3.3.2 Alfalfa

In the case of the alfalfa, it was observed that the succulence detected in the first 3 weeks of growth was quickly replaced after this period by toughened stems and stalks before maturity and maximum mass had been achieved by this species. The total top mass of the alfalfa at this point was lower than that of the cowpeas and vetch plants at 35 days. The alfalfa was observed to flower before the other species. This could have resulted in a buildup of resistant tissue such as cellulose and hemicellulose in the shoots, resulting in woody stems (section 2.8.1). This would also have caused a lowering of water content. These factors may have contributed to the low index of succulence determined, compared with the other species grown (Table 3.1). Looking toward the main experiment, indications were that the alfalfa may have also acquired high levels of lignin at an early age (section 2.8.1). The speed of decomposition would be significantly reduced if incubation were to begin after 35 days of growth. Though the alfalfa root mass was seen to be relatively high (Table 3.2), the lack of shoot succulence (Table 3.1) signified a possible reduction in the speed of decomposition of such plant parts (Yadvinder-Singh *et al.* 1992). Because the aim in this study was that of incubating easily decomposed material from species that rapidly acquired biomass, it was decided to eliminate alfalfa from the upcoming main experiment.

3.3.3 Clover

Clover plants under the prevailing glasshouse conditions exhibited a susceptibility to direct heat, seedling establishment was slow, and shoot growth proved to be relatively slow and minimal in comparison to the cowpeas and vetch. It was thus decided that clover without protection from direct heat could not be successfully grown up to the mass levels needed in the hot South Australian summer field conditions. Therefore clover on its own was also eliminated from the main experiment. It was decided however, that if clover could be grown with a crop that provided adequate shade, it could be suitable as a green manure crop.

3.3.4 Vetch

In the trials, the vetch plant was regarded as the most appropriate to be incorporated because it demonstrated the greatest and most rapid shoot growth in the prevailing conditions, and abundant root growth and nodulation (including the greatest amount of lateral root extension). Similar results with respect to the acquisition of relatively substantial levels of dry weight by the vetch species had been reported by Mayfield *et al.* (1994) from field studies at various sites in South Australia (Table 3.3), where the dry weight acquired by the vetch was found to be 40% greater than that of the alfalfa.

Table 3.3. Dry Weight (t/ha) of Tops of Legumes at Harvest at Two Locations in South Australia (after Mayfield et al., 1994)

Plant	Halbury	Blyth
vetch	10.70	9.27
weeds	0.46	5.02
alfalfa	6.20	6.27
weeds	0.76	8.90

3.4 Conclusion

As a result of all of the above-mentioned field results, in addition to those of the present investigation there seemed to be evidence for the potential of vetch as (1) a shade plant for clover, and (2) an appropriate green manure for red brown earths in South Australia. Two varieties of green manure were consequently chosen for further study: (1) clover/vetch treatment, and (2) vetch only.

Chapter 4

Green manuring in non-sodic red brown earths

4.1 Introduction

Because microaggregates are normally in the "resilient" category, regardless of soil management practices (section 2.7.1) the effects of soil management practices are more quickly reflected on macroaggregates (250µm - 5mm), the stability of which is necessary for a seed bed (section 2.7.2). Removal of crops and crop residues lead to the death of the bacteria which the crop had been supporting mainly through the nutrients from root exudates and dead roots (section 2.7.1). However, under permanent pasture, where plants remain alive throughout the year, gel production maintains aggregate stability (section 2.7.2). As previously stated, because green manure supplies plant derived soil-binding gums via its decomposition (section 2.7.3), it is reasonable to assume that green manure can thereby increase the stability of macroaggregates. However, it has been shown that the speed of decomposition of green manure in soils depends on the water content of the soils, and several authors have stressed several advantages of aerobic conditions in soils (section 2.8.4). The greatest rate of decomposition occurs at a water content that is lower than the field capacity of the soils (section 2.8.4).

The hypothesis to be tested therefore, is as follows: *When green manure is incorporated into a red brown earth at a water content below field capacity, it increases the structural stability of macroaggregates.* In order to evaluate the effects of all treatment combinations on the stability of the red brown earths, three measurements were adopted: water stability of aggregates, water retention and hydraulic conductivity. The treatments should however, include the incubaton of the green manure in the red brown earth at various water regimes, for each measurement. Three water regimes were chosen for incubation of (1) shoots, and (2) shoots + roots, incorporated into soils.

4.2 Methodology

4.2.1 Treatments

The following treatment particulars were adopted:

(1) Plant parts incubated: shoots only, shoots + roots.

(2) Three types of red brown earth based on previous management viz: wheat fallow, continuous wheat, and permanent pasture.

(3) Water regimes: wet/dry, field capacity, 80% field capacity

4.2.2 Plant Parts Incubated: "Shoots Only" & "Shoots + Roots"

The plant parts chosen as green manure treatments were (a) shoots, (b) shoots & roots, because of the difference in quality of green manure between root material and young shoots, and consequently the possibly differing effects on their rates of decomposition (section 2.9.5), which affects the extent of soil structural stabilization.

4.3 Materials and Methods

4.3.1 Soils and Preparation

Preparation of soils and growth of plants were conducted in the same manner as that outlined in chapter 3. Based on the yield of dry matter in the preliminary experiments and amounts required for incorporation, the number of plants per pot was increased here, from 10 to 20. This necessitated an increase in the diameter of the pots to accommodate the added plants. However the mass of soil was kept at 1 kg. The added advantage of shallower pots was that better permeation of roots occurred throughout the soil because vertical root extension was restricted and so lateral growth was increased, thereby branching and making contact with a greater number of soil particles.

After the harvesting of the shoots on the same day, the plant parts were cut into 3 cm lengths to increase the area of contact with soil particles. As it was anticipated that the incorporation process of the plant parts would entail a time period of at least one week, immediately after harvest the needed aliquots (of 80 grams for each 1 kg of soil) were placed into plastic bags and tightly sealed against desiccation until the time of incorporation, a few hours later.

Incorporation was achieved by spreading thin layers of soil between alternate thin bands of fresh plant parts. Equal weights of stems and leaves were applied for the "Shoots Only" treatment, while for the "Shoot/Root" treatment, equal weights of shoots + leaves, and roots were imbedded. After incorporation, the surface of the soil was firmly tamped down, simulating the action of a roller under field conditions, to facilitate better contact between soil particles and the potentially decomposing substrate.

4.3.2 Incubation

A temperature of 25°C was maintained in a controlled-light growth chamber consisting of a sealed walk-in cabinet. Four replicates of each treatment were randomly arranged on tables and the following water regimes applied to the replicates during the incubations:

(1) Wet/dry Regime
(2) Field capacity Regime
(3) 80 % Field capacity Regime

4.3.3 Wet/dry Regime

A watering regime consisting of alternately wetting and drying the soil during ten day periods was applied as follows:

A timed calibrated dripper system, up to the level of field capacity, was used once per week. The soil, having been covered with inert plastic mulch was separated from that mulch by a layer of stiff nylon cloth which rested on the soil surface to prevent slaking and dispersion and to spread the water out evenly across the top of each pot. The nylon mesh further slowed the entry of water into the soil. This whole device also helped to reduce evaporation of water from the top surface of the soil. However, as an added precaution against water loss, the pots were then covered with plastic sheeting tightly over the next two days until total equilibration had been achieved. Water contents remained constant during the 7 day rewetting period, and this was checked at the beginning and end. After three days the plastic sheeting was removed, along with the plastic mulch and nylon cloth, which allowed a 4 - day drying period, after which the mulch was replaced and the wetting phase resumed.

4.3.4 Field Capacity Regime

The mass of water needed for maintaining field capacity was calculated, and added. Soil water content was held at field capacity values by placing plastic sheeting (0.1mm thick) over the pots for the duration of 4,6,8, and 12 week incubations.

4.3.5 80% Field Capacity Regime

The procedure of watering was the same as that for the Field Capacity Regime (above) except that the amount of water added was 20 per cent less.

4.3.6 Assessment of Structural Stability

Three techniques were used to assess the soil structural stability of the various treatments:

water stable macroaggregation
water retention and
hydraulic conductivity.

4.3.6.1 Water Stable Macroaggregation

The method of Kemper and Rosenau (1986) was adapted as follows:

All samples were exposed after 4, 6, 8, & 12 week incubations until air dry. The soils were then gently crushed with a wooden mallet and then passed through a 5 mm sieve. Four subsamples of 25 grams were then taken from each replicate. The samples were then placed on a nest of sieves of the following mesh diameters: 1 mm, 500μm, 250μm and 125μm. Samples were slowly lowered into a cylinder of distilled water until the water made contact with the bottom of the soil layer and then immersed in the cylinder and oscillated vertically at a stroke length of 2 cm with a frequency of 30 strokes per minute for 5 minutes. The material was then carefully washed from each sieve into containers, oven dried at 105 degrees for 48 hours and then each re-weighed.

WSMA was calculated as the amount of material left on the 250µm sieve plus the amount left on all sieves above this size; this was then corrected for the weight of sand > 250µm and expressed as a percentage of the original weight of aggregates:

$$\text{WSMA} = \frac{\{\text{Wt. stable soil } [>250\mu m] - \text{Sand } [>250\ \mu m]\} \times 100}{\text{Initial soil weight - sand weight } (>250\mu m)}$$

4.3.6.2 Water Retention

Air-dried aggregates were equilibrated and measured, based on the method of Klute (1986). The amount of water retained in soils as a result of each soil treatment was determined by the pressure plate apparatus and sintered funnel assemblies with a range of suctions applied to the soils at: 0.1kPa, 1kPa, 10kPa, 100kPa suction respectively.

4.3.6.3 Hydraulic Conductivity

For the determination of the rate of water movement through the soil, the saturated hydraulic conductivity (K_S) was determined for each treatment utilising a constant hydraulic head in the following manner: 50 gm of loose oven dried aggregate were placed in a perspex cylinder. The soil was first settled by a "drop" technique whereby each cylinder was dropped a fixed number of times from a fixed height. The soil was then fitted with a nylon mesh stretched over the bottom opening of the cylinders and wetted by capillary action. The soil surface was protected from the direct impact of the hydraulic head by using a filter paper. A constant head of 15 cm of water was maintained on each replicate, over a period of 7 hours during which 14 measurements were taken every 30 minutes of the amount of water conducted (q, cm^3) in that time period (t, h) period. The 7 hour period was needed because of the characteristically long time taken for a constant flow to be achieved in many unstable soils. The K_S (cm h^{-1}) of 4 replicates for each treatment was calculated as:

$$K_S = q(L) / H(At)$$

where q was the volume of water (cm^3) collected per unit time, t (h), A (cm^2) was the cross-sectional area of the cylinder, L was the length of the sample, and H (hydraulic head) was (L + 15 cm).

4.4 Results and Discussion

4.4.1 Saturated Hydraulic conductivity

4.4.1.1 Effect of water regime

The effect of soil water content on decomposition of organic matter is reflected in the hydraulic conductivity of the soil samples. As can be seen (Table 4.1), all water regimes caused significant increases in K_S of soils, but the increases for the permanent pasture soils at 80% field capacity had the greatest magnitude. This indicates that decomposition and formation of organic binding agents and thus some stabilization of soil structure had taken place in all soils, but to a greater extent in the pasture soil held at 80% of field capacity. At this water content decomposition of green manure was efficient in the presence of both adequate moisture and oxygen. At all water regimes OM increased Ks related to the controls.

4.4.1.2 Effect of different parts of green manure plants

The increases in K_S in all instances were significantly higher than the control (Table 4.2). The K_S increases for the "shoots only", over that of the "shoots + roots", though consistent, were generally not statistically significant. A high proportion of undecomposed stems, and roots (for the shoot + root treatments) was observed in the soils after each incubation, even after 12 weeks, for all treatments. The succulent shoot material probably decomposed faster in the soils, and in the process released a greater quantity of binding agents, thereby causing aggregation and greater porosity. The resistant root and lower stem material on the other hand, which included complex compounds such as suberins (in the roots), would have needed more time to decompose; the effects on soil structure of "shoot + root" would therefore not be up to the levels attained by the "shoot only" treatment. Thus after the succulent leaves had been decomposed, further decomposition was slow for the resistant stems, particularly in the wheat fallow and continuous wheat soils.

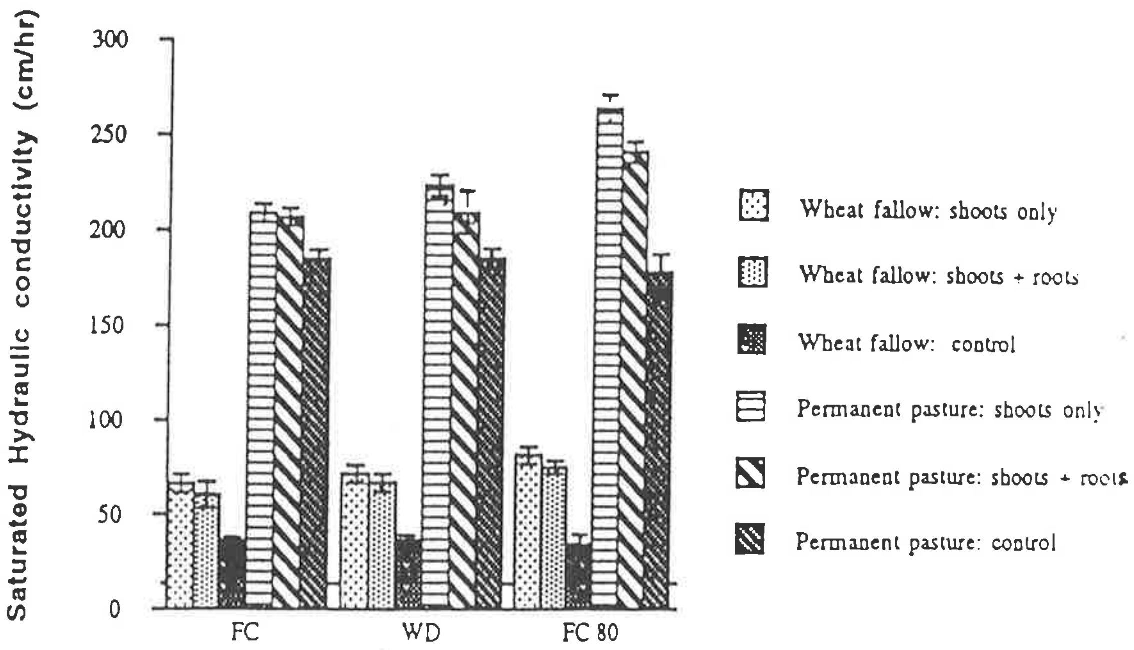
Table 4.1. The Effect of Water Regime, Green Manure from Different Plant Parts, and Prior Soil Management on the Hydraulic Conductivity (cm/hr) of a Red Brown Earth.

Water regime*	Treatment	Soil management		
		WF	*CW*	*PP*
WD	S	71^{e}	69^{f}	223^{ab}
	S+R	66^{f}	68^{f}	209^{c}
	Control	36^{g}	37^{g}	185^{d}
FC	S	66^{f}	79^{e}	209^{c}
	S+R	59^{f}	60^{f}	206^{c}
	Control	36^{g}	36^{g}	184^{d}
FC80	S	81^{e}	82^{e}	263^{a}
	S+R	75^{e}	75^{e}	241^{ab}
	Control	34^{g}	35^{g}	178^{d}

* Water regime of soils were: WD = wet/dry, FC = field capacity, FC80 = 80% of FC Shoots = "S", Shoots+Roots = "S+R", WF = wheat fallow, CW = continuous, PP = permanent pasture. Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's H.S.D. test.

Figure 4.1

The effect of water regime during incubation, green manure plant part, and prior soil management system on hydraulic conductivity of a red-brown earth.



Water Regime: WD = wet/dry, FC= field capacity, FC 80 = 80% FC

Table 4.2. Effect of Leguminous Green Manure, Prior Soil Management and Period of Incubation on the Hydraulic Conductivity (cm/hr) of a Red Brown Earth.

Treatment	Soil mgmt.	Weeks of Incubation			
		4	6	8	12
Shoot: *(20 t/ha)*	WF	45^{l}	75^{ji}	82^{hi}	89^{h}
	CW	63^{jk}	75^{ji}	81^{hi}	87^{hi}
	PP	210^{d}	220^{c}	239^{b}	259^{a}
Control (o t/ha)	WF	40^{l}	38^{l}	38^{l}	36^{l}
	CW	39^{l}	38^{l}	39^{l}	37^{l}
	PP	181^{f}	185^{f}	181^{fg}	184^{f}
Shoot + root: *(20 t/ ha)*	WF	42^{l}	68^{j}	74^{ji}	83^{hi}
	CW	43^{l}	68^{j}	75^{ji}	84^{hi}
	PP	202^{de}	210^{d}	225^{c}	238^{b}
Control (0 t/ha)	WF	40^{l}	38^{l}	38^{l}	36^{l}
	CW	39^{l}	38^{l}	39^{l}	37^{l}
	PP	181^{f}	185^{f}	181^{fg}	183^{f}

Column values followed by different letters in shoot or root are significantly different. ($P < 0.05$) as determined by Tukey's H.S.D test.

Figure 4.2

The effect of length of incubation period on the saturated hydraulic conductivity of a red-brown earth from different management systems.

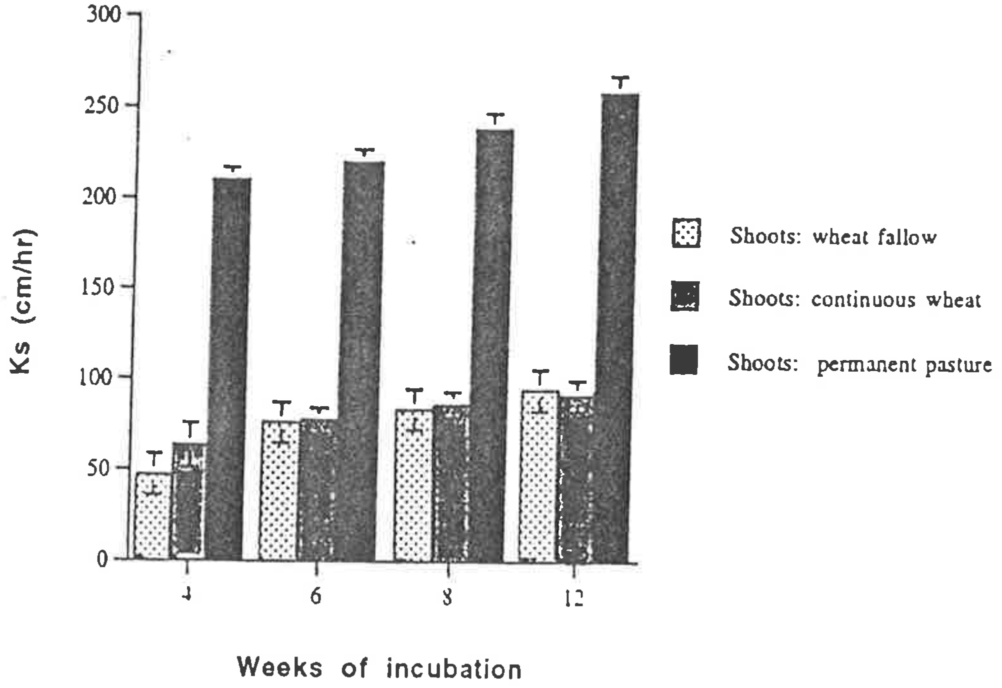


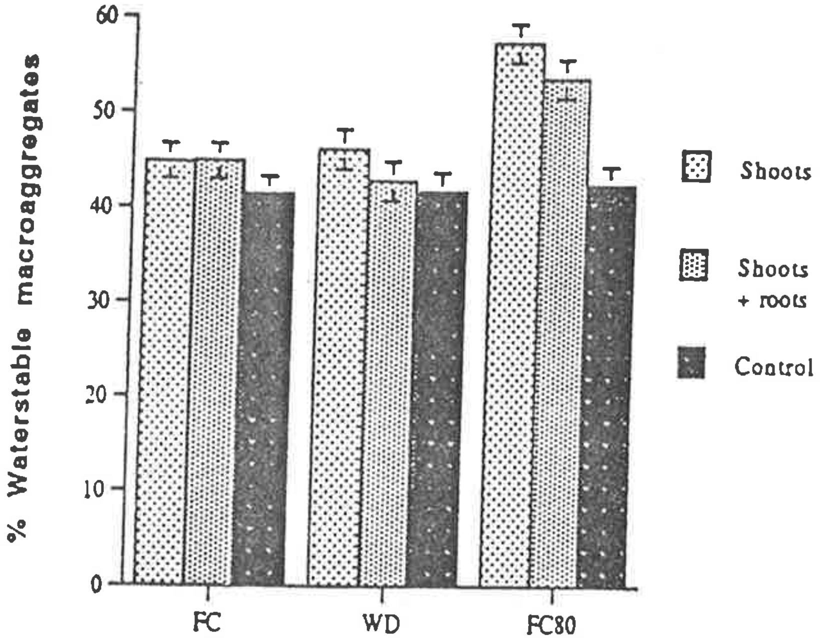
Table 4.3. Effects of Leguminous Green Manure on the Percentage of Waterstable Macroaggregates in a Red Brown Earth Under Different Water Regimes.

			Water regime	
Green manure	t /ha	WD	F/C	FC80
Shoot	20	47^b	46^b	58^a
Control	0	42^b	41^b	42^b
Shoot + root	20	43^b	45^b	54^a
Control	0	42^b	41^b	42^b

Column values followed by different letters in shoot or root are significantly different ($P < 0.05$) as determined by Tukey's H.S.D test.

Figure 4.3

The effect of green manure plant part and water regime under which it was incubated on the stability of macroaggregates in a red-brown earth.



Water regime:
WD = wet/dry, FC = field capacity, FC80 = 80% field capacity

Figure 4.4

The effect of time and green manure plant part on the water stability of macroaggregates in a red-brown earth at 80% field capacity.

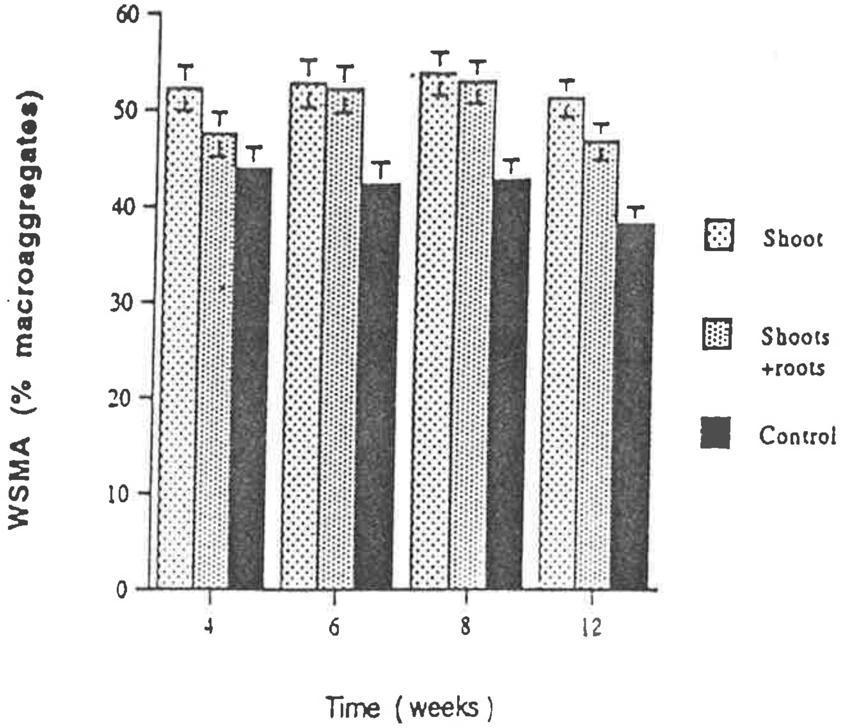


Table 4.4. The Effect of Prior Soil Management and Green Manure from Different Plant Parts on WSMA of a Red-brown Earth.

Green manure *(t/ha)*	Soil management WF	 CW	 PP
shoot			
20	45^{cd}	44^{cd}	66^{a}
0	37^{d}	35^{d}	54^{b}
shoot + root			
20	42^{cd}	42^{cd}	62^{a}
0	37^{d}	35^{d}	54^{b}

Significance (P < F)` from ANOVA) = .01. Column values followed by different letters in shoot or root are significantly different ($P < 0.05$) as determined by Tukey's H.S.D test.

Table 4.5. The Effect of Different Parts of Green Manure Plants and Water Regime During Incubation on the Water Retention (vol. %) of a Red Brown Earth.

Treatment	Potential (- kPa)	Water regime		
		WD	FC	FC80
S	10^{-1}	47^{a}	48^{a}	49^{a}
	10^{0}	37^{b}	36^{b}	37^{b}
	10^{1}	26^{c}	26^{c}	26^{c}
	10^{2}	15^{d}	15^{d}	16^{d}
S+R	10^{-1}	48^{a}	47^{a}	48^{a}
	10^{0}	37^{b}	36^{b}	37^{b}
	10^{1}	26^{c}	25^{c}	25^{c}
	10^{2}	14^{d}	14^{d}	15^{d}
Control	10^{2}	48^{a}	47^{a}	48^{a}
	10^{1}	34^{b}	37^{b}	37^{b}
	10^{0}	24^{c}	26^{c}	25^{c}
	10^{-1}	13^{e}	13^{e}	13^{e}

Column values followed by different letters in shoot or root are significantly different; ($P < 0.05$) as determined by Tukey's H.S.D test.

Table 4.6. The Effect of Leguminous Green Manure, Prior Soil Management and Water Regime During Incubation on the Water Retention of a Red Brown Earth.

Treatment	Potential (- kPa)	Water regime		
		WD	FC	FC80
WF	10^{-1}	44^{b}	44^{b}	45^{b}
	10^{0}	36^{cd}	36^{cd}	37^{c}
	10^{1}	25^{ef}	25^{ef}	26^{ef}
	10^{2}	13^{gh}	12^{gh}	13^{gh}
CW	10^{-1}	45^{b}	44^{b}	45^{b}
	10^{0}	33^{cd}	36^{cd}	37^{c}
	10^{1}	26^{ef}	25^{ef}	24^{ef}
	10^{2}	13^{gh}	13^{gh}	14^{gh}
PP	10^{-1}	54^{a}	54^{a}	56^{a}
	10^{0}	38^{c}	38^{c}	38^{c}
	10^{1}	26^{ef}	28^{e}	27^{ef}
	10^{2}	16^{g}	16^{g}	17^{g}

Column values followed by different letters in shoot or root are significantly different; ($P < 0.05$) as determined by Tukey's H.S.D.

Table 4.7. Effect of Green Manure on the Organic Carbon Content (ppm) of a Red-brown Earth.

Green manure (t/ ha)	Permanent Pasture	Wheat Fallow	Continuous Wheat
20	2.8^a	1.4^b	1.4^b
0	2.7^a	1.3^b	1.2^b

($P < 0.05$) as determined by Tukey's H.S.D.

4.4.1.3 Effect of Time of Incubation on Ks

Table 4.2 shows that saturated hydraulic conductivity of the samples changed during the incubation period and that the control showed no signifcant differences during the 12 week incubation period. As the incubation proceeded, substantial increases in K_S occurred in the wheat fallow and continuous wheat soils at weeks 4 and 6. However, after that, between weeks 8 and 12, no further significant increases occurred in the K_S of the continuous wheat and wheat fallow replicates. For the soils with a history of permanent pasture, the more significant increases were of a greater magnitude than those of soils with histories of wheat fallow and continuous wheat. Whereas the increases in K_S for the wheat fallow and continuous wheat soils levelled off at week 8, the increases for the permanent pasture soils continued throughout the 12 weeks of incubation. Nevertheless increases of the highest magnitudes took place at 4 weeks, and amongst the permanent pasture soils. This trend is in agreement with the observations of Mason, (1977), who found that differences in N mineralisation rates of incubated green manure were relatively small up to the third week of incubation, after the largest increases in the first week.

4.4.1.4 Effect of prior soil management history

Increases in K_S are seen to be highest amongst the treatments on permanent pasture soil (Table 4.2; Figure 4.2). The K_S for the permanent pasture soils was always higher than that of the cultivated soils by several orders of magnitude. The improvement in K_S was more substantial than for the cultivated soils. Obviously there is no effect of mineralogy. It is also seen (Table 4.2) that significant increases in K_S began at 4 weeks of incubation in pasture soils, whereas in the cultivated soils the increases began only after 6 weeks.

4.4.2 Macroaggregate Stability

4.4.2.1 Effect of water regime

Generally, the measurements of water-stability of macroaggregates (WSMA) showed no significant differences between the wet/dry treatment and soil held at field capacity with that of the controls. The only significant difference seen is for the "shoots only" treatment , in soils held at 80% field capacity (Table 4.3; Figure 4.3). For this treatment, a small improvement in organic carbon was observed following the incubations (Table 4.7). As in the K_S, the increasing trend in macroaggregation was probably due to greater aeration and reduced waterlogging at this water regime. Whereas the increase in WSMA was not generally statistically significant, increase in K_S was significant at all water regimes. A possible explanation for the lack of significance of the WSMA results could be that the method of determining WSMA may have been too severe. It is known that macroaggregates are more susceptible than microaggregates to breakdown under prolonged physical stresses, particularly for the more recently formed aggregates (Tisdall and Oades, 1982; Varadachari & Ghosh, 1983). Thus aggregates formed as a result of the treatments here, may have been destroyed via the impact of the wet sieving applied in this study. This could have partially masked some improvements in WSMA. On the other hand, the process of measuring saturated hydraulic conductivity of soils involved substantially lower levels of physical agitation. The treatments however, could have caused some changes in microaggregation and porosity, which could have contributed to the increase in K_S. K_S therefore seems to be a more precise parameter, compared with WSMA, for determining minute changes in soil structure.

4.4.2.2 Effect of different parts of green manure plants.

At 80% field capacity, the soil samples incubated with the shoot material exhibited a substantially higher level of macroaggregate stability than that incubated with the shoot + root (Table 4.3; Figure 4.3). These increases were significant only for the permanent pasture soils. This is discussed later. These data, again as in the case of hydraulic conductivity, show the effect of the quality of added organic matter on the soil sample.

4.4.2.3 Effect of time

In the present study, aggregate stability first showed a consistent, though not statistically significant increase up to week 8, then decreased at later stages of the incubation (Figure 4.4). At week 12 for the "shoots only" treatment, a significant increase above the control was observed. As the stability of the control decreased by week 12, a trend of increasing stability for the treatments became more marked, particularly for the shoots only treatment. As observed in the case of K_S, at 12 weeks of incubation such increases in WSMA, above those of the controls were significantly less than that those attained at week 4, when highest increases were recorded. Similarly, increased aggregate stability in the first two weeks of incubation was obtained by Swift (1992) by adding glucose to the red-brown earths of southern Australia. This also seems to agree with Muneer and Oades (1989) who found that following an initial application of glucose, the gain in structural improvement stopped with no further addition of substrate.

4.4.2.4 Effect of prior management history

There were no significant increases in WSMA amongst either of the previously cultivated soils, but significant increases for the permanent pasture soils occurred (Table 4.4). Due to the extensive root systems of pasture plants, the upper soil horizon in old pastures is almost all rhizosphere (Connell and Hadfield, 1961). A higher level of biological activity, compared to cultivated soils improved the soil structure. Among the three original soils, the microfloral population would therefore have been highest in the permanent pasture soils. The additions of green manure seemed to have triggered and greatly facilitated the production of binding agents in the pasture soils. This is in agreement with the observations of Swift, (1992), where additions of a readily decomposeable organic substrate stimulated the activity of greater number of indigenous microorganisms in pasture soils compared with the other soils. The cultivated soils contained a lower level of organic matter owing to the dried out and resistant nature (probably comparitively highly lignaceous) of the organic fraction in the cultivated soils. As this "priming" effect was greater in the pasture soils, a greater amount of binding agents was released, thereby leading to more significant increases the stability of aggregates.

4.4.3 Water Retention

Differences in the amounts of water retained amongst the treatments were not significant. (Table 4.5, 4.6). The soils are mainly fine-grained, with high clay content. Therefore normally, relatively high water retention of these soils reflect their clay content. The water regimes of incubation of green manure did not cause significant differences in water retention of the soils in this study. The only statistically significant trend seen is that of the higher rate of water retention as it relates to prior soil management (Table 4.6). This is exhibited by the pasture soil compared with those of the cultivated ones.

4.5 Conclusions

The experiments led to the following conclusions:

Aggregate stability is increased by green manure. Improvements in this parameter bring about improvements in water movement or retention. Green manure maintains soil organic matter levels under particular, though not well-defined soil conditions.

Non-sodic red brown earths show significant increases in saturated hydraulic conductivity when incubated with leguminous green manure under a regime of continuous oxygen and moisture supply at 80 % field capacity, as compared to other water regimes. However such increases are most substantial for soils previously under a management system of permanent pasture.

Green manure added at 20 t/ha did not stabilise aggregates of either the wheat fallow or continuous wheat rotations of the red brown earth against 5 minutes of wet-sieving. However, such stability was significant in the permanent pasture soils. Therefore, at application rates of 20 t ha $^{-1}$, leguminous green manure is not effective as an agent for the improvement of the structure of a red brown earth which had been previously under a cultivation system for several decades, compared to soils previously under pasture management during the same period.

The effects of the duration of incubation time on red brown earths indicate that the effects of green manure on the structural stability of such soils begin to decrease after the initially applied substrate has been consumed by microorganisms.

The saturated hydraulic conductivity of red brown earths incubated with green manure showed greater increases than those increases involving macroaggregate stability. Increases in the K_S of the soils also lasted for a longer period of the incubation time.

Chapter 5

Green manuring in calcareous sodic soils

5.1 Introduction

The experimental work in this chapter concerns the action of green manures on calcareous, sodic sub-soils of high pH, from two localities. The chief needs of such subsoils are to acquire and maintain adequate water and aeration for plants. Warkentin (1982) stated, that to maintain aggregate stability in a "clayey" soil it is necessary for clay minerals to remain in a flocculated state as microaggregates. The organic matter within microaggregates normally is physically inaccessible to microorganisms, and hence not subject to rapid decomposition (section 2.7.1). However, the low levels of native carbon resulting mainly from poor growth conditions caused by sodicity causes a lack of such organic matter in sodic soils, thereby exacerbating the effects of sodicity in causing poor soil structure (section 2.6). Thus in sodic subsoils, the spontaneous movement of clay particles seals pores, thereby reducing infiltration (Rengasamy and Olsson, 1992) .

Among other factors, flocculation is enhanced by the presence in the soil of polyvalent cations, organic matter and minimum disturbance (Muneer and Oades, 1989), but flocculation of clay particles must be accompanied by cementation to reduce dispersion (section 2.9.1). It has been reported that in combination with organic matter, calcium compounds added to sodic surface-soils reduce dispersion and increase macroaggregation (section 2.9.4). Such results can be achieved in calcareous soils, even without the artificial addition of a calcium source. It has been shown that organic acids, acting in a calcareous soil will release Ca^{++}, thereby leading to a higher EC of the soil solution (section 2.9.4). This reduces dispersion in such soils. But it has been observed that if the soils are already sodic, introduction of organic matter without removal of Na^{+} may not reduce dispersion, thereby decreasing aggregate stability (Rengasamy and Olsson, 1991). It is therefore appropriate that an anticipated programme of green manuring should be preceded by preliminary experiments to determine (1) the plant species most suited to such soil conditions, and (2) the response of the soil to pretreatment with gypsum (which has been known also to facilitate root proliferation) by replacing the Na^{+} attached to clay paticles, with Ca^{++}. Measurement of changes in aggregate stability will include those used previously for non-sodic soils (section 4). Because measurement of soil stability in clay soils can be determined by permeability measurements (Warkentin, 1982), any significant accompanying decrease in dispersion of clay particles would be expected to be reflected in increased permeability of such soils. Thus, of particular significance is the hydraulic conductivity of the treated sodic subsoils.

The hypothesis for this chapter is as follows:
When used in sodic subsoils pre-treated with gypsum, green manure will increase macroaggregation and microaggregation.

5.2 Materials and Methods

5.2.1 Properties of Soils

Table 5.1 shows the main features of two subsoils obtained from a 15 - 30 cm depth of a sodic red-brown earth from (1) Strathalbyn and (2) Two Wells, South Australia. The pH readings (> 9) were obtained from 1:5 soil /water ratio extracts. The high sodium adsorption ratios (SAR > 8) of both subsoils gave rise to spontaneous dispersion (section 2.6.2.3). Because of the high pH, each subsoil could be expected to contain $CaCO_3$, $MgCO_3$ and Na_2CO_3. However, it is seen that there are much lower levels of exchangeable cations and electrical conductivity for the Strathalbyn subsoil, athough it contains more than three times as much native $CaCO_3$ as the Two Wells soil. This indicates that $CaCO_3$ in Strathalbyn is mostly insoluble, and hence suggests the possible effectiveness of organic acids from decomposing green manure to solubilise the $CaCO_3$, thereby releasing Ca ions into the soil solution.

Table 5.1. Properties of Calcareous, Sodic Soils (15 - 30 cm)

Properties	Strathalbyn	Two Wells
Soil pH (H_2O)	9.1	9.4
EC (dS. m^{-1})	0.25	0.52
Organic carbon (%)	0.56	0.47
CEC (m mol_c kg^{-1})	45	310
SAR	8.5	9
CaCO3 (%, w/w)	14	4
Particle size distribution		
Sand (%)	45	27
Silt (%)	16	26
Clay (%)	39	47
Clay mineralogy (% of clay fraction)		
Illite	28	32
Kaolinite	14	18
Quartz	15	4
Randomly interstratified minerals	43	45

5.2.2 Assessment of Soil Structural Stability

In addition to the measurements of water-stable aggregation, hydraulic conductivity, and water retention (section 4), additional techniques for determining changes in microstructure are described below.

5.2.2.1 Spontaneous dispersion

Distilled water was slowly and carefully added down the side of a vial, to 25 grams of air-dry soil aggregates without disturbing the soil. The flask was then left to stand for 24 hours. The water above the soil was then stirred for 15 seconds and 10 ml of clay suspension removed using a pipette. The clay obtained by spontaneous dispersion of the soil was calculated as a percentage of the total soil weight on an oven-dry basis.

5.2.2.2 Mechanical Dispersion

For the determination of mechanical dispersible clay, the samples prepared as previously were placed in an "end over end" mechanical shaker for 24 hours. After 8 hours of standing, 10 ml of the suspension was removed and then oven-dried for 24 hours. The mechanically dispersed clay was calculated as a percentage of total oven-dry soil.

5.2.2.3 Particle size analysis of dispersed material

Particle size analysis of the suspension, measures the average size of soil particles after mechanical dispersion. Because clay particles can be bound together into floccules by cements (Warkentin, 1982; Emerson, 1983), the size of these are therefore an indication of the level of aggregation of clay particles caused by treatments. After soils were mechanically dispersed (1: 5 soil water), particle size distribution was measured in suspensions by using a NICOMP model C370 submicron particle sizer version 5. The standardisation was done using 0.09μm latex rubber spheres. The values were within 5% error.

5.2.2.4 Electrophoretic Mobility

Because dispersion is reduced by lowering the repulsive charges of the clay particles, the measurement of particle charge and their mobility reveals the effect of the treatments on clay dispersion. This is because organo-mineral complexing neutralises such charges, thereby lowering the electrophoretic mobility of particles.

The $-\zeta$ potential may be considered as a remote effect of the surface charge of the particles. The Smoluchowski equation below is related to the electrophoretic mobility of the particles (Pashley, 1985) by:

$$\zeta = 4\pi \eta \mu_e / \varepsilon$$

where ζ is the zeta potential in mV, η is the electrophoretic mobility (mm s^{-1} v^{-1} cm^{-1}), μ_e is the viscosity of the medium, and ε is the dielectric constant. For aqueous media at 20° C, the relation between electrophoretic mobility and the $-\zeta$ potential is 12.85 mV per mobility unit.

The $-\zeta$ potential was measured using a Malvern Zetamaster, Zetamaster particle electrophoresis analyser. All $-\zeta$ potential measurements were at a constant temperature (20° C) and with a constant field strength of 80 V cm-1. Measurements were carried out over a 30 second run time and the final values used were the averages of 10 runs. Suspensions of dispersed clays (0.1 g dm^{-3}) were prepared in reverse osmosis (RO) water. The $-\zeta$ potential measurements in this study were all negative, indicative of the anionic charge on the clay surfaces causing the clay to migrate toward the cathode.

5.2.2.5 Waterstable Macroaggregation, Water Retention, and Saturated Hydraulic Conductivity

Water-stable macroaggregation, water retention at different suctions and hydraulic conductivity were measured according to the procedures described in section 4.3.

5.2.3 Treatments

5.2.3.1 Rate of Gypsum Application

The equivalent of 20 t/ha of gypsum was added to soil in half of the number of pots, the other half being “no gypsum” controls.

5.2.3.2 Soil Pre-treatment

The sodic soils were sifted through a 5 mm sieve and then thoroughly hand-mixed with gypsum while at air dry. The pots were lined on the inside with a fine meshed nylon cloth to reduce losses of clay particles during the proposed drainage. The soil was placed in pots of dimensions 12 cm deep, 50 cm wide and 80 cm long (plate 5.1). The soils were then wetted up to saturation. Six, weekly leaching cycles followed, where the water was slowly added from a timed dropper onto a layer of inert plastic granules resting on a nylon cloth placed on the soil surface. This contraption reduced the mechanical impact of the water drops on the soil. At the end of the six week leaching period the soils were air-dried and plants were grown.

5.3 Growth Responses on Sodic Soils

5.3.1 Results of Gypsum Pre-treatment

The soils pre-treated with gypsum substantially increased in friability in contrast to the no-gypsum (control) soils. Readings taken with a hand penetrometer confirmed these observations (Table 5.2). This condition persisted throughout the six weeks of the leaching regime.

Table 5.2. Effect of Gypsum Treatment on Penetrometer Resistance (Mpa *) of Soils at Air-dry.*

Pot Number	Gypsum	No Gypsum
	Two Wells	
1	1.5^{b}	3.5^{a}
2	1.3^{b}	3.5^{a}
3	0.7^{cd}	3.4^{a}
	Strathalbyn	
4	1.5^{b}	3.6^{a}
5	0.8^{cd}	3.9^{a}
6	0.7^{cd}	4.0^{a}

Values followed by different letters are significantly different. Tukey's HSD ($P < .05$)

5.3.2. Results of Plant Growth on Sodic Soils

Based on the average (of 5 replicates) weight of plant roots from each treatment, all plants exhibited a trend of reduced root growth on the sodic soils (Table 5.3). However, it is seen that root growth in the gypsum treated sodic soils was more substantial than that of the control sodic soils (Table 5.3). The lower root weights (Table 5.3), is largely attributed to the lack of adequate aeration in the root zones of plants in these soils, and mechanial impedance which greatly restricted root elongation. It was found that in both soils, the cowpea roots were the most underdeveloped and were devoid of any root nodules. The roots of the other legumes contained nodules, with the greatest amounts observed on the vetch plant, which also had acquired greatest root mass. A visual inspection revealed that the vetch roots were the longest of all species. They proliferated a greater volume of soil than the other root systems, thereby having gained access to more soil water. This seems at least in part, to be responsible for the more luxuriant growth of the vetch as compared with the other species.

Table 5.3. Comparison of Average Root Weights (g/pot) of Plants Grown in Two Calcareous Sodic Sub-soils (15-30cm (0-15 cm depth)

Plants	Gypsum-treated	No gypsum
	Two Wells	
Vetch	1.25^{c}	1.09^{c}
Cowpeas	1.09^{d}	0.91^{c}
Clover	1.34^{c}	0.72^{de}
	Strathalbyn	
Vetch	2.16^{bc}	1.86^{b}
Cowpeas	0.95^{d}	0.56^{e}
Clover	1.23^{c}	0.92^{d}

Column values followed by different letters are significantly different ($P < .05$) determined by Tukey's HSD test.

5.3.3 Shoot Development

Several conditions contributed to growth problems on the sodic soils. The tops of the cowpeas, exhibited unhealthy growth on the sodic soil from Two Wells (Plate 5.4) and were unsuitable to be used as a green manure. Chemical analysis showed that shoot material of the cowpeas suffered from boron deficiency (Plate 5.3) which caused the drying out of the leaves and consequently a decrease in succulence on the Two Wells soil.

On the other hand, the vetch plant, which exhibited a greater hardiness and resistance to adverse soil conditions, acquired a greater biomass than observed for the cowpeas, clover and alfalfa plants. It was found that the clover plant also grew more healthily whilst shaded by the vetch plants.

Plate 5.1

Set-up of Pot Experiments

Plate 5.2

Visual appearance of sodic soils
treated with gypsum (left) and no gypsum on the right.

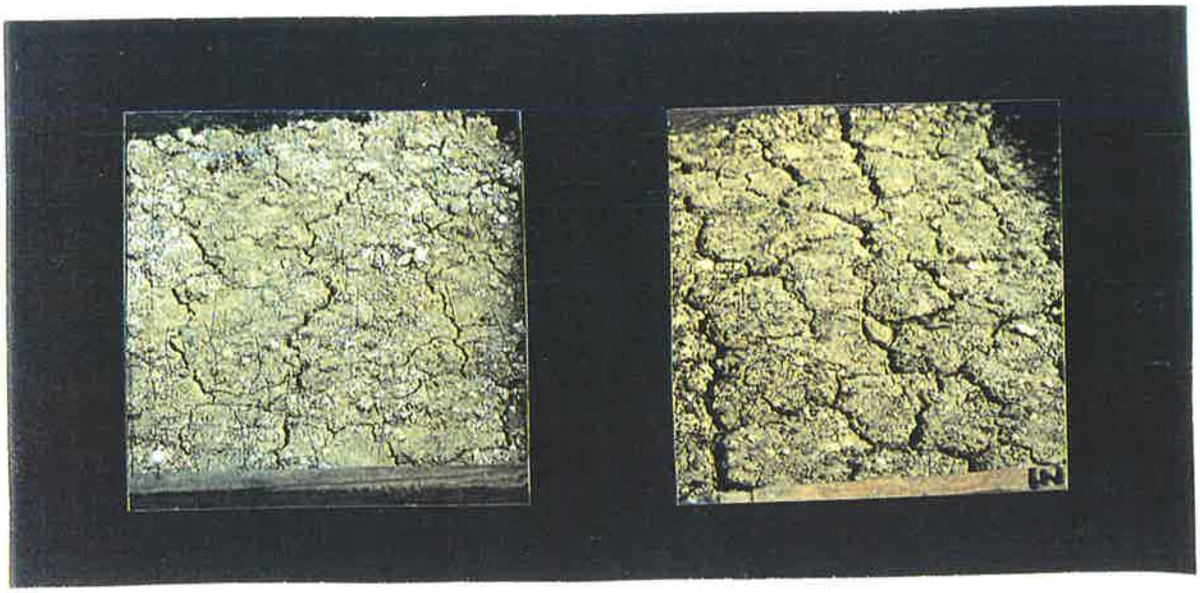


Plate 5.3

Evidence of boron deficiency in cowpeas (*Vigna sinensis*) in Two Wells soil.

Plate 5.4

Loss of succulence at 8 days after symptoms of boron deficiency in cowpeas in Two Wells soil.

Plate 5.5

80% field capacity treated soil (Strathalbyn)
at 4 weeks incubation with green manure and gypsum.

Plate 5.6

Undecomposed parts of vetch (*Vicia sativa*) due to high lignin content.

Plate 5.7

Appearance of treated soils (Strathalbyn) at 12 weeks after K_s measurements.

(A) Gypsum with no green manure
(B) Gypsum with green manure
(C) No gypsum, no green manure
(D) No gypsum with green manure

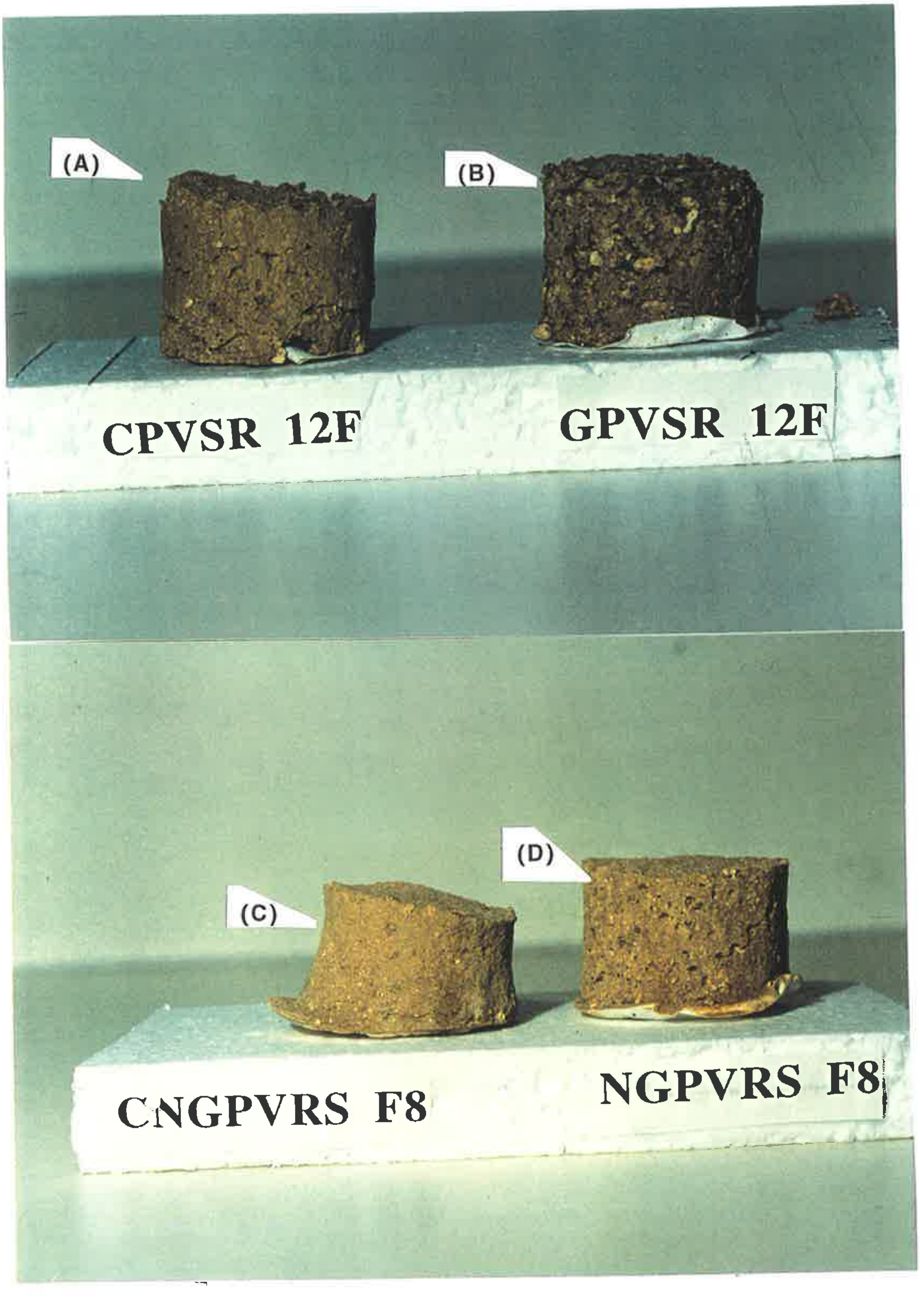


Plate 5.8

Appearance of treated Two Wells soil at 12 weeks after K_s measurements

(A) Gypsum + green manure

(B) Gypsum only

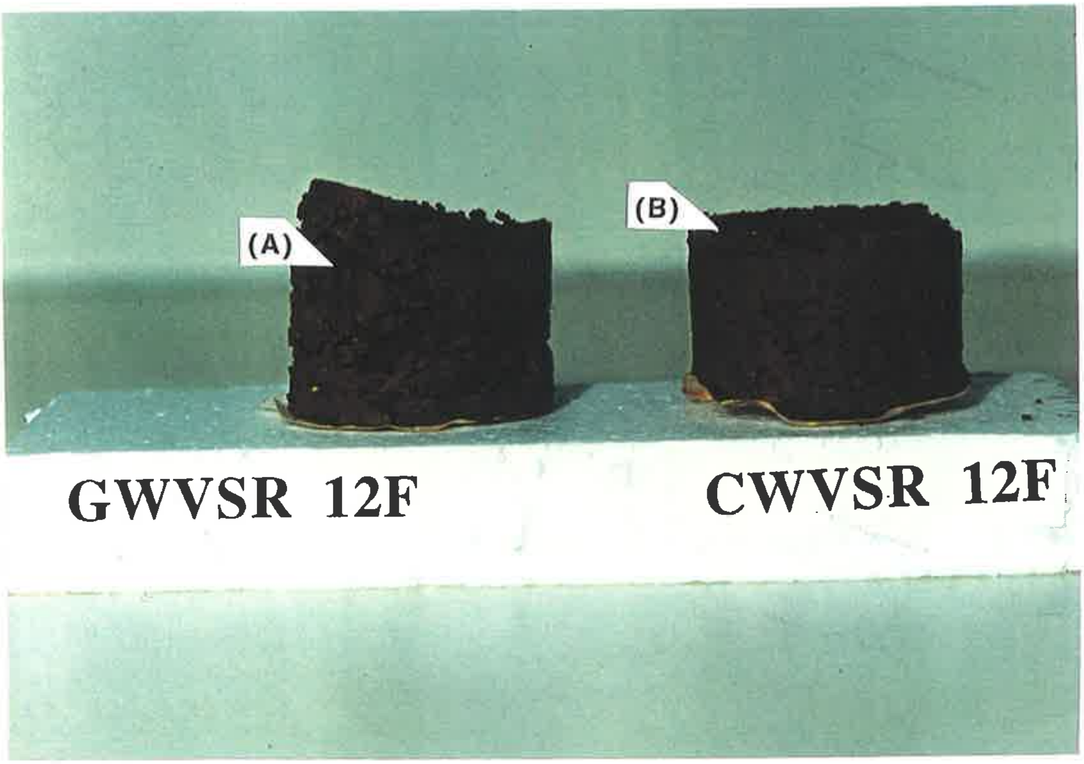


Plate 5.9

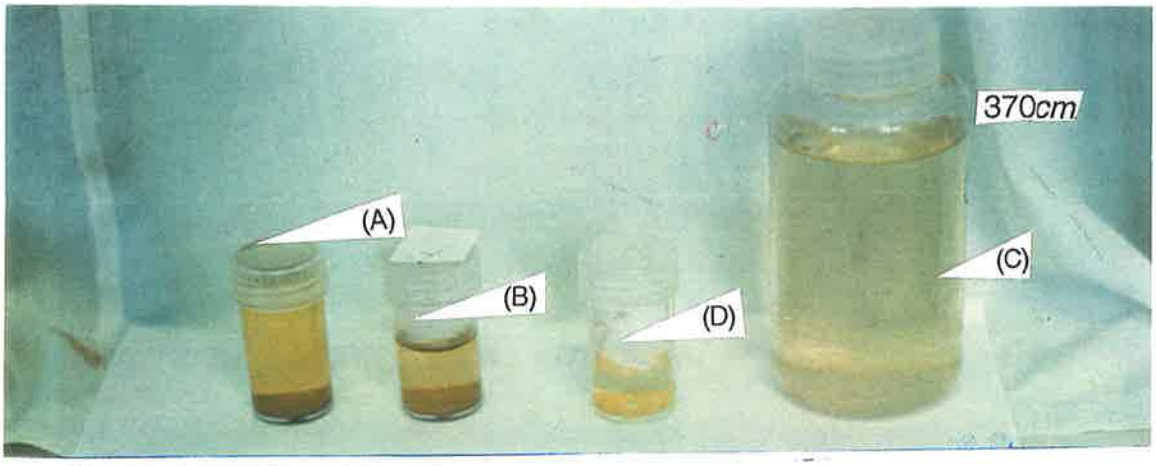


Plate 5.9a Total quantity of leachates after no gypsum-green manure treatments.

(A) Two Wells
(B) Two Wells control
(C) Strathalbyn
(D) Strathalbyn control

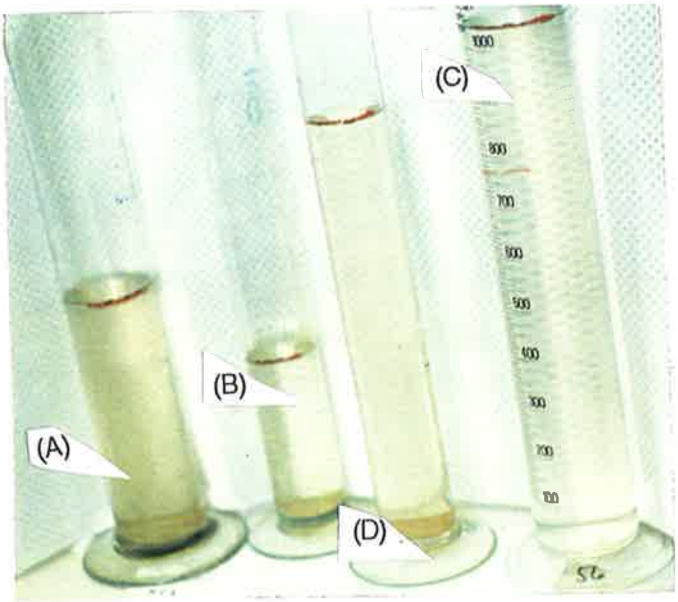


Plate 5.9b Total quantity of leachates after gypsum + green manure treatments.

(A) Two Wells
(B) Two Wells control
(C) Strathalbyn
(D) Strathalbyn control

Table 5.4. Comparison of Average Shoot Weights (g/pot) of Plants Grown in Calcareous Sodic Soils (15-30 cm depth)

	Sodic soils	
Plants	Gypsum-treated	No gypsum
	Two Wells	
Vetch	2.20^{c}	2.09^{c}
Cowpeas	1.86^{de}	1.35^{ef}
Clover	2.20^{c}	1.65^{e}
	Strathalbyn	
Vetch	2.88^{bc}	2.11^{c}
Cowpeas	1.45^{ef}	1.06^{f}
Clover	2.10^{c}	1.95^{cd}

Column values followed by different letters are significantly different ($P < .05$) determined by Tukey's HSD test.

5.4 Incubations

For the incubations of green manure and gypsum in the sodic soils, the procedure adopted in section 4 of this study was followed. The following treatments were used:

1. gypsum 20 t/ha
2. gypsum 20 t/ha + green manure 20 t/ha
3. green manure 20 t/ha
4. control (no gypsum, no green manure)

5.5 Results and Discussion

5.5.1 Response of soils to gypsum treatment and leaching

Gypsum treatments increased friability and macroporosity. Even though cracks in the soil were also apparent for the "no gypsum" treatments, such cracks were not interconnected, as indicated by very low infiltration and high penetrometer resistance. For the "no gypsum" pots during attempted leaching, there was no drainage from the soil as the soil pores were immediately sealed. Spontaneous dispersion of the clays caused a blockage of pores, leading to a total restriction of water movement throughout the lower part of the soil. However in the gypsum treated pots, interconnection was adequate enough to facilitate leaching and draining of the soils within 24 hours.

5.5.2 Hydraulic conductivity

5.5.2.1 Green manure treatment

Green manure increased K_S in all soils (Table 5.5; Table 5.6) thereby signifying an effectiveness of green manure improving the porosity of sodic soils.

Table 5.5. The Effect of Green Manure Only and Water Regime, on the Hydraulic Conductivity (cm/hr) of Two Calcareous Sodic Soils (Average Values).

Green manure Component	t/ha	*Water regime* WD	FC	80%FC
shoot	20	122^{b}	112^{bc}	159^{a}
control	0	0^{d}	0^{d}	0^{d}
shoot + root	20	113^{bc}	111^{bc}	150^{a}
control	0	0^{d}	1^{d}	3^{d}

Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's HSD test.

Table 5.6. Effects of Different Parts of Green Manure Plants and Duration of Incubation on the Hydraulic Conductivity (cm/hr) of Two Calcareous Sodic Soils (Average Values).

		Weeks of Incubation			
Green manure	t/ha	4	6	8	12
Shoots (control)	0	0^c	0^c	3^c	0^c
	20	101^b	104^b	114^b	206^a
Shoots+roots (control)	0	0^c	0^c	3^c	3^c
Shoots + roots	20	98^b	101^b	109^b	201^a

Column values followed by different letters are significantly different ($P < .05$) determined by Tukey's HSD test.

Table 5.7. The Effect on Hydraulic Conductivity (cm/hr) of Water Regime and Gypsum at Incubation with Green Manure on Calcareous Sodic Soils (Average Values).

Water regime at Incubation	Gypsum	No gypsum *(control)*
WD	176^{b}	48^{c}
FC	168^{b}	42^{c}
80%FC	214^{a}	77^{c}

Column values followed by different letters are significantly different (*P* < .05) as determined by Tukey's HSD test.

Table 5.8. The Effect on Hydraulic Conductivity (cm/hr), of Gypsum, Different Parts of Green Manure Plants and Water Regime at Incubation on Two Calcareous Sodic Soils (Average Values).

		Water Regimes of Incubation		
Green manure	t/ha	WD	FC	FC 80
		Gypsum		
[Control]	0	145^{d}	144^{d}	145^{d}
Shoot	20	200^{b}	192^{bc}	254^{a}
[Control]	0	145^{d}	144^{d}	145^{d}
Shoot + root	20	196^{b}	191^{bc}	243^{a}
		No gypsum		
[Control]	0	0.7^{f}	0.0^{f}	0.6^{f}
Shoot	20	44^{e}	33^{e}	84^{e}
[Control]	0	0.7^{f}	0.3^{f}	0.6^{f}
Shoot + root	20	39^{e}	32^{e}	58^{e}

Column values followed by different letters in "shoots" or "shoots + roots" are significantly different ($P < .05$) as determined by Tukey's HSD test.

Table 5.9. The Effect of Gypsum + Green Manure on the Hydraulic Conductivity (cm/hr) of Two Calcareous Sodic Soils, vs Water Regime.

Water Regime	Weeks of Incubation			
	4	6	8	12
		GM + G		
		Two Wells		
Wet/dry	140^{d}	143^{d}	148^{d}	148^{d}
Field Capacity	134^{d}	143^{d}	144^{d}	144^{d}
80% Field Capacity	172^{c}	170^{c}	174^{c}	195^{bc}
		Strathalbyn		
Wet/dry	147^{d}	147^{d}	149^{d}	155^{d}
Field capacity	145^{d}	140^{d}	146^{d}	151^{d}
80% Field capacity	172^{c}	175^{c}	179^{c}	278^{a}

GM + G = gypsum + green manure

Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's HSD test.

Table 5.10. The Effect of Gypsum and Green Manure, on the Hydraulic Conductivity (cm/hr) of Two Calcareous Sodic Soils at 80% Field Capacity.

Soil Additive	Weeks of Incubation 4	6	8	12
		Two Wells		
G	168^{bc}	170^{bc}	168^{bc}	174^{b}
GM - G	38^{de}	43^{d}	58^{d}	108^{c}
-G -GM	0^{f}	0^{f}	0^{f}	0^{f}
		Strathalbyn		
G	185^{ab}	195^{a}	195^{a}	214^{a}
GM -G	107^{d}	110^{d}	116^{d}	178^{b}
-G -GM	0^{f}	0^{f}	3^{f}	7^{f}

G = gypsum, GM = green manure, -GM= no green manure, -G = no gypsum

Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's HSD test.

However, comparison of the soils incubated with succulent shoots only, with those incubated with shoots + roots showed no significant differences in K_S for the soils during the incubation period (Table 5.5). Generally there was an increasing trend with a longer incubation (Table 5.6).

5.5.2.2 Green manure + gypsum

When green manure was incubated in gypsum-treated soils (Table 5.9), the K_S of the soils increased significantly above that of either treatment applied singly (Table 5.10). In this study the organic matter had been added to the soil in a fresh state. However, the gypsum-only treatment exhibited a higher K_S than that of the green manure only treatment (Table 5.10). Both gypsum and green manure were therefore effective in increasing the K_S of the soil, but gypsum singly was more effective. Gypsum treatment resulted in the removal of Na^+ as indicated by SAR values (Table 5.19). This is discussed in detail later.

5.5.2.3 Effect of water regime

For both sodic soils, incubation at 80% of their field capacity increased K_S to a substantially higher level than did the field capacity and wet/dry treatments (Table 5.9). This was probably related to the better aeration and sufficiency of oxygen in the soils, as found for the Urrbrae soils discussed earlier here, in section 4.4.1.1. However, this result applied only to the gypsum+green manure treatment (Table 5.7). For the green-manure only treatments (Strathalbyn only), a result comparable to that of the gypsum-only treatment was achieved only after 12 weeks (Table 5.10). This is discussed later (5.5.2.4). Thus, for the gypsum-only treatments, though the increase in K_S attained during the pre-treatment had been maintained during the incubation, the K_S was not significantly improved further at any time over the 12 week incubation period (Table 5.10) for any of the water regimes. The absence of decomposing green manure in the gypsum only treatment caused a lower level of porosity.

Amongst the no-gypsum soil held at field capacity, poor aeration inhibited decomposition, whilst for the alternately wetted and dried replicates, the lower layers of soil in the containers probably remained dry for substantially longer periods. In the first case this caused anaerobic conditions which interrupted oxygen supply for prolonged periods and in the second case a lack of adequate moisture to support soil microorganisms. Decomposition of green manure was thereby curtailed, thus causing a reduction in the release of soil-binding cements.

5.5.2.4 Effect of period of incubation

After 12 weeks, it was found that in all treatments, there was a general trend of decreasing magnitude of K_S with time (Tables 5.9, 5.10), as follows:

(gypsum + green manure) > gypsum > green manure > control

For both sodic soils, the increase in K_S for the green manure + gypsum treatment during the period 9 -12 weeks is seen to have been greater than that of each of the preceding 2 week periods, but significantly for the Strathalbyn soil (Tables 5.9, 5.10). More $CaCO_3$ (14%) in Strathalbyn soil contributed to a higher Ca^{++} in soil solution compared to the soil solution of Two Wells soils ($CaCO_3$ 3%) (Tables 5.15 - 5.21). The need for the presence of divalent cations in the sodic soil in order for inherent clay materials to remain in a flocculated state, as the Na^+ ions are replaced by the Ca^{++}, has been stated by Muneer and Oades (1987), Baldock *et al.* (1994) and Shanmuganathan and Oades, (1984). By week 12, the indigenous $CaCO_3$ had probably become sufficiently solubilised under the continuous action of organic acids and H_2CO_3. H_2CO_3 had been formed as an indirect result of the increased CO_2 under continuously moist soil conditions (i.e. at 80% field capacity) caused by the increased respiration of microorganisms in response to the presence of green manure as a substrate. It is thus possible that because considerable time (even under the prevailing conditions of adequate heat and moisture) was needed for such reactions to substantially occur, a dramatic rise in K_S was observed only towards the end of the incubation period. However for the Strathalbyn soil the K_S of the green manure had approached that of the the gypsum-only treatment by week 12 of the incubation. This is a departure from the trend seen earlier in the incubation, when the green-manure-only treatment consistently exhibited a lower K_S than that of either of the gypsum-without-green-manure or the gypsum + green manure treatment. This was a highly significant trend, which gives support to the suggestion that the green manure acted synergistically in the late stages of the incubation with the native calcium in both sodic subsoils (but moreso in the Strathalbyn subsoil), to increase K_S.

5.5.3 Measurement of Macroaggregation

For the gypsum-only treatments, there is no significant difference in stability of macroaggregation and there are no clear trends (Table 5.12). Even under conditions of 80% field-capacity water regime, the water-stable macro-aggregation WSMA was not significantly improved. In this study, the subsoils used can be classified as cracking clays (plate 5.2). Similar results, in terms of macroaggregation were obtained by Coughlan (1984), in a survey of cracking clays in central Queensland. He found that none of the water stability measurements used (hydraulic conductivity was not utilised in that study) were significantly correlated with organic matter. Another reason may be related to the fact that gypsum acting alone does not seem to improve the macroaggregation of soils (Baldock, 1994). The role of gypsum is to flocculate the clay particles. As has been found by other workers (Baldock, 1994; Muneer and Oades, 1987), Ca^{++} in soil solution do not improve macroaggregation. In this study, the addition of green manure to the gypsum-treated soils also made no difference in macroaggregate stability. Generally, in other studies, calcium and organic matter have been shown to improve macroaggregation in non-sodic soils. However, in sodic soils Ca^{++} improve clay flocculation and domain formation. Further aggregation of domains by organic matter may take place over a longer period of time than used in this study. It appears that the role of green manure is in providing organic acids to dissolve $CaCO_3$, rather than aggregation of clay domains (macroaggregation).

Table 5.11. Effect of Green Manure ± Gypsum on the Organic Carbon Content (ppm) of Two Calcareous Sodic Subsoils.

Green manure (t/ ha)	Gypsum	No gypsum
	20 (t/ha)	--
Two Wells		
20	0.85^{a}	0.52^{c}
0	0.48^{d}	0.48^{d}
Strathalbyn		
20	0.62^{b}	0.49^{d}
0	0.48^{d}	0.48^{d}

Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's HSD test.

Table 5.12. The Effect of Green Manure ± Gypsum on the Percentage of Waterstable Macroaggregates in Two Calcareous Sodic Soils.

Green Manure (t/ha)	Weeks of Incubation 4	8	12
		Strathalbyn	
		Gypsum-treated	
20	36^{a}	34^{a}	32^{a}
0	35^{a}	38^{a}	35^{a}
		No-Gypsum treated	
20	30^{a}	37^{a}	35^{a}
0	35^{a}	38^{a}	35^{a}
		Two Wells	
		Gypsum-treated	
20	37^{a}	36^{a}	32^{a}
0	34^{a}	37^{a}	35^{a}
		No-Gypsum treated	
20	34^{a}	36^{a}	38^{a}
0	36^{a}	37^{a}	40^{a}

Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's HSD test.

5.5.4 Water Retention

There was no significant differences in water retention (Table 5.13, 5.14). The water retention readings up to a potential of 10^2 - kPa was consistent with the results on macroaggregation.

5.5.5 Dissolved Cations

The Strathalbyn soils contained 14% CaCO3. The soils were tested for the presence of dissolved cations at 4, 8 and 12 weeks, against controls. According to the chemical analyses for dissolved cations of the 1:5 soil : water suspensions of the soils, the Ca^{++} t 8 & 12 weeks was significantly higher in treatments for the Strathalbyn soils than that of any other time in the incubation, and for the treatments of the Two Wells soils (Tables 5.16 - 5.17). In addition, at the end of 12 weeks, for the Strathalbyn soils, the magnitude of increases of K_s under the influence of green manure only, were almost as that of gypsum alone (Table 5.9).

Because the rate of applied gypsum had been the same in all soils, the extra Ca^{++} found in the Strathalbyn soil at 12 weeks must have come from the indigenous $CaCO_3$ in that soil. It is interesting to note that after the 4th week of incubation, no further significant changes in K_s were observed until the measurement at week 12. This is in agreement with Swift (1992), who found that a simple, water-soluble substrate decayed quickly in soils with their maximum effect on soil physical properties (such as aggregate stability) being exhibited somewhere between 4 and 8 weeks of incubation. In the present study, the substantial increase in Ca^{++} and Mg^{++} at week 12 was attributed to the dissolution of native $CaCO_3$ (which was shown to have occurred towards the end of the incubation) in the soil.

Table 5.13. The Effect of Green Manure ± Gypsum and Water Regime During Incubation on the Water Retention of a Calcareous Sodic soil from Two Wells.

Treatment	Potential (- kPa)	Water regime		
		WD	FC	FC80
GM, G	10^{-1}	61^{a}	58^{a}	61^{a}
	10^{0}	47^{b}	45^{b}	43^{b}
	10^{1}	33^{c}	35^{c}	38^{c}
	10^{2}	23^{d}	19^{de}	26^{d}
GM, - G	10^{-1}	60^{a}	60^{a}	57^{a}
	10^{0}	47^{b}	45^{b}	47^{b}
	10^{1}	34^{c}	35^{c}	39^{c}
	10^{2}	23^{d}	25^{d}	26^{d}
- GM, G	10^{-1}	57^{a}	58^{a}	60^{a}
	10^{0}	45^{b}	44^{b}	46^{b}
	10^{1}	35^{c}	36^{c}	36^{c}
	10^{2}	19^{de}	18^{de}	25^{d}
- GM, - G	10^{-1}	58^{a}	59^{a}	56^{a}
	10^{0}	45^{b}	44^{b}	47^{b}
	10^{1}	34^{c}	34^{c}	36^{c}
	10^{2}	23^{d}	21^{d}	23^{d}

G = gypsum, **GM** = green manure, **- GM**= no green manure, **- G** = no gypsum

Column values followed by different letters in shoot or root are significantly different; ($P < 0.05$) as determined by Tukey's H.S.D.

Table 5.14 The Effect of Green Manure ± Gypsum and Water Regime During Incubation on the Water Retention of a Calcareous Sodic soil from Strathalbyn.

Treatment	Potential (- kPa)	Water regime		
		WD	FC	FC80
GM, G	10^{-1}	60^{a}	55^{a}	58^{a}
	10^{0}	45^{b}	42^{b}	47^{b}
	10^{1}	33^{c}	35^{c}	38^{c}
	10^{2}	24^{d}	22^{d}	27^{d}
GM, - G	10^{-1}	58^{a}	60^{a}	59^{a}
	10^{0}	45^{b}	44^{b}	47^{b}
	10^{1}	39	35^{c}	34^{c}
	10^{2}	23^{d}	27^{d}	24^{d}
- GM, G	10^{-1}	58^{a}	61^{a}	57^{a}
	10^{0}	46^{b}	46^{b}	45^{b}
	10^{1}	35^{c}	35^{c}	36^{c}
	10^{2}	23^{d}	18^{de}	25^{d}
- GM, - G	10^{-1}	58^{a}	56^{a}	58^{a}
	10^{0}	46^{b}	44^{b}	47^{b}
	10^{1}	35^{c}	35^{c}	36^{c}
	10^{2}	19^{de}	25^{d}	23^{d}

G = gypsum, **GM** = green manure, **- GM**= no green manure, **- G** = no gypsum

Column values followed by different letters in shoot or root are significantly different; ($P < 0.05$) as determined by Tukey's H.S.D.

Table 5.15. Effect of Green Manure ± Gypsum on the Soluble Calcium (ppm) of Two Calcareous Sodic Soils.

Green manure (t/ ha)	Gypsum	No gypsum
	(20 t/ha)	(0 t/ha)
	Two Wells	
20	265^b	47^d
0	185^c	0.52^e
	Strathalbyn	
20	355^a	43^d
0	195^c	0.52^e

Significance (*P* < F from ANOVA) = .05. Column values followed by different letters are significantly different (*P* < .05) determined by Tukey's HSD test.

Table 5.16. The Effect of Green Manure, Sampling Site and Time, on the Soluble Calcium (ppm) of Two Calcareous Sodic Soils.

	Weeks of Incubation		
Green manure (t/ha)	4	8	12
		Two Wells	
20	264^{b}	360^{a}	271^{b}
0	28^{e}	35^{e}	29^{e}
		Strathalbyn	
20	325^{b}	374^{a}	370^{a}
0	16^{e}	22^{e}	15^{e}

Significance (P < F from ANOVA) = .001. Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's HSD test.

Table 5.17. The Effect of Green Manure ± Gypsum on the Soluble Calcium (ppm) in Two Calcareous Sodic Soils (Average Values).

Green Manure	Weeks of Incubation		
(t/ha)	4	8	12
		Gypsum-treated	
20	231^{c}	305^{b}	411^{a}
0	24^{e}	15^{e}	15^{e}
		No Gypsum-treated	
20	158^{cd}	310^{b}	330^{b}
0	21^{e}	42^{e}	28^{e}

Significance (P < F from ANOVA) = .001. Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's HSD test.

Table 5.18. The Combined Effect of Green Manure ± Gypsum on the Magnesium (ppm) of Two Calcareous Sodic Soils (Average Values).

Green Manure	Weeks of Incubation		
	4	8	12
(t/ha)		<u>*Gypsum*</u>	
20	75^a	59^a	41^a
0	18^c	5^c	9^c
(t/ha)		<u>*No gypsum-treated*</u>	
20	34^b	83^a	69^a
0	4^c	19^c	11^c

Significance ($P < F$ from ANOVA) = .001. Column values followed by different letters are significantly different ($P < .05$) as determined by Tukey's HSD test.

Table 5.19. The Combined Effect of Green Manure and Sampling Site on the Soluble Magnesium (ppm) of Two Calcareous Sodic Soils.

Green Manure t/ha	Two Wells	Strathalbyn
20	55^a	66^a
0	11^b	11^b

Significance (*P* < F from ANOVA) = .001. Column values followed by different letters are significantly different (*P* < .05) as determined by Tukey's HSD test.

Table 5.20. The Combined Effect of Green Manure, Time, and Sampling Site on the Electrical Conductivity (dS/m) of Two Sodic Subsoils.

Green manure (t/ha)	Weeks of Incubation 4	 8	 12
		Two Wells	
20	1.1^{b}	2.0^{a}	1.6^{b}
0	0.7^{e}	1.0^{c}	0.6^{d}
		Strathalbyn	
20	1.6^{b}	1.8^{a}	2.5^{a}
0	0.6^{d}	1.6^{b}	0.8^{e}

Significance (P < F from ANOVA) = .001. Column values followed by different letters are significantly different (P < .05) as determined by Tukey's HSD test.

Table 5.21. The Combined Effect of Gypsum + Green Manure, and Time, on the Electrical Conductivity (ds/m) of Two Calcareous Sodic Soils (Average Values).

	Weeks of Incubation		
Green Manure (t/ha)	4	8	12
		Gypsum (20 t/ha)	
20	2.2^{a}	1.7^{b}	1.3^{bc}
0	0.8^{c}	0.9^{c}	0.7^{c}
		No Gypsum	
20	1.0^{c}	2.6^{a}	2.2^{a}
0	0.5^{cd}	1.8^{b}	0.6^{cd}

Significance (P < F from ANOVA) = .001. Column values followed by different letters are significantly different (P < .05) as determined by Tukey's HSD test.

5.5.6 Hydraulic Conductivity as Related to the Factors of Clay Dispersion

The major factor affecting the hydraulic conductivity in sodic soils is the dispersed clay. Even as little as 1% of the total clay when dispersed affects the hydraulic conductivity by blocking micro-channels in the soil mass (Rengasamy *et al.* 1984). The improvement in K_S, by the addition of either green manure alone or green manure + gypsum, is mainly due to the prevention of clay dispersion. Since macroaggregation in sodic soils by these treatments has not changed significantly, prevention of clay dispersion seems to be the major mechanism. This is in agreement with Warkentin (1982) who found that wet sieving to measure size distribution of stable aggregates > .5 mm is not a valid test for the stability of clayey soil structure, but that the significant aspect of stability of clayey soil is the permanence of fissures or pores. This importance of pore stability is clearly seen from the significant negative correlation between mechanically dispersed clay and K_S in this study (Tables 5.23a, 5.23b, 5.23c).

Clay dispersion is reduced by lowering SAR and increasing EC of the soil solution (Quirk and Schofield, 1955; Rengasamy and Olsson, 1991; Sumner, 1993;). In the present study, addition of gypsum has increased EC and lowered SAR in both soils (Tables 5.23a, b, c). Similarly, green manure alone has also reduced the SAR and increased EC (Tables 5.23a, b, c), particularly in Strathalbyn soils. The acid production, either as organic acids or as H_2CO_3 from CO_2 evolution during green manure decomposition resulted in the dissolution of $CaCO_3$ present in the soil. This process led to the increase of Ca^{++} in solution, which simultaneously reduced SAR and increased EC. Thus, the beneficial reaction of protons from green manuring depended on the products of green manure decomposition and indigenous $CaCO_3$ in the soil. Because the Strathalbyn soil contained more indigenous $CaCO_3$ (14%) than the Two Wells soil (3% $CaCO_3$), more Ca^{++} was released from the Strathalbyn soil.

The above mechanism is substantiated by the reduction of pH in both soils after green manuring (Table 5.22). The significant negative correlations between pH and EC (Figure 5.2, Table 5.23a), and positive correlations between pH and SAR (Table 5.23a; Figure 5.3), confirm this. The reduction of pH from 9.36 to 8.32 after 12 weeks of addition of green manure in Strathalbyn soils, and from 9.65 to 8.12 in Two Wells led to an increase in K_S from 5 to 147, and 0 to 145 cm/hr, respectively (Figure 5.22). The reduction of pH, thus, seems to be a major factor in the reclamation of sodic soils.

As seen from Table 5.23a, the clay dispersion is significantly reduced by the green manure treatment. The properties of the clays are also altered. The clay particles have been aggregated by the green manure into a size range of 30µm. Even though macro-

Table 5.22. Mean values of soil parameters for treatment effects (average values) *key, p. 142

		pH	EC	TCC	spdis	mcdis %	zeta	z mob	ps (nm)	SAR	cm/hr	% wsa
1	12 week	8.32	1.67	2331	0.02	0.45	-20	-1.4	778	2.77	147	35
2	12 week control	9.36	0.68	596	0.14	2.45	-20	-1.5	533	5.29	5	35
3	8 week	8.87	1.54	2311	0.18	0.86	-14	-1	687	5.4	90	37
4	8 week control	9.13	0.98	907	0.28	1.54	-13	-1	451	6.06	1	38
5	4 week	8.96	1.03	1002	0.86	0.76	-20	-1.5	420	6.1	50	30
6	4 week control	9.35	0.97	296	0.23	4.67	-19	-1.5	348	7.35	0	35
7	12 week	7.86	3.55	1064	0.13	0.24	-15	-1	14962	0.98	279	32
8	12 week control	8.21	2.51	700	0.19	0.32	-16	-1.2	417	1.4	180	37
9	8 week	8.49	2.19	1259	0.12	0.26	-14	-1	5984	1.4	200	34
10	8 week control	8.82	1.97	422	0.22	0.3	-20	-1.4	487	2.3	150	31
11	4 week	8.55	2.15	2287	0.01	0.47	-13	-0.9	10229	1.46	180	36
12	4 week control	8.82	1.86	946	0.61	2.97	-16	-1.8	567	2.5	145	38
13	12 week control	8.52	1.65	1553	0.09	1.68	-24	-1.8	996	4.8	40	38
14	12 week control	9.65	0.52	567	0.65	2.22	-34	-2.5	165	8.05	0	40
15	8 week	8.04	1.02	2648	0.14	1.83	-28	-2	503	4.86	20	36
16	8 week control	9.6	0.5	1024	0.22	3.36	-33	-2.4	231	8.9	0	37
17	4 week	8.77	3.1	895	0.18	1.55	-19	-1.4	562	5.32	10	34
18	4 week control	9.71	1.8	475	0.43	5.78	-24	-1.8	413	8.9	0	36
19	12 week	8.12	2.26	1841	0.07	0.15	-15	-1.1	29997	0.95	180	32
20	12 week control	8.34	2.14	696	0.23	0.23	-15	-1.1	823	1.3	85	35
21	8 week	8.32	1.32	1629	0.11	0.25	-16	-1	35818	0.95	160	36
22	8 week control	8.84	1.15	444	0.18	0.25	-15	-1.1	1408	1.3	80	37
23	4 week	8.83	2.4	1778	0.08	0.18	-14	-1	25828	1.12	136	37
24	4 week control	8.91	1.8	645	0.43	0.2	-14	-1.04	2382	1.35	76	34

Strathalbyn Soil			Two Wells Soil		
Green manure / no gypsym					
Treatment	1	12 week	Treatment	13	12 week
	2	12 week control		14	12 week control
	3	8 week		15	8 week
	4	8 week control		16	8 week control
	5	4 week		17	4 week
	6	4 week control		18	4 week control
Green manure + gypsum					
Treatment	7	12 week	Treatment	19	12 week
	8	12 week control		20	12 week control
	9	8 week		21	8 week
	10	8 week control		22	8 week control
	11	4 week		23	4 week
	12	4 week control		24	4 week control

Table 5.23a.Linear Correlation Matrix of Green Manure Treatment Effects for Measured Parameters (Combined Values)

	pH	EC	TCC	spdis %	mcdis %	zeta	z mob	ps (nm)	SAR	cm/hr	% wsa
pH	1										
EC	-0.60	1.00									
TCC	-0.52	0.10	1.00								
spdis %	0.48	-0.33	-0.46	1.00							
mcdis %	0.69	-0.41	-0.34	0.31	1.00						
zeta	-0.45	0.53	0.08	-0.28	-0.53	1.00					
z mob	-0.50	0.53	0.16	-0.42	-0.64	0.95	1.00				
ps (nm)	-0.41	0.30	0.36	-0.37	-0.39	0.34	0.43	1.00			
SAR	0.77	-0.59	-0.23	0.41	0.80	-0.71	-0.72	-0.52	1.00		
cm/hr	-0.72	0.68	0.29	-0.35	-0.64	0.57	0.59	0.53	-0.82	1.00	
% wsa	0.32	-0.37	0.07	-0.03	0.31	-0.27	-0.34	-0.16	0.27	-0.34	1.00

Key:

pH = pH
EC = electrical conductivity
TCC = total cation capacity
spdis % = spontaneous dispersion
mcdis % = mechanical dispersion
zeta = zeta potential
z mob = electroph. mobility
ps (nm) = particle size
SAR = sodium adsorption ratio
cm/hr = K_S
% wsa = % WSMA

Table 5.23b. **Strathalbyn soil**

	pH	EC	TCC	spdis %	mcdis %	zeta	z mob	ps (nm)	SAR	cm/hr	% wsa
pH	1										
EC	-0.92	1.00									
TCC	-0.36	0.16	1.00								
spdis %	0.32	-0.31	-0.34	1.00							
mcdis %	0.70	-0.56	-0.45	0.23	1.00						
zeta	-0.30	0.39	0.38	-0.26	-0.25	1.00					
z mob	-0.42	0.41	0.45	-0.56	-0.58	0.74	1.00				
ps (nm)	-0.64	0.75	0.26	-0.37	-0.39	0.47	0.58	1.00			
SAR	0.84	-0.86	-0.23	0.37	0.63	-0.30	-0.29	-0.58	1.00		
cm/hr	-0.93	0.96	0.29	-0.31	-0.64	0.33	0.35	0.70	-0.94	1.00	
% wsa	0.14	-0.15	0.24	-0.25	0.32	0.53	0.10	-0.24	0.06	-0.19	1.00

Key:

pH = pH
EC = electrical conductivity
TCC = total cation capacity
spdis % = spontaneous dispersion
modis % = mechanical dispersion
zeta = zeta potential
z mob = electroph. mobility
ps (nm) = particle size
SAR = sodium adsorption ratio
cm/hr = K_S
% wsa = % WSMA

Table 5.23c. **Two Wells soil**

	pH	EC	TCC	spdis %	mcdis %	zeta	z mob	ps (nm)	SAR	cm/hr	% wsa
pH	1										
EC	-0.35	1.00									
TCC	-0.67	0.02	1.00								
spdis %	0.61	-0.27	-0.60	1.00							
mcdis %	0.67	-0.25	-0.26	0.48	1.00						
zeta	-0.52	0.68	0.03	-0.27	-0.60	1.00					
z mob	-0.55	0.63	0.05	-0.47	-0.70	0.94	1.00				
ps (nm)	-0.42	0.22	0.48	-0.49	-0.49	0.45	0.56	1.00			
SAR	0.72	-0.42	-0.22	0.37	0.84	-0.89	-0.87	-0.54	1.00		
cm/hr	-0.57	0.34	0.29	-0.26	-0.58	0.76	0.69	0.76	-0.85	1.00	
% wsa	0.48	-0.46	-0.18	0.45	0.34	-0.53	-0.48	-0.34	0.41	-0.33	1.00

Key:

pH = pH
EC = electrical conductivity
TCC = total cation capacity
spdis % = spontaneous dispersion
modis % = mechanical dispersion
zeta = zeta potential
z mob = electroph. mobility
ps (nm) = particle size
SAR = sodium adsorption ratio
cm:hr = K_S
% wsa = % WSMA

Figure 5.1

The relationship between electrical conductivity and SAR of the green manure-treated soils

$y = 3.877x^{(0.881)}$ (r = 0.694)

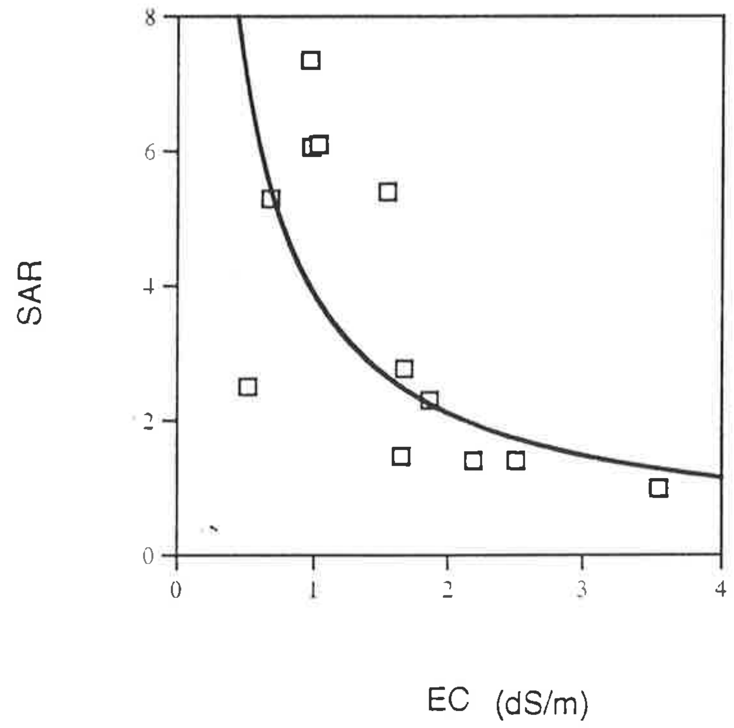


Figure 5.2

The relationship between EC and pH in the green manure-treated soils

$y = -1.501x + 14.797 \quad (r = 0.926)$

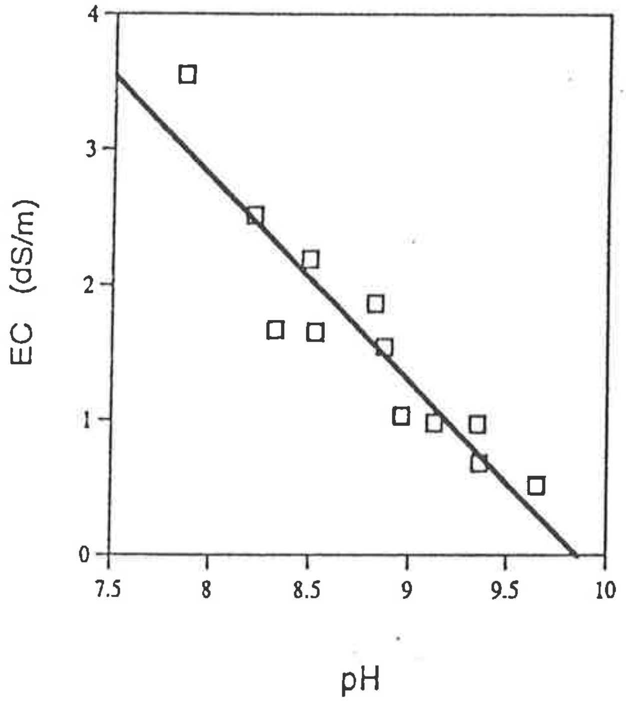


Figure 5.3

Relationship between pH and SAR in the green manure-treated soils

$$y = 0.001 * 10^{0.420x}$$

(r =0.728)

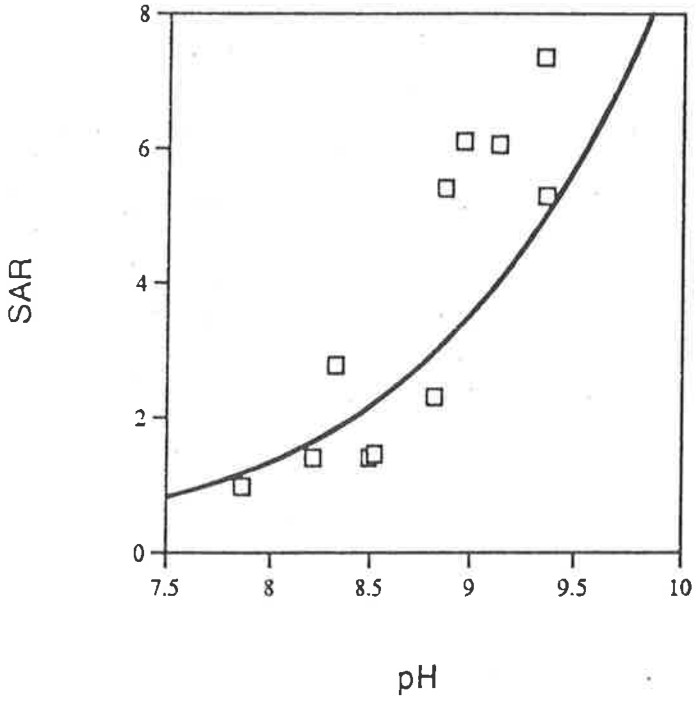


Figure 5.4

The relationship between pH and particle size (nm) in the green manure-treated soils

$y = -5041.726x + 48435.233$

$(r = -0.41)$

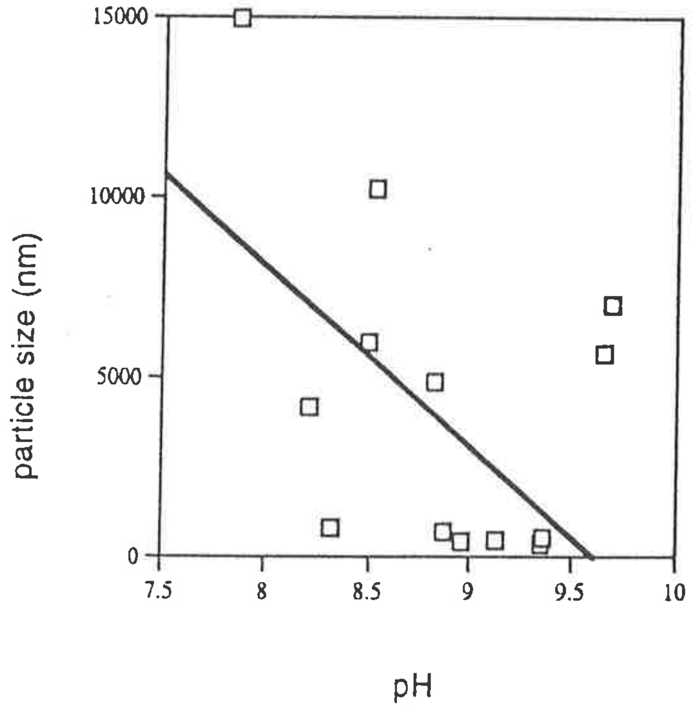


Figure 5.5

The relationship between pH and saturated hydraulic conductivity (cm/hr) in the green manure-treated soils

$$y = 1.1440E+1x^{(.184)}$$

(r = 0.549)

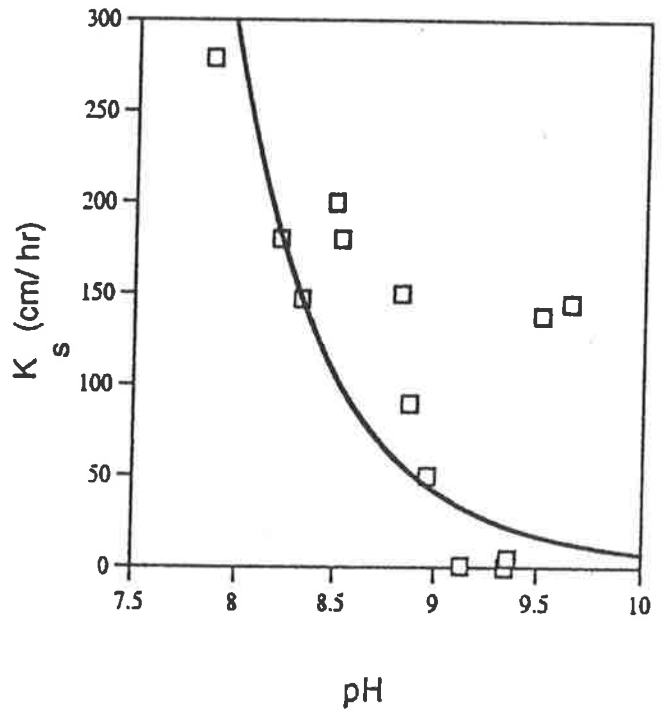


Figure 5.6

The relationship between particle size and saturated hydraulic conductivity for the green manure-treated soils

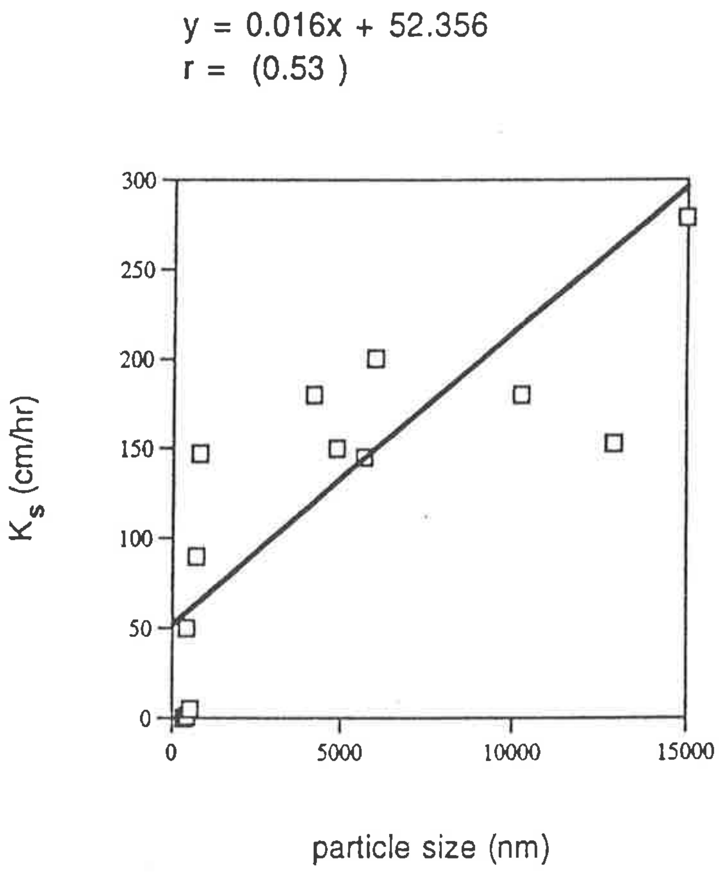


Figure 5.7

The relationship between particle size and SAR
for the green manure-treated soils

$y = 102.756x^{(0.473)}$

(r = 0.94)

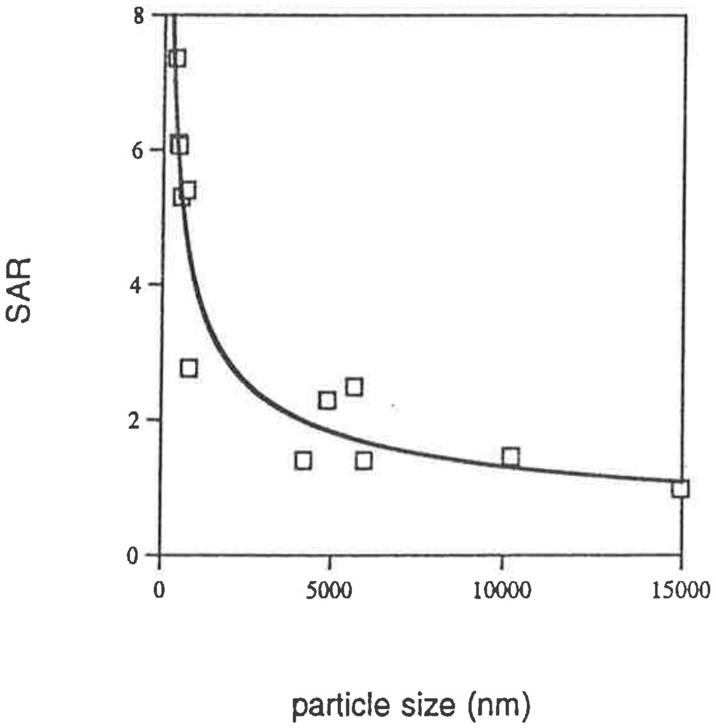


Figure 5.8

The relationship between mechanical dispersion and SAR of the green manure-treated soils

$$y = 3.315x^{0.517} \qquad (r = 0.753)$$

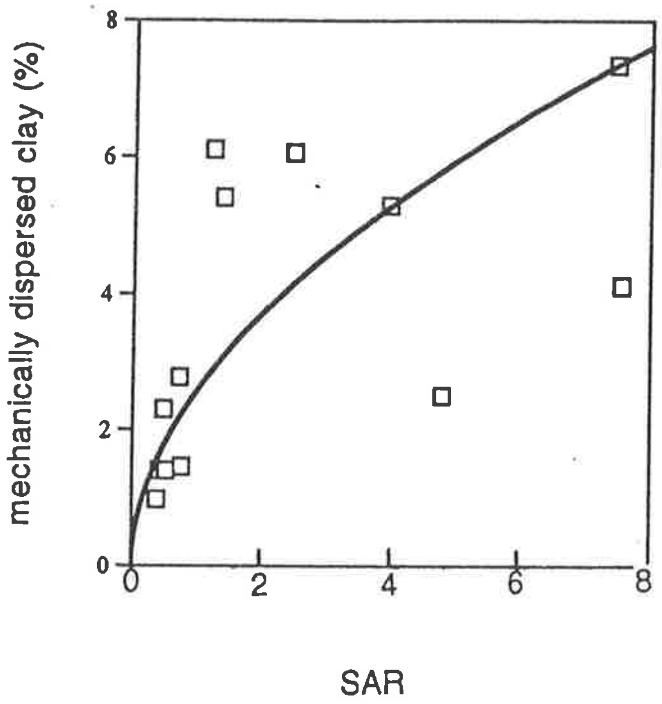


Figure 5.9

The relationship between mechanical dispersion and particle size of the green manure-treated soils

$$y = 1514.308x^{(0.837)}$$

(r = 0.612)

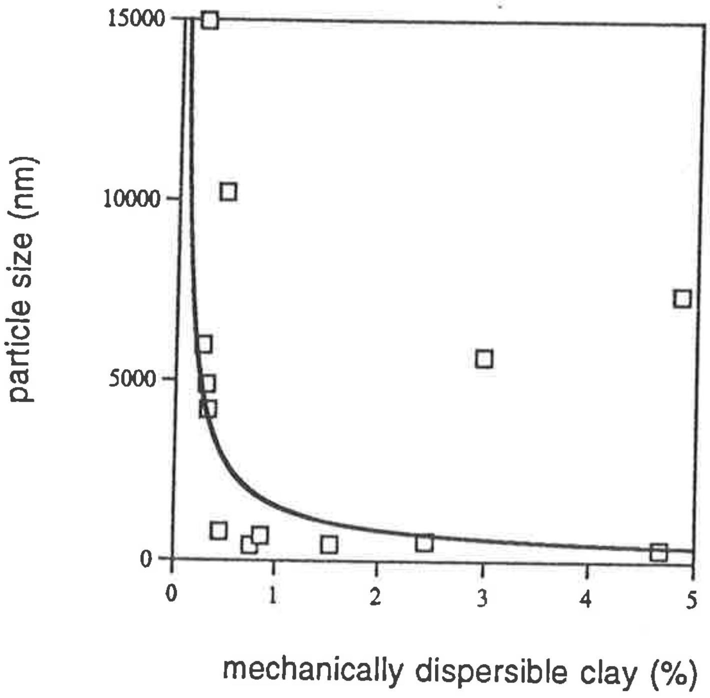
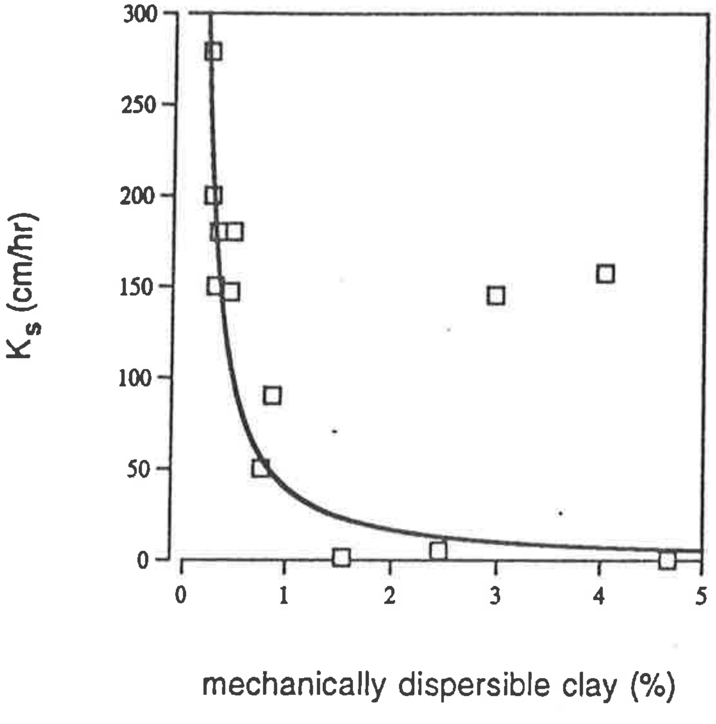


Figure 5.10

The relationship between mechanical dispersion and saturated hydraulic conductivity of the green manure-treated sils

$y = 39.369x^{(1.263)}$ (r = 0.639)



aggregation in the size range of >250 µm is not improved, clay particles have been assembled into clusters, by green manuring. The average size of dispersed materials in control soils are < 0.5µm, whereas, after green manuring, the average particle size has gone up to 30µm. This clearly shows that the products of decomposition, organic molecules and Ca^{++}, interacted with clay particles to form stable clusters.

The zeta potential and negative electrophoretic mobility of the clay particles (Table 5.23a; Appendix 2) support the above conclusion on clay aggregation. The zeta potential is a measure of the level of negative charge (which causes mutual repulsion) on clay particles (section 5.2.2.4). Thus the greater the negative charges of adjacent particles, the greater their mutual repulsion and hence, mobility. Thus the zeta mobility, (or electrophoretic mobility) varies directly with the zeta potential. As clay aggregation increased, as evidenced by the "particle" size increase, the zeta potential and mobility decreased (Table 5.19). This is because an increase in clustering of negatively charged clay crystals and domains into larger units result in the decrease of negative charges. These linkages between clay particles could have been caused by the action of the above-mentioned polyvalent ions (Ca^{++}) released amongst the clay crystals and domains, in addition to that of organic cements released by the decomposing green manure.

The major change occurring in the sodic soils is that of the hydraulic conductivity. This is due to the creation of tight clusters of the crystals and domains, where the accompanying reduction in the amount of loosely held clay particles in the soil caused a decrease in clay dispersion (Table 5.23a). The formation of clusters of clay particles thus seem to be the major factor increasing the K_S in the sodic soils. Thus the major effect of green manuring on the sodic soils is on the microstructure of the soils, by the formation of bigger clay particle clusters.

5.6 Conclusions

The effect of green manure in sodic soils was examined with and without the addition of gypsum. The addition of green manure together with gypsum improved permeability of the sodic soil used in this study. Incorporation of gypsum increased the K_S of the soil. The additive effect of green manure and gypsum on K_S was considered to result from the influence on soil pH which resulted in the release of protons, solubilization of the native $CaCO_3$ and leaching of Na_2CO_3. As a result of these extra protons in the soils, flocculation of the clay particles increased, along with a concommitant decrease in dispersion, leading to the creation of clay clusters and an improvement in the soil porosity.

5.7 General Conclusions

In the present study, the efficiency of green manure to ameliorate the degraded structure of non-sodic and sodic soils was investigated. In the latter soils, the effect of green manure was examined with and without the addition of gypsum. Results of the pilot experiments conducted to determine suitability of the common vetch alfalfa *(Medicago sativa)*, cowpea *(Vigna sinensis)* and white clover *(Trifolium repens)* to be used as a green manure showed the potential of common vetch *(Vicia sativa)*. This is because of its high index of succulence (as succulence is known to be related to efficiency of decomposition), and high biomass.

In non-sodic Urrbrae soils, the improvement due to green manuring on water stable macroaggregation (WSMA), and water retention at -100 kPa potential were not statistically significant. At application rates of 20 t ha $^{-1}$, leguminous green manure is not effective as expected for the improvement of the structure of a red brown earth which had been previously under a continuous cultivation or fallow/cultivation system for several decades, compared to soils previously under pasture management during the same period. The measurements showed a significant soil structural improvement in the Urrbrae soil which had previously been under permanent pasture treatment. Further, green manure when incubated at 80% field capacity substantially improved the K_S and WSMA of the permanent pasture non-sodic soil. The ideal moisture condition for increasing aggregate stability seems thus to be that of a continuous moisture regime at a water content less than the field capacity of the soil. Water regime is therefore an important factor in the efficiency of green manure in improving soil structure. Nevertheless, the utility of further improving the physical properties of a soil which for decades had been under permanent pasture (which implies already good structure) is questionable.

In sodic subsoils, saturated hydraulic conductivity values were improved by green manuring under all conditions. In sodic soils, generally, the improvement in K_S was in the following order of treatments: gypsum + green manure > gypsum > green manure > control. As in the non-sodic soils, the sodic subsoils incubated at 80% field capacity showed greatest increases. The differences in water retention and water stable macroaggregation measurements were not statistically significant. In sodic subsoils, green manure increased the cations Ca^{++} and Mg^{++} in solution and the electrical conductivity, whereas pH was reduced. Before the treatments, a high level of exchangeable Na^{+} resulted in low permeability in the sodic subsoils. A marked decrease in pH was observed in Strathalbyn subsoil containing 14% $CaCO_3$, due to the dissolution of native $CaCO_3$ probably by organic acids and H_2CO_3 from CO_2 produced by green manure. The combination of these changes reduced the sodium adsorption ratio (SAR) of these soils considerably, leading to significant improvements in permeability of the subsoils.

Though the release of biological binding agents from decomposing freshly incorporated plant matter such as green manure can lead to increases in soil porosity, permeability and soil aggregation, green manure did not improve macroaggregation in sodic soils, yet the non-sodic soils which had a previous history of permanent pasture improved markedly in macroaggregation. In sodic soils however, stabilisation occurred at the microstructure level. The average size of dispersed materials in control soils were < 0.5µm, whereas after green manuring, the average particle size increased up to 30µm. The products of decomposition of green manure were both organic compounds and the release of Ca^{++}, which aggregated the clay particles and stabilized the domains. Thus, the effect of green manure on sodic soils containing $CaCO_3$ markedly differs from non-sodic soils. The results of this experiment promise the use of green manure as an economic ameliorant for sodic soils with $CaCO_3$ and high pH. In non-sodic soils the effect of green manure on the improvement of soil structure may take a longer time. In short term experiments, such as the present study, the improvements were only minor.

Further research is needed to determine: (1) Long term effects of green manure on soil structure, particularly non-sodic soils, (2) the effect of green manure on the production of organic acids through bacterial activity and the efficiency of pH reduction. (3) the methods of reclaiming subsoil sodicity in the field by using green manure.

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Appendices

Key to Appendices 1 and 2

Strathalbyn Soil			**Two Wells Soils**		
		Green manure / no gypsum			
Treatment	1	12 week	Treatment	13	12 week
	2	12 week control		14	12 week control
	3	8 week		15	8 week
	4	8 week control		16	8 week control
	5	4 week		17	4 week
	6	4 week control		18	4 week control
		Green manure + gypsum			
Treatment	7	12 week	Treatment	19	12 week
	8	12 week control		20	12 week control
	9	8 week		21	8 week
	10	8 week control		22	8 week control
	11	4 week		23	4 week
	12	4 week control		24	4 week control

Appendix 1

Electrophoretic Mobility as Determined by the Malvern Zetamaster

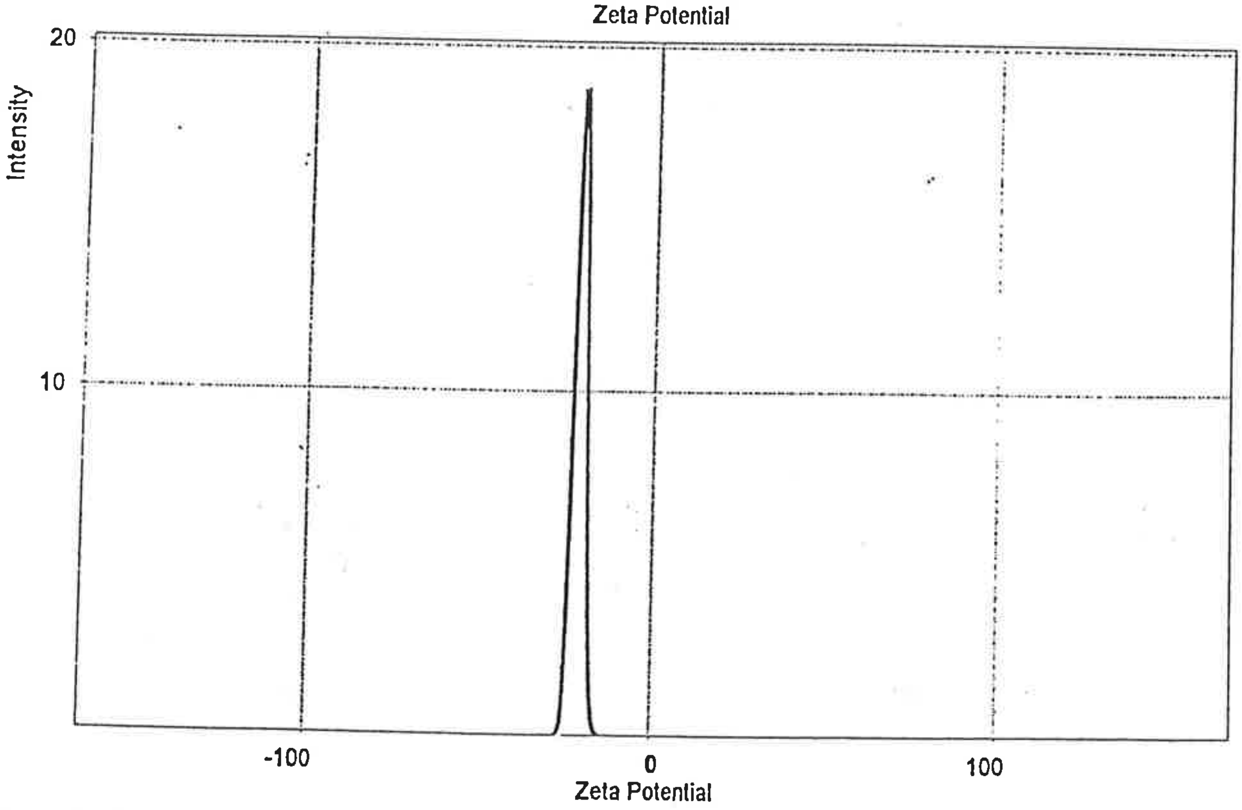
Appendix 1

Electrophoretic Mobility as Determined by the Malvern Zetamaster

1

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	3704.0	-1.533	-21.0	1.7	01:41:27
2	17.0	3498.5	-1.525	-20.8	1.7	01:41:57
3	17.0	3383.1	-1.419	-19.2	1.6	01:42:27
4	17.0	3470.6	-1.531	-20.7	1.7	01:42:58
5	17.0	3213.0	-1.550	-21.2	1.7	01:43:29
6	17.0	3704.0	-1.533	-21.0	1.7	01:41:27
7	17.0	3498.5	-1.525	-20.8	1.7	01:41:57
8	17.0	3383.1	-1.419	-19.2	1.6	01:42:27
9	17.0	3470.6	-1.531	-20.7	1.7	01:42:58
10	17.0	3213.0	-1.550	-21.2	1.7	01:43:29
Average		3453.8	-1.511	-20.6	1.6	
+/-		168.6	0.050	0.8	0.0	

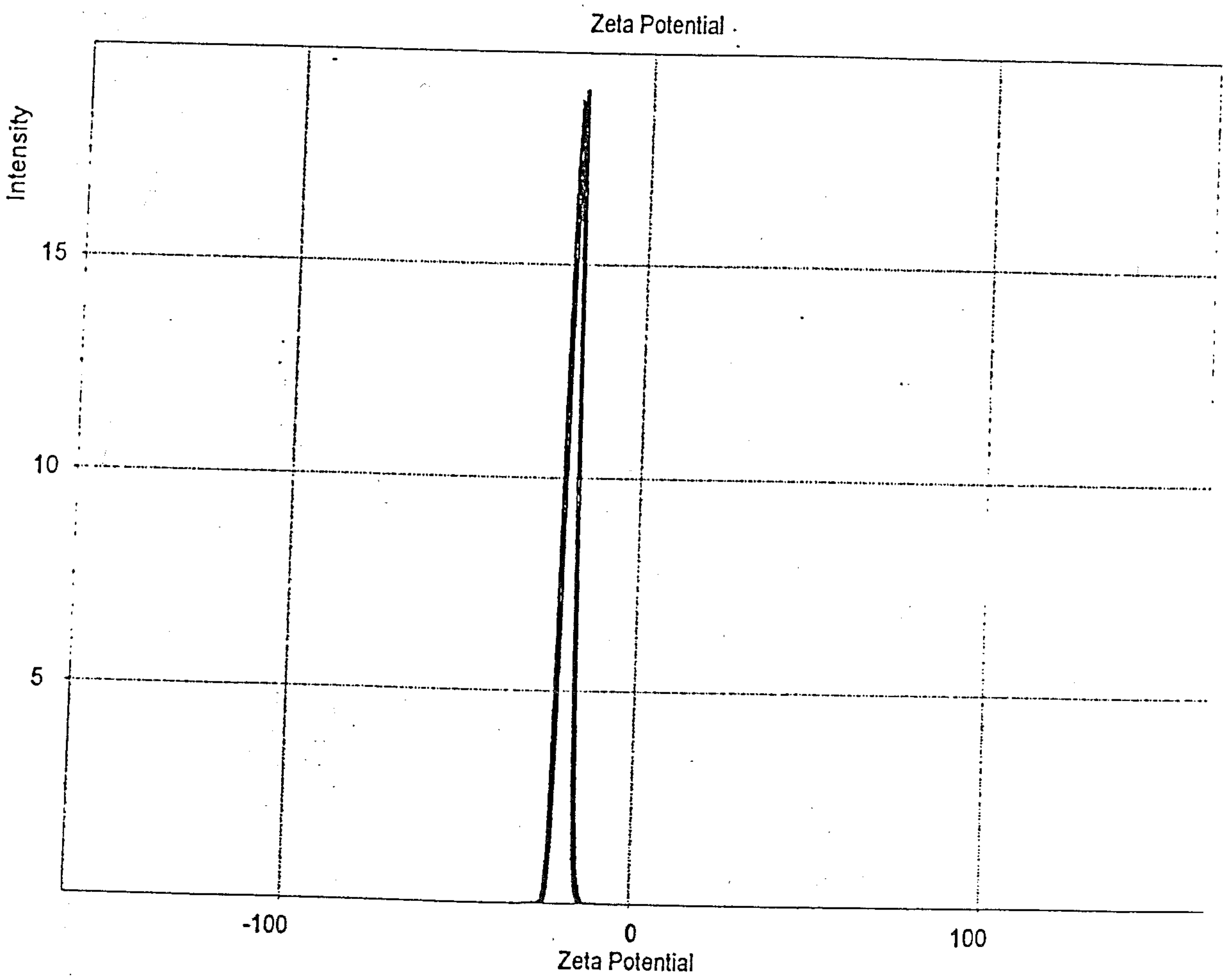


Malvern Instruments England
ZetaMaster Version PCS: v1.24 Wednesday 16 August 1995

2

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	3367.3	-1.536	-21.1	1.7	01:50:17
2	17.0	3349.8	-1.478	-20.1	1.6	01:50:47
3	17.0	3065.5	-1.529	-21.1	1.6	01:51:18
4	17.0	3116.2	-1.500	-20.3	1.6	01:51:48
5	17.0	3082.7	-1.579	-21.4	1.7	01:52:18
Average		3196.3	-1.524	-20.8	1.6	
+/-		149.4	0.038	0.6	0.0	



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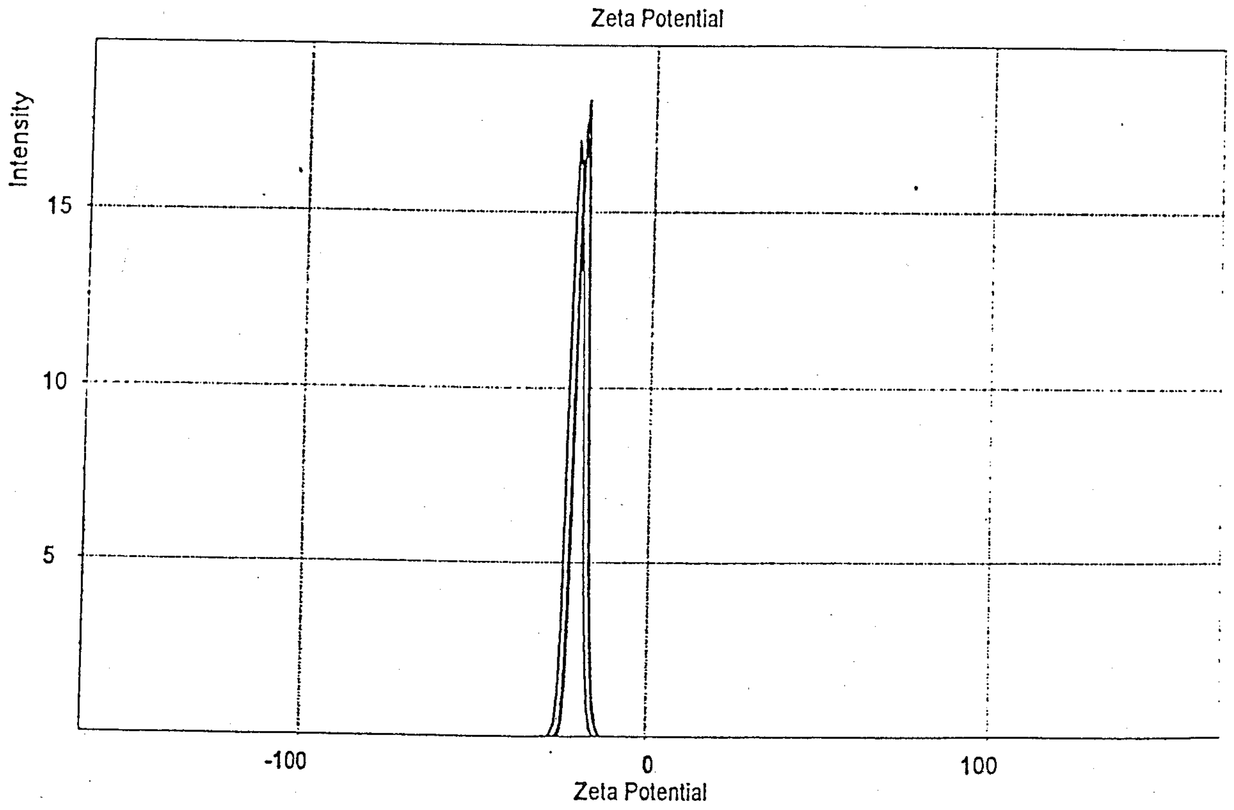
2

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2576.6	-1.469	-21.0	1.7	19:56:47
2	17.0	2497.2	-1.512	-21.9	1.8	19:57:17
3	17.0	2630.6	-1.401	-20.4	1.7	19:57:47
4	17.0	2587.4	-1.369	-20.0	1.7	19:58:17
5	17.0	2618.7	-1.402	-20.5	1.8	19:58:47
6	17.0	2576.6	-1.469	-21.0	1.7	19:56:47
7	17.0	2497.2	-1.512	-21.9	1.8	19:57:17
8	17.0	2630.6	-1.401	-20.4	1.7	19:57:47
9	17.0	2587.4	-1.369	-20.0	1.7	19:58:17
10	17.0	2618.7	-1.402	-20.5	1.8	19:58:47
Average		2582.1	-1.431	-20.7	1.8	
+/-		49.3	0.055	0.7	0.1	



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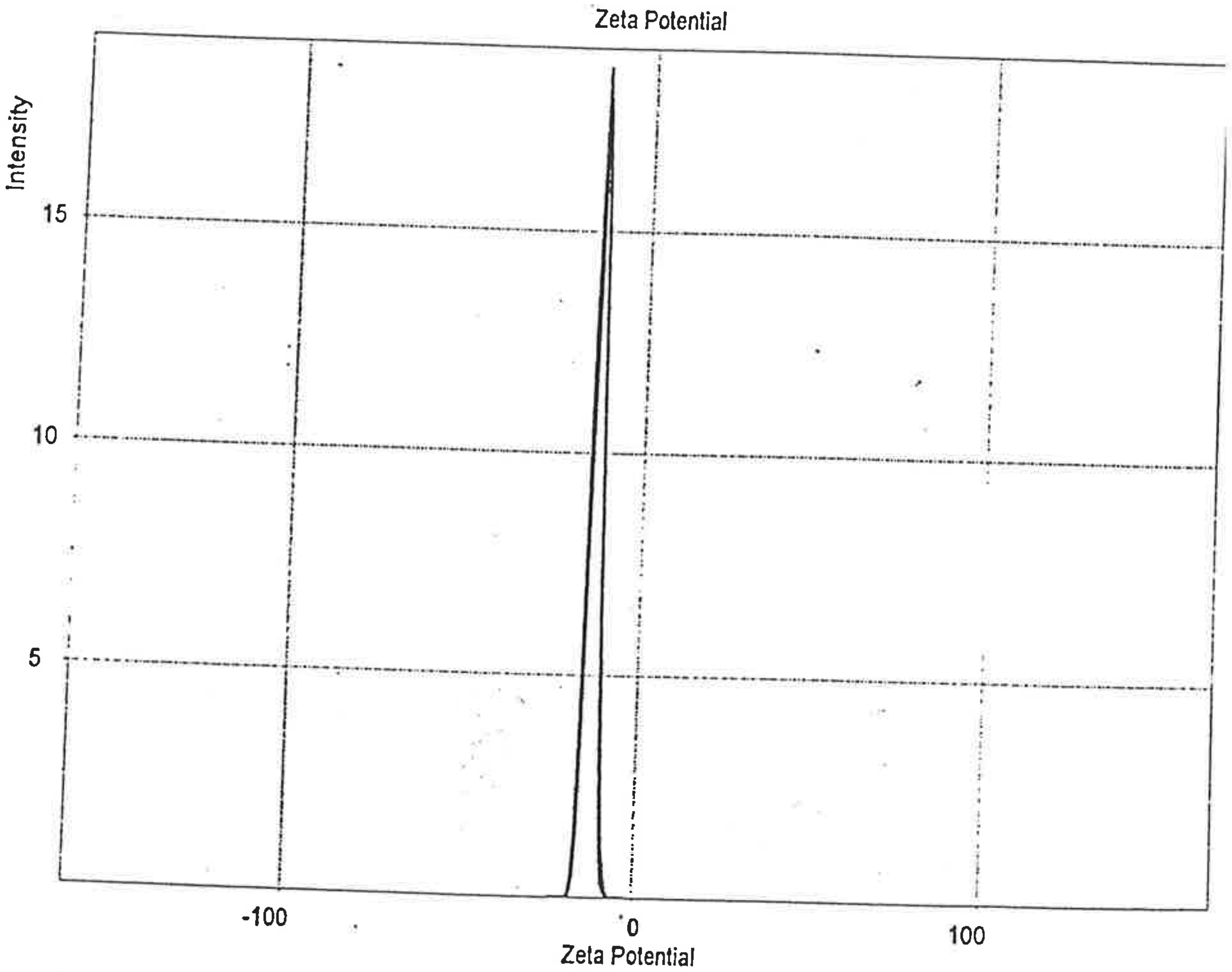
3

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2280.9	-0.997	-14.2	1.8	20:23:23
2	17.0	2608.1	-0.985	-14.0	1.7	20:23:53
3	17.0	2873.7	-0.975	-13.7	1.7	20:24:24
4	17.0	2835.9	-1.023	-14.4	1.7	20:24:58
5	17.0	2861.3	-1.019	-14.4	1.7	20:25:28
Average		2692.0	-1.000	-14.1	1.7	
+/-		254.2	0.021	0.3	0.0	



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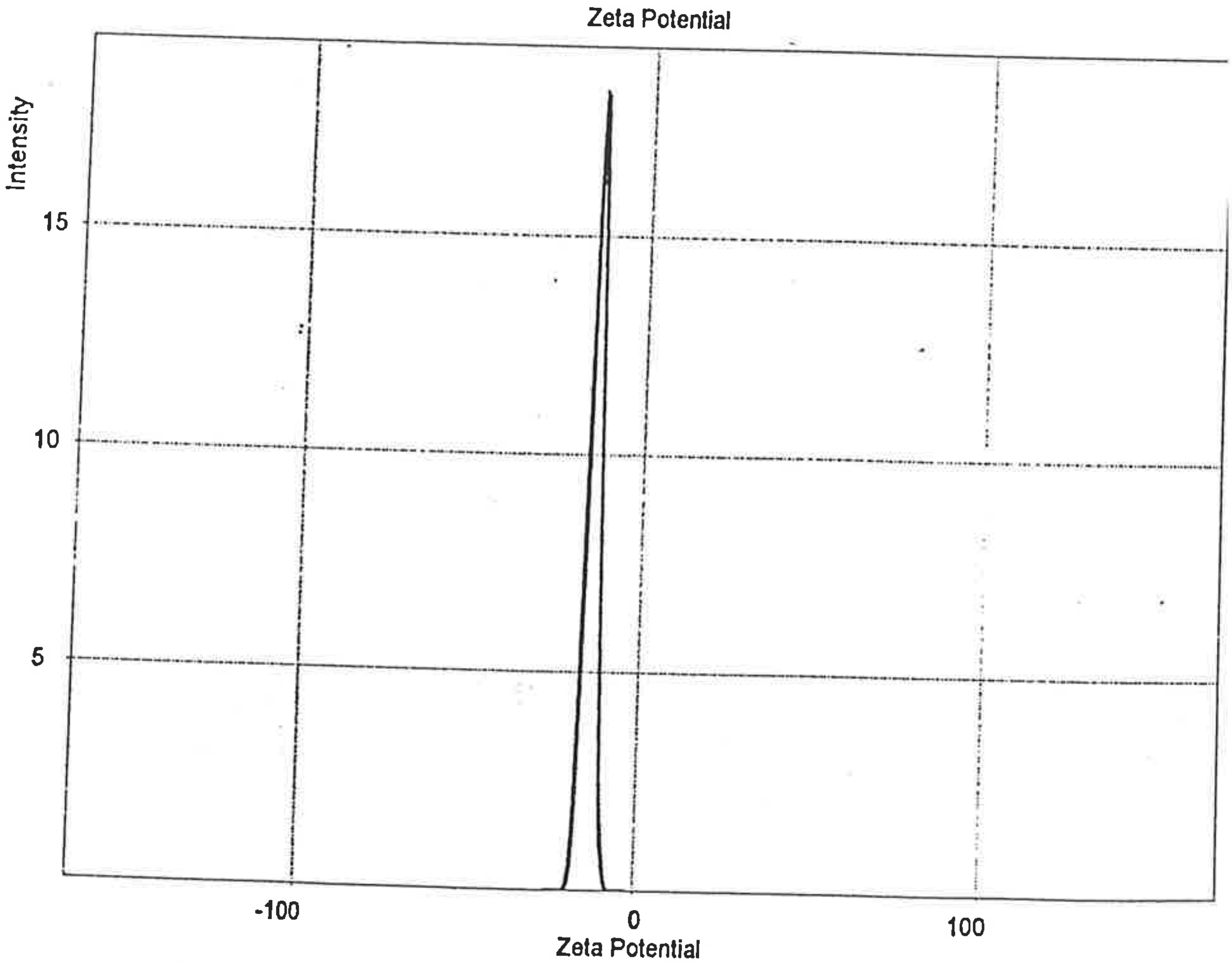
4

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2776.4	-0.986	-13.6	1.8	20:31:41
2	17.0	2982.8	-0.963	-13.1	1.7	20:32:11
3	17.0	2873.5	-0.972	-13.6	1.7	20:32:41
4	17.0	3114.5	-0.978	-13.6	1.7	20:33:12
5	17.0	2701.5	-0.978	-13.6	1.7	20:33:43
Average		2889.7	-0.975	-13.5	1.7	
+/-		164.1	0.009	0.2	0.0	



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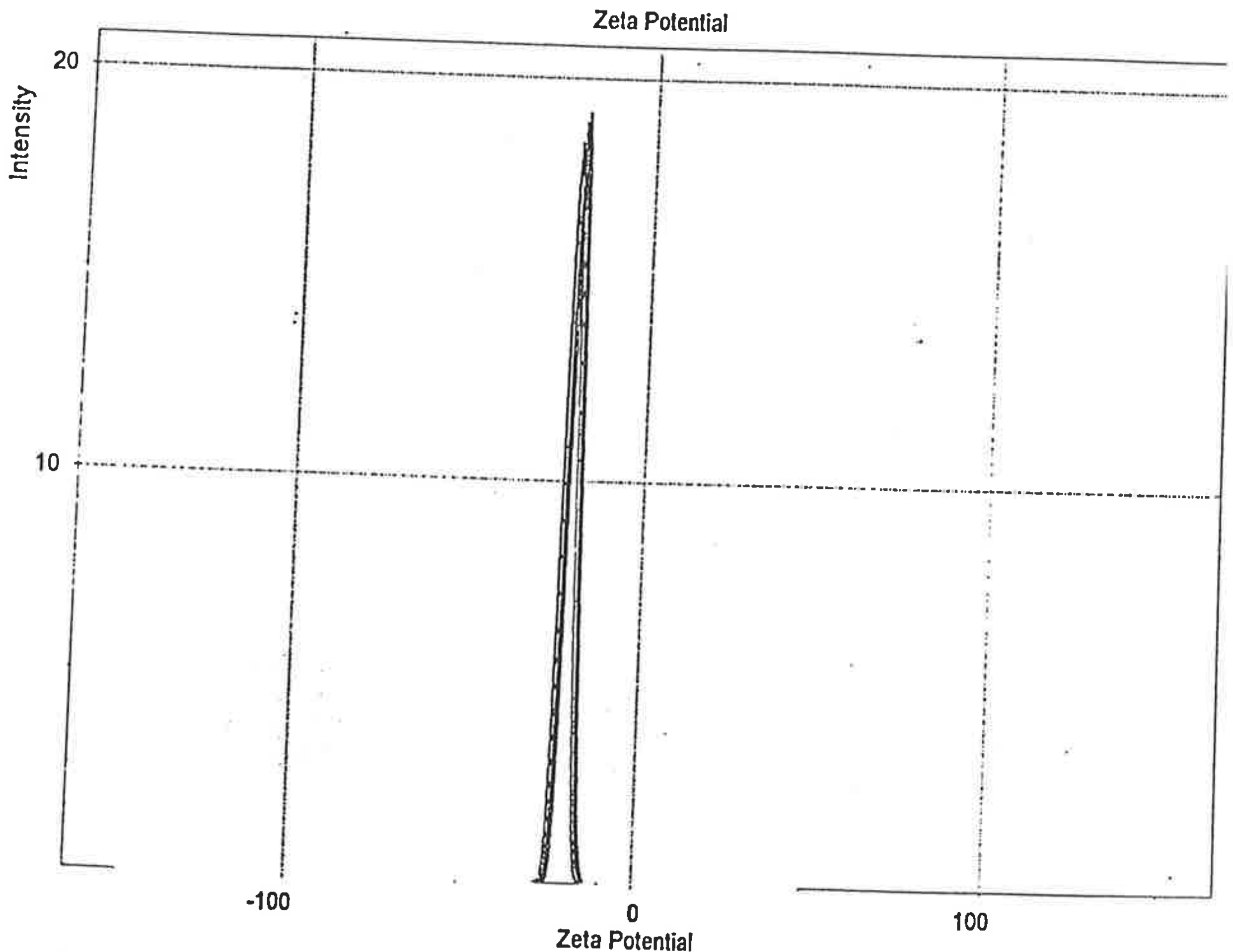
5.

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	3730.4	-1.458	-20.4	1.6	20:43:38
2	17.0	3612.2	-1.418	-19.6	1.6	20:46:12
3	17.0	3709.1	-1.543	-21.5	1.7	20:46:43
4	17.0	3374.2	-1.524	-21.1	1.7	20:47:13
5	17.0	3786.0	-1.451	-20.2	1.7	20:47:44
6	17.0	3802.3	-1.508	-21.1	1.8	20:48:14
Average		3669.0	-1.484	-20.6	1.7	
+/-		159.4	0.048	0.7	0.1	



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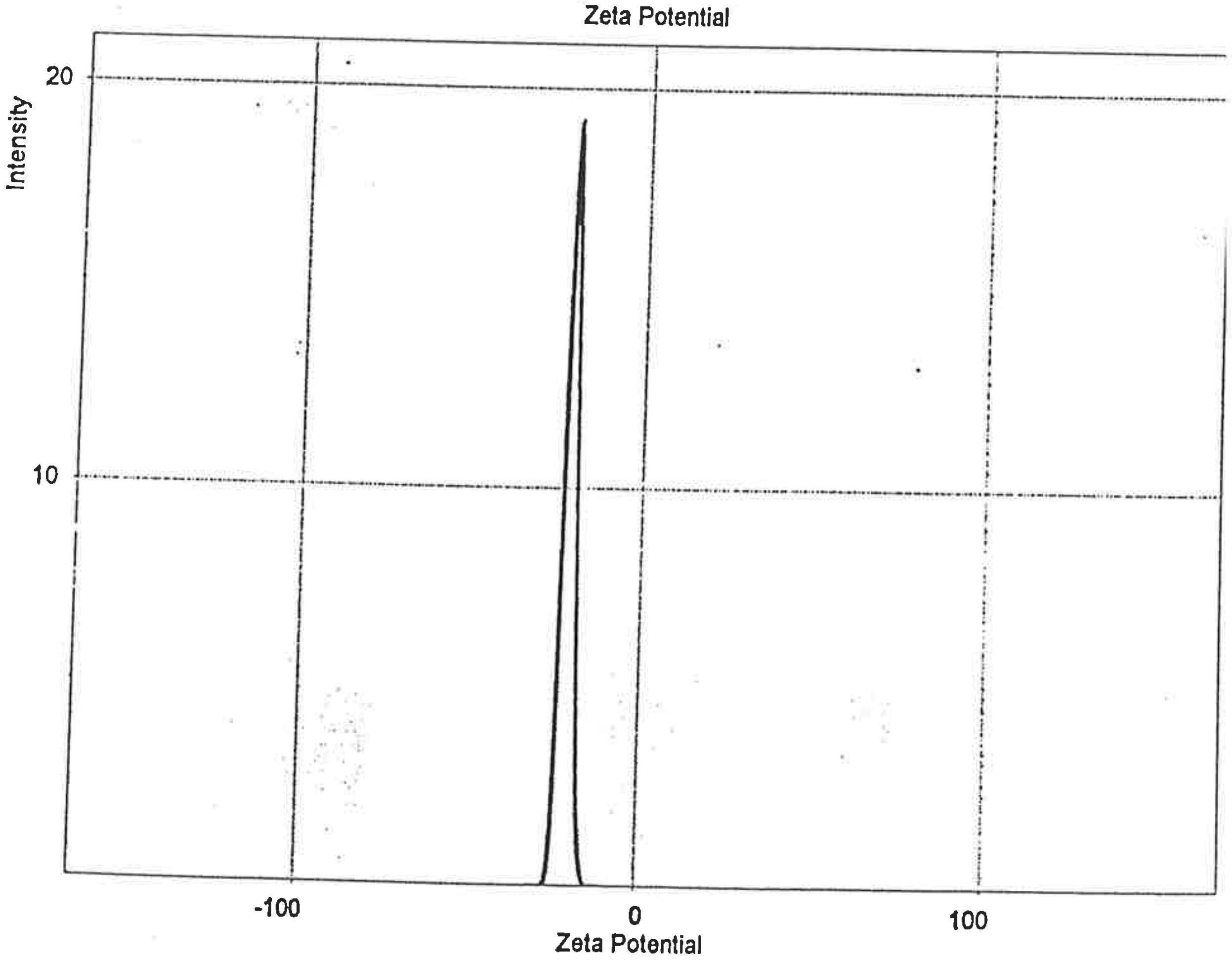
6

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2396.0	-1.418	-19.3	1.6	20:58:35
2	17.0	2419.6	-1.464	-20.0	1.6	20:59:06
3	17.0	2336.7	-1.429	-20.0	1.7	20:59:36
4	17.0	2339.1	-1.392	-19.4	1.6	21:00:07
5	17.0	2463.1	-1.445	-19.9	1.7	21:00:37
Average		2390.9	-1.430	-19.7	1.6	
+/-		54.0	0.028	0.3	0.0	



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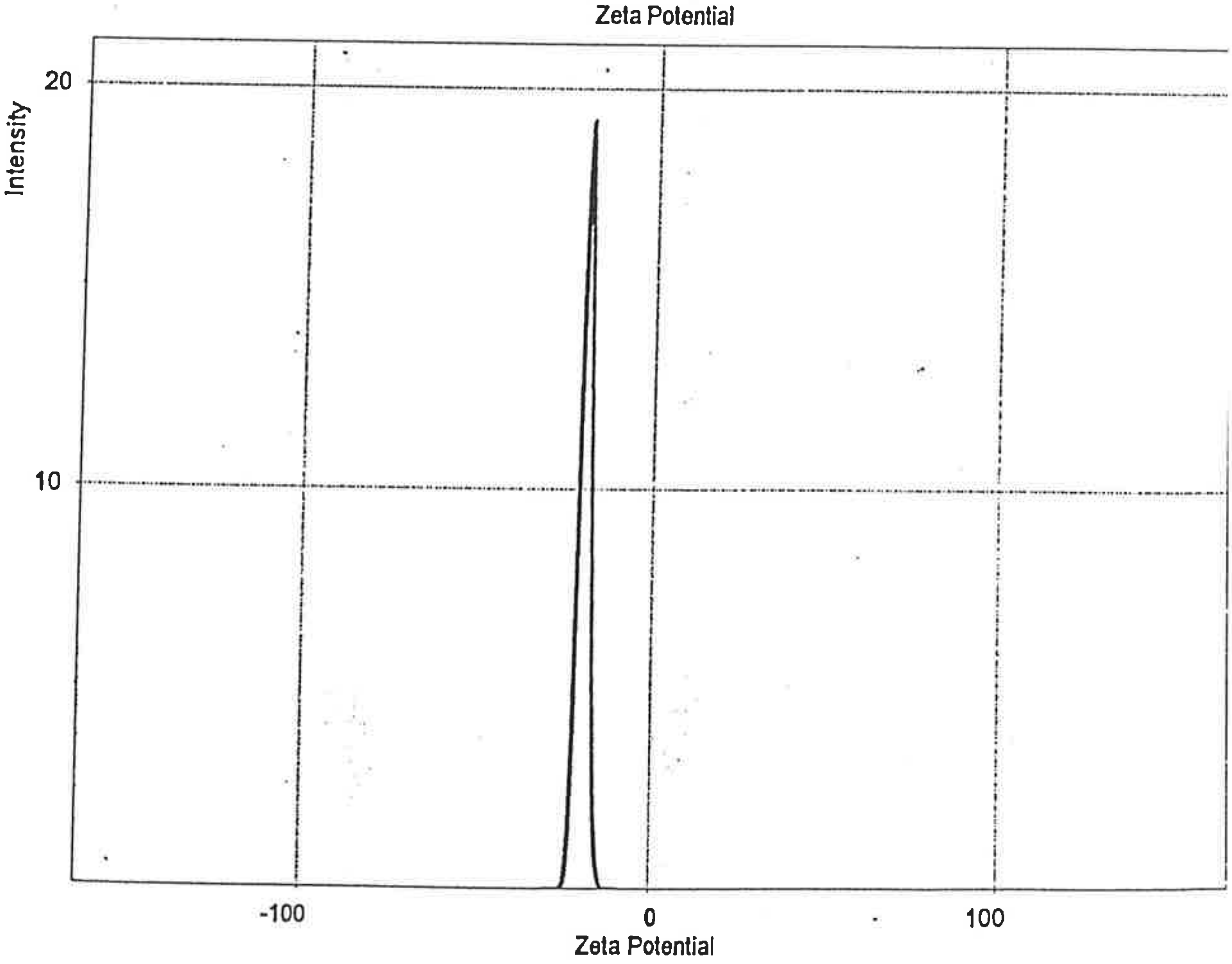
ZetaMaster Version PCS: v1.24 Wednesday 16 August 1995

6

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2396.0	-1.418	-19.3	1.6	20:58:35
2	17.0	2419.6	-1.464	-20.0	1.6	20:59:06
3	17.0	2336.7	-1.429	-20.0	1.7	20:59:36
4	17.0	2339.1	-1.392	-19.4	1.6	21:00:07
5	17.0	2463.1	-1.445	-19.9	1.7	21:00:37
Average		2390.9	-1.430	-19.7	1.6	
+/-		54.0	0.028	0.3	0.0	



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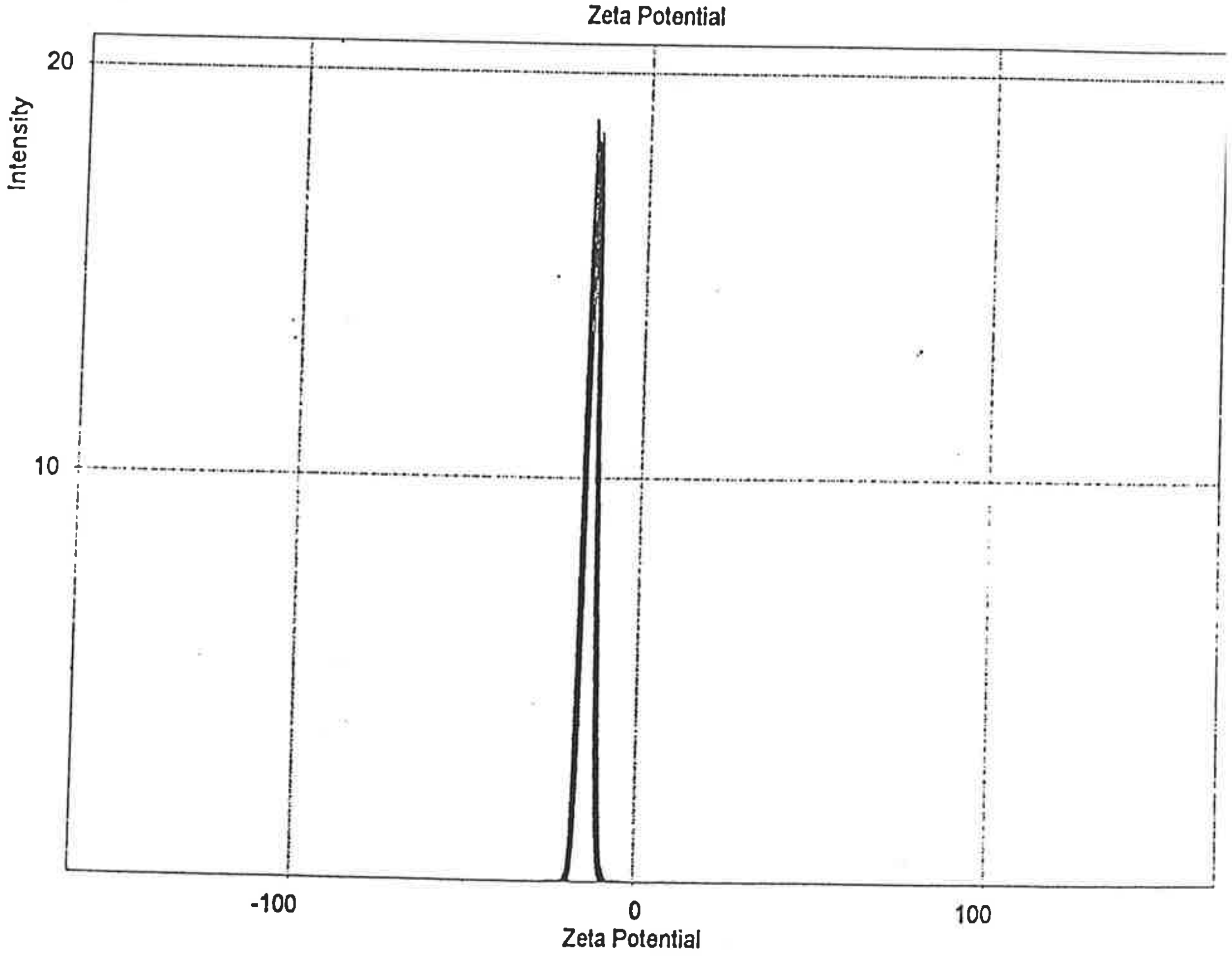
7

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2435.1	-1.140	-15.7	1.7	21:10:47
2	17.0	3279.7	-1.023	-14.2	1.7	21:11:17
3	17.0	2514.8	-1.069	-14.7	1.7	21:11:47
4	17.0	2290.3	-1.118	-15.3	1.7	21:12:18
5	17.0	2537.9	-1.154	-15.7	1.7	21:12:49
Average		2611.6	-1.101	-15.1	1.7	
+/-		385.8	0.054	0.7	0.0	



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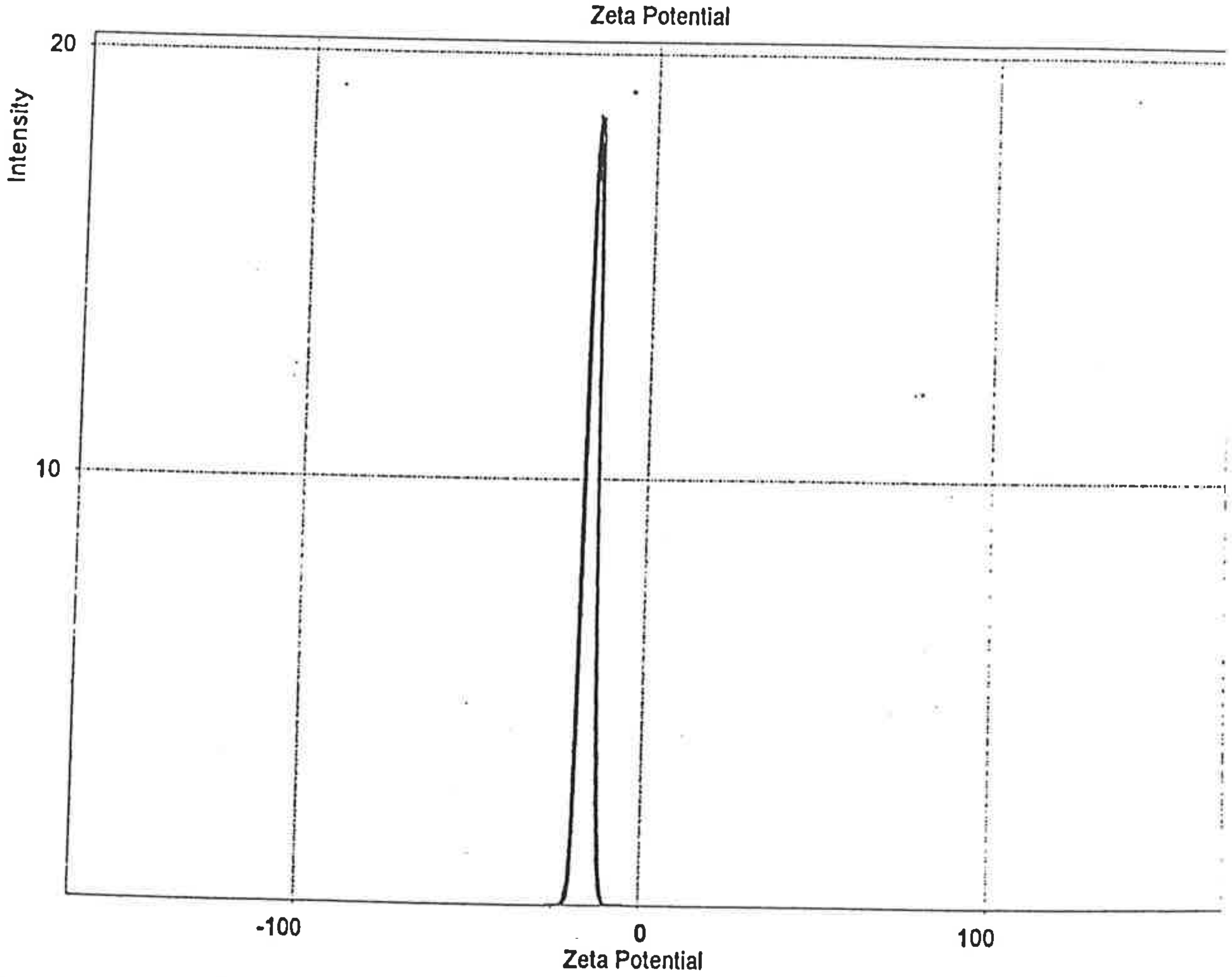
8

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2618.0	-1.181	-16.1	1.7	21:36:34
2	17.0	2177.6	-1.150	-16.1	1.7	21:37:04
3	17.0	2302.2	-1.118	-15.4	1.7	21:37:35
4	17.0	2653.6	-1.162	-15.9	1.7	21:38:05
5	17.0	2433.3	-1.139	-15.6	1.7	21:38:36
Average		2436.9	-1.150	-15.8	1.7	
+/-		203.2	0.024	0.3	0.0	



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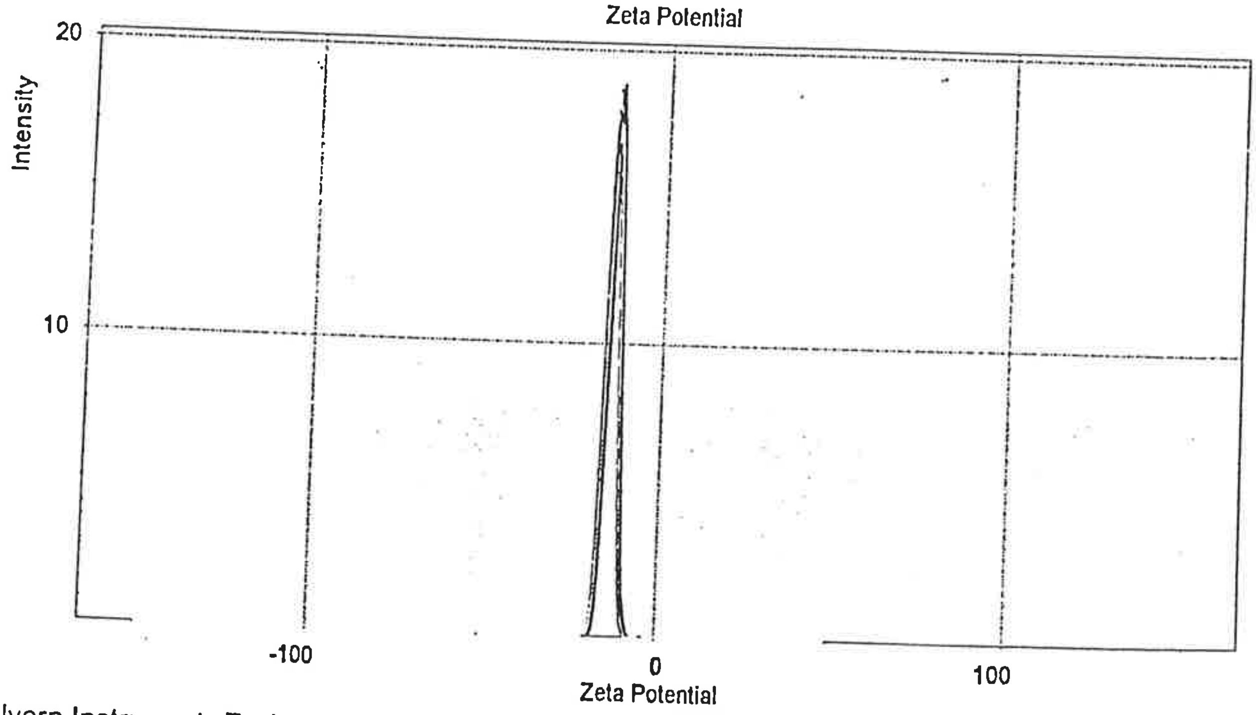
9

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	1949.6	-1.038	-14.3	1.7	22:19:25
2	17.0	1816.2	-1.071	-14.7	1.6	22:19:55
3	17.0	2019.4	-1.001	-13.7	1.7	22:20:26
4	17.0	2048.3	-0.981	-13.4	1.7	22:20:56
5	17.0	1807.8	-1.064	-14.5	1.7	22:21:27
6	17.0	1949.6	-1.038	-14.3	1.7	22:19:25
7	17.0	1816.2	-1.071	-14.7	1.6	22:19:55
8	17.0	2019.4	-1.001	-13.7	1.7	22:20:26
9	17.0	2048.3	-0.981	-13.4	1.7	22:20:56
10	17.0	1807.8	-1.064	-14.5	1.7	22:21:27
11	17.0	2221.3	-1.064	-14.4	1.7	22:28:19
12	17.0	2175.9	-1.007	-13.6	1.7	22:28:50
13	17.0	2608.3	-1.094	-14.9	1.7	22:29:20
Average		2022.2	-1.037	-14.2	1.7	
+/-		222.8	0.038	0.5	0.0	



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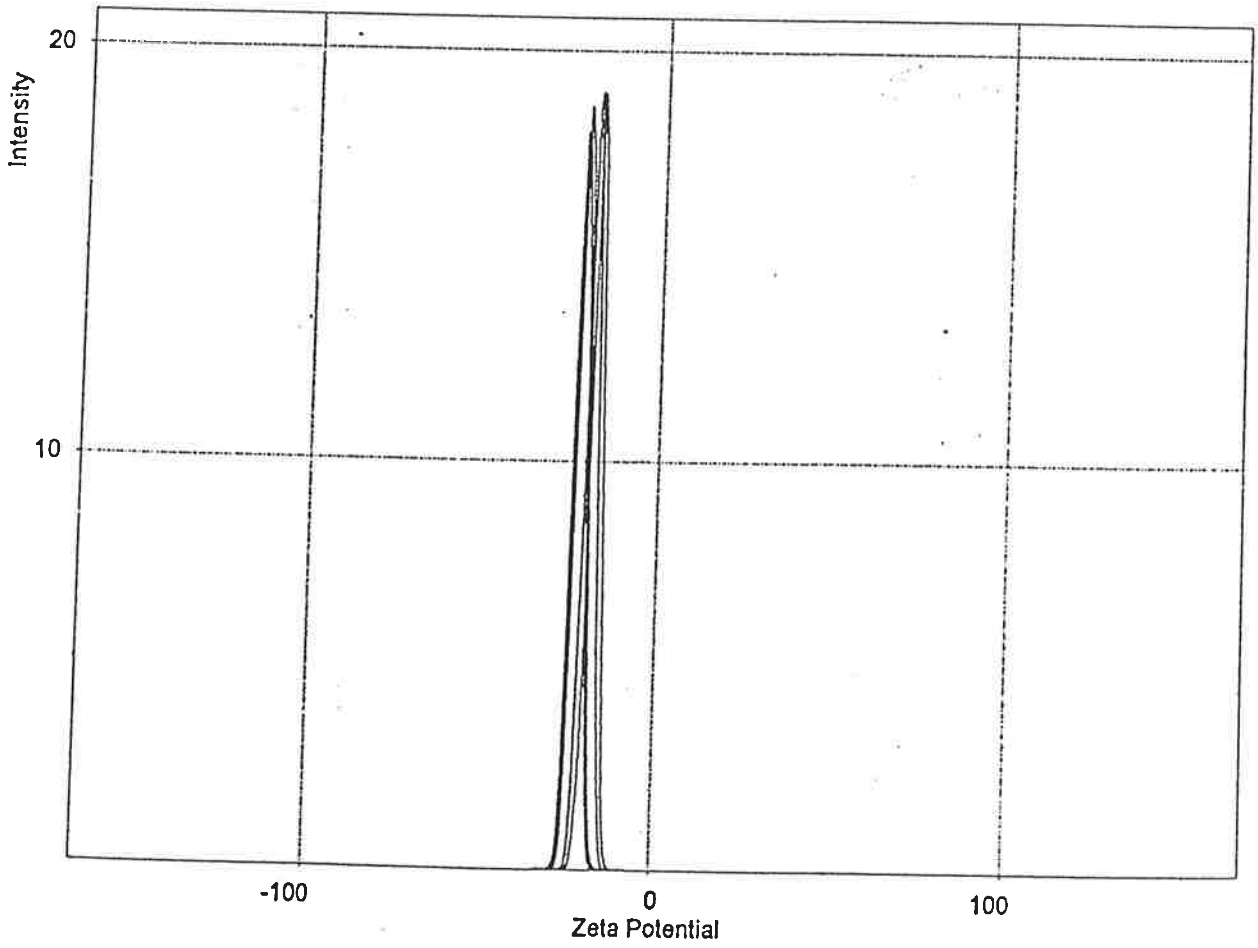
10

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	1887.4	-1.256	-17.3	1.6	08:21:14
2	17.0	1906.6	-1.538	-21.2	1.7	08:21:45
3	17.0	1879.4	-1.575	-21.9	1.7	08:22:15
4	17.0	1852.3	-1.359	-18.6	1.6	08:22:45
5	17.0	1845.3	-1.366	-18.6	1.7	08:23:16
Average		1874.2	-1.419	-19.5	1.7	
+/-		25.3	0.134	1.9	0.0	

Zeta Potential



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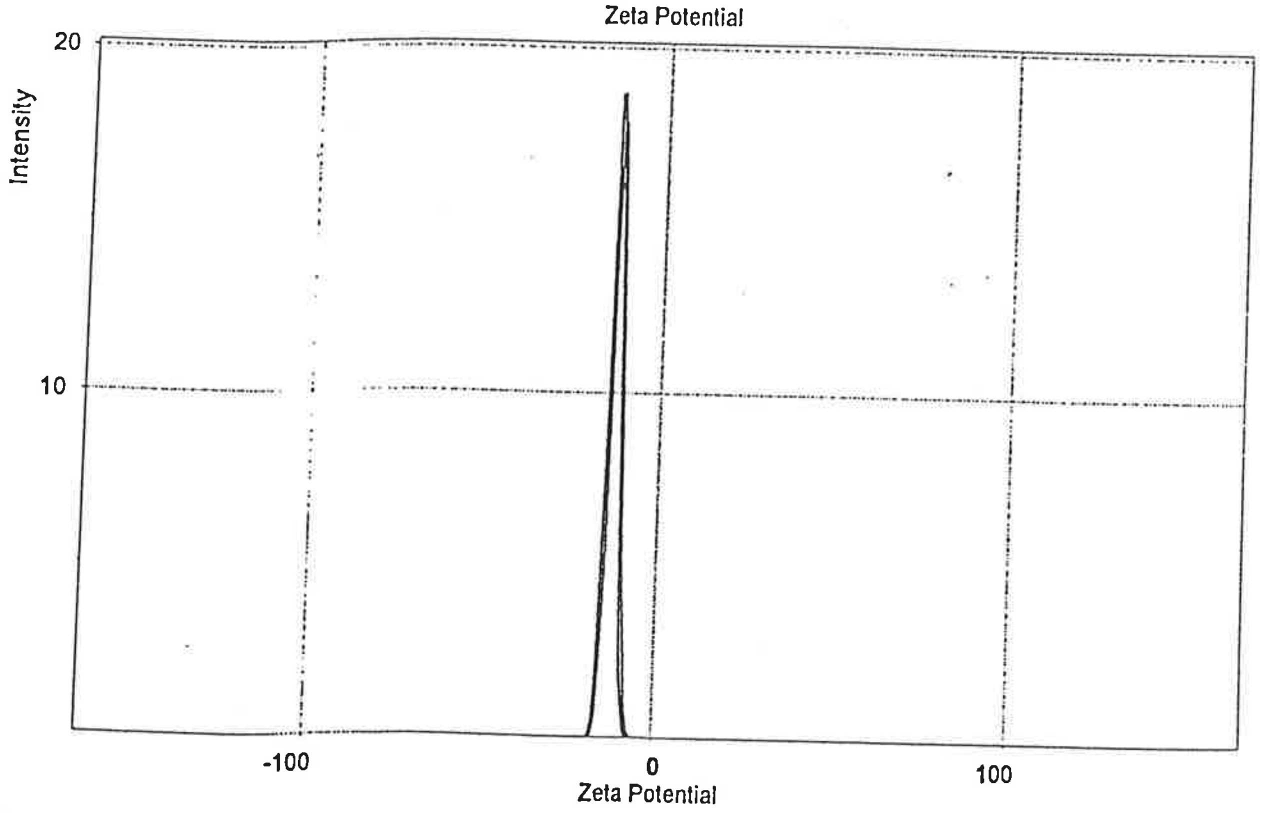
11

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2589.9	-0.988	-13.5	1.7	02:25:24
2	17.0	2920.7	-0.892	-12.3	1.7	02:25:54
3	17.0	3134.0	-0.957	-13.2	1.7	02:26:24
4	17.0	2745.9	-0.969	-13.2	1.6	02:26:54
5	17.0	2496.1	-0.955	-13.1	1.6	02:27:25
6	17.0	2589.9	-0.988	-13.5	1.7	02:25:24
7	17.0	2920.7	-0.892	-12.3	1.7	02:25:54
8	17.0	3134.0	-0.957	-13.2	1.7	02:26:24
9	17.0	2745.9	-0.969	-13.2	1.6	02:26:54
10	17.0	2496.1	-0.955	-13.1	1.6	02:27:25
Average		2777.3	-0.952	-13.1	1.7	
+/-		241.8	0.034	0.4	0.0	



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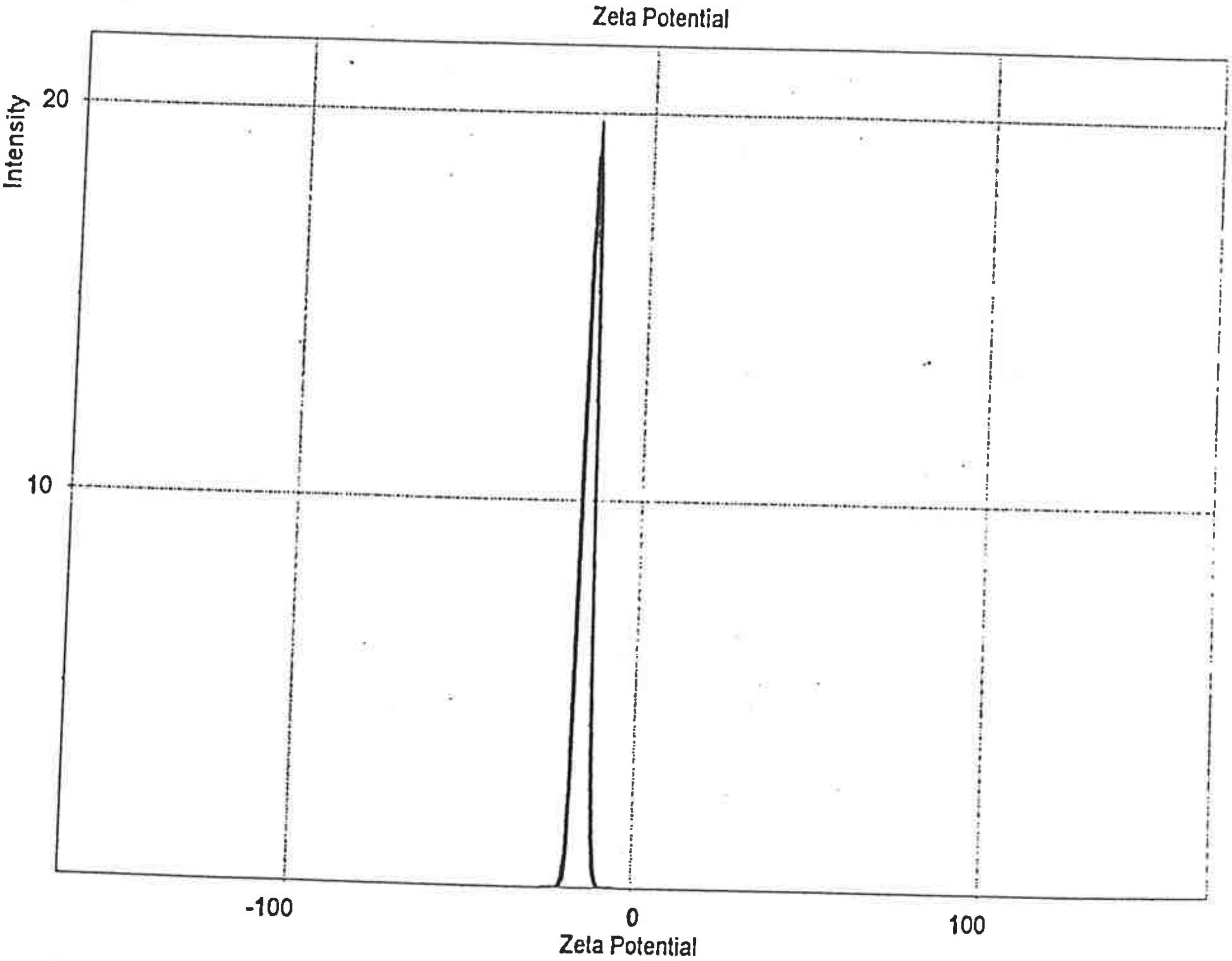
12

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	3021.2	-1.153	-15.8	1.6	23:09:05
2	17.0	3503.7	-1.170	-15.9	1.6	23:09:36
3	17.0	3187.0	-1.202	-16.2	1.6	23:10:06
4	17.0	3260.2	-1.156	-15.7	1.6	23:10:37
5	17.0	3083.8	-1.209	-16.5	1.6	23:11:07
Average		3211.2	-1.178	-16.0	1.6	
+/-		187.7	0.026	0.3	0.0	



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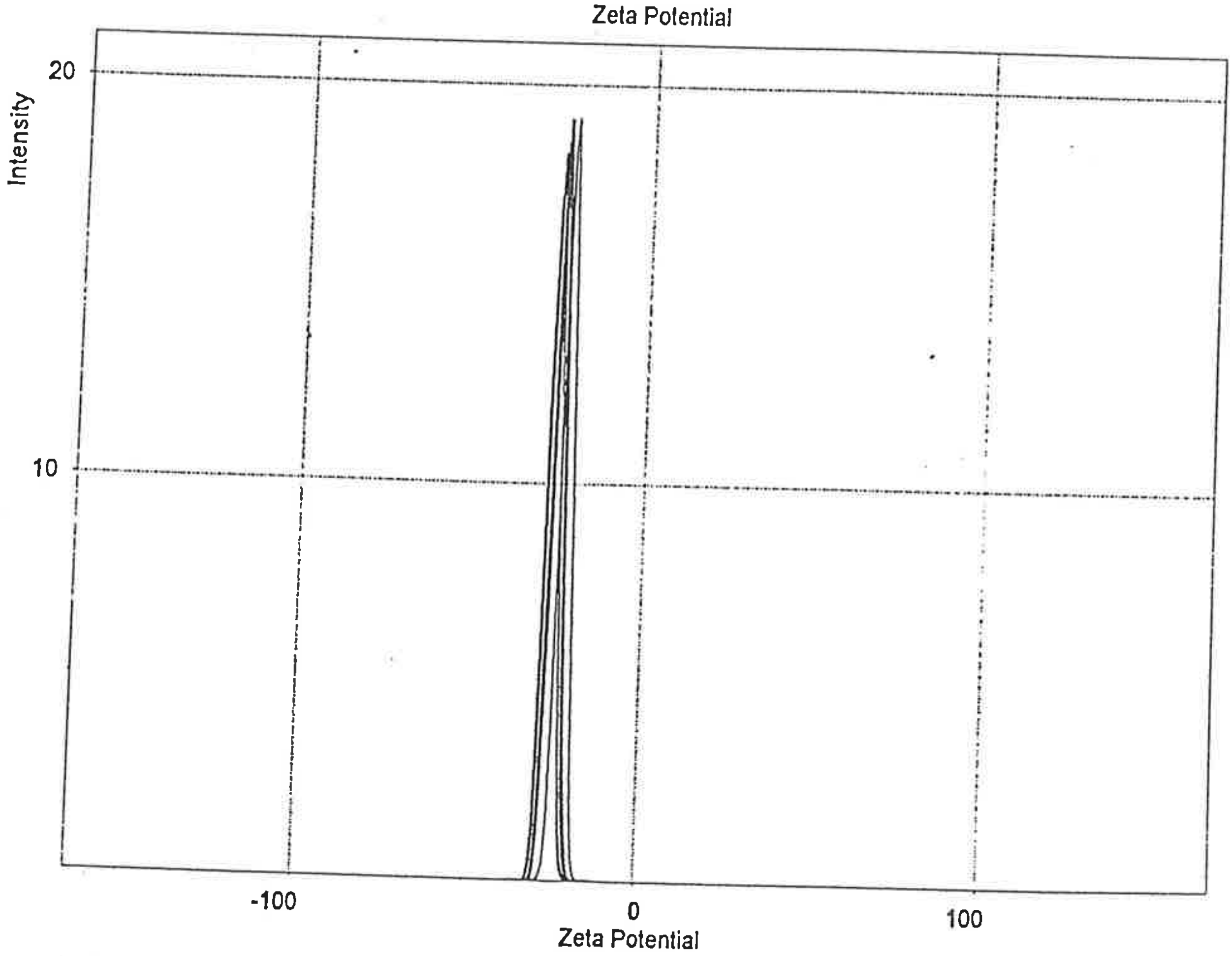
13

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2020.2	-1.641	-22.4	1.6	23:17:48
2	17.0	2003.7	-1.801	-25.0	1.7	23:18:19
3	17.0	2001.8	-1.904	-26.1	1.7	23:18:49
4	17.0	2010.4	-1.798	-24.6	1.6	23:19:20
5	17.0	1998.5	-1.792	-24.5	1.7	23:19:50
Average		2006.9	-1.787	-24.5	1.7	
+/-		8.6	0.094	1.3	0.0	



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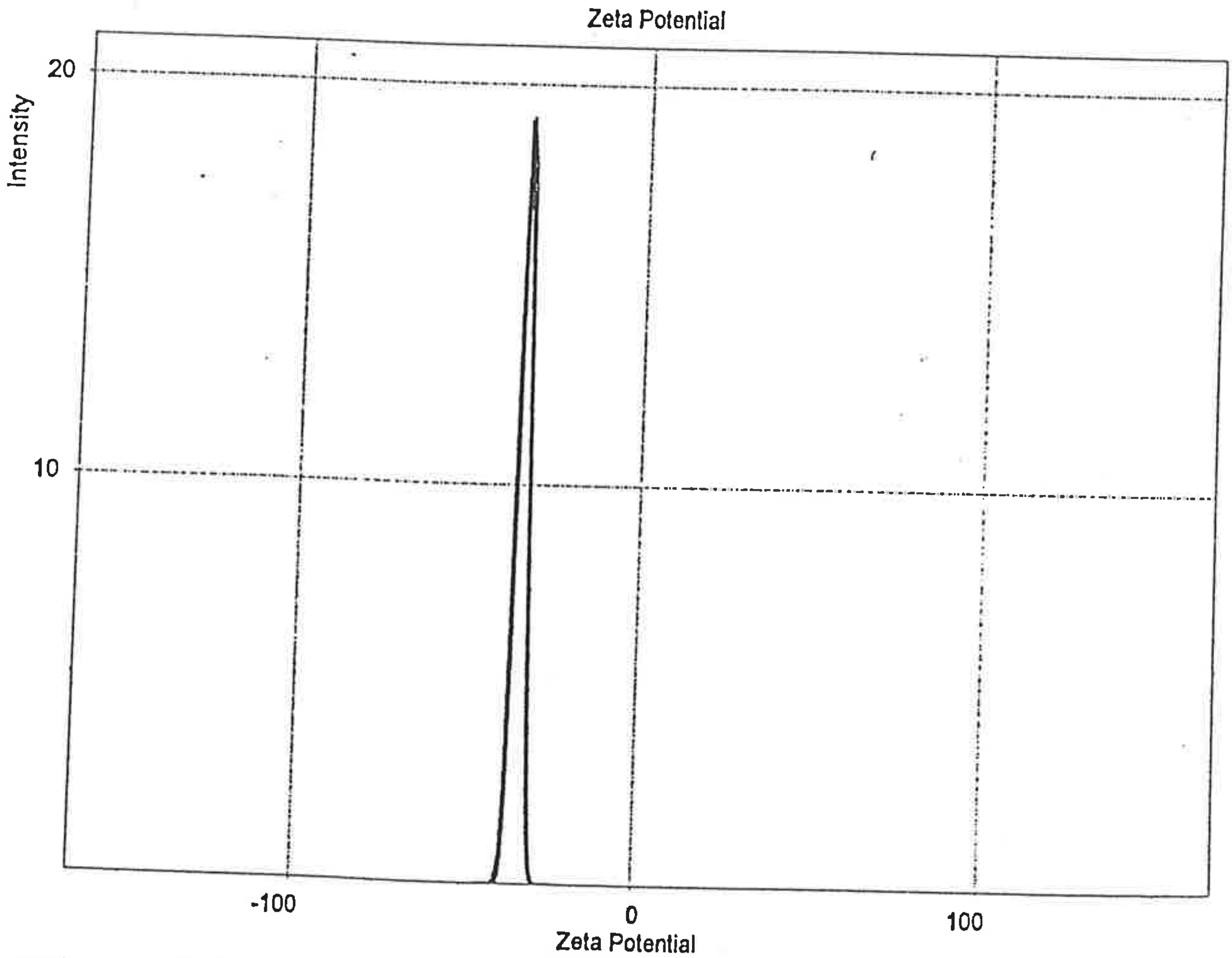
14

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2010.0	-2.545	-34.4	1.6	23:43:40
2	17.0	2013.9	-2.569	-34.5	1.7	23:44:11
3	17.0	2012.6	-2.531	-34.3	1.6	23:44:41
4	17.0	2027.6	-2.534	-34.5	1.7	23:45:12
5	17.0	2009.6	-2.482	-33.7	1.6	23:45:42
Average		2014.7	-2.532	-34.3	1.6	
+/-		7.4	0.032	0.3	0.0	



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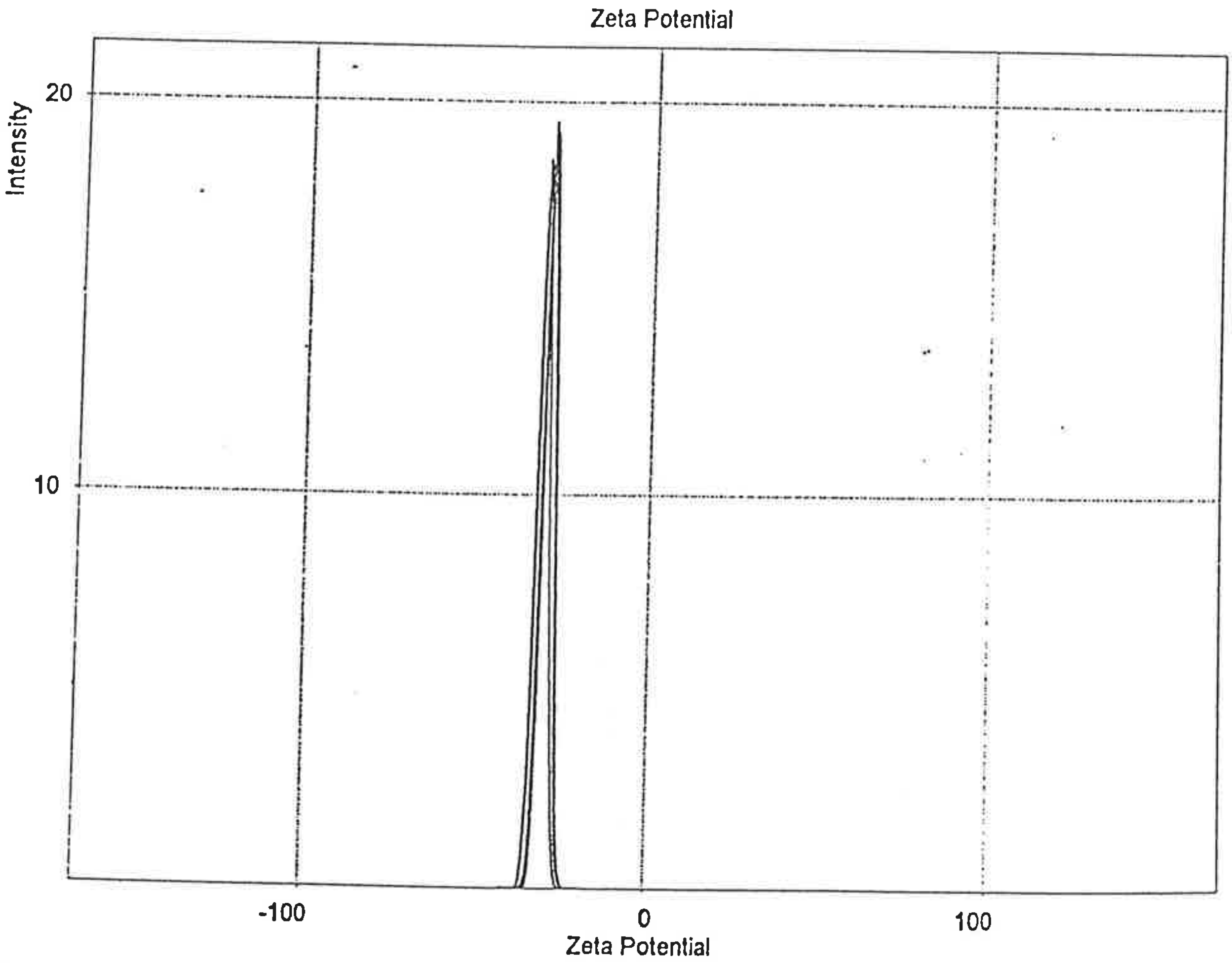
15

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	3018.6	-2.075	-28.2	1.6	23:52:39
2	17.0	3113.5	-2.112	-28.5	1.6	23:53:10
3	17.0	3087.5	-2.040	-28.1	1.6	23:53:40
4	17.0	3164.9	-2.186	-29.9	1.7	23:54:11
5	17.0	3113.0	-2.056	-28.6	1.6	23:54:41
Average		3099.5	-2.094	-28.6	1.6	
+/-		53.3	0.058	0.7	0.0	



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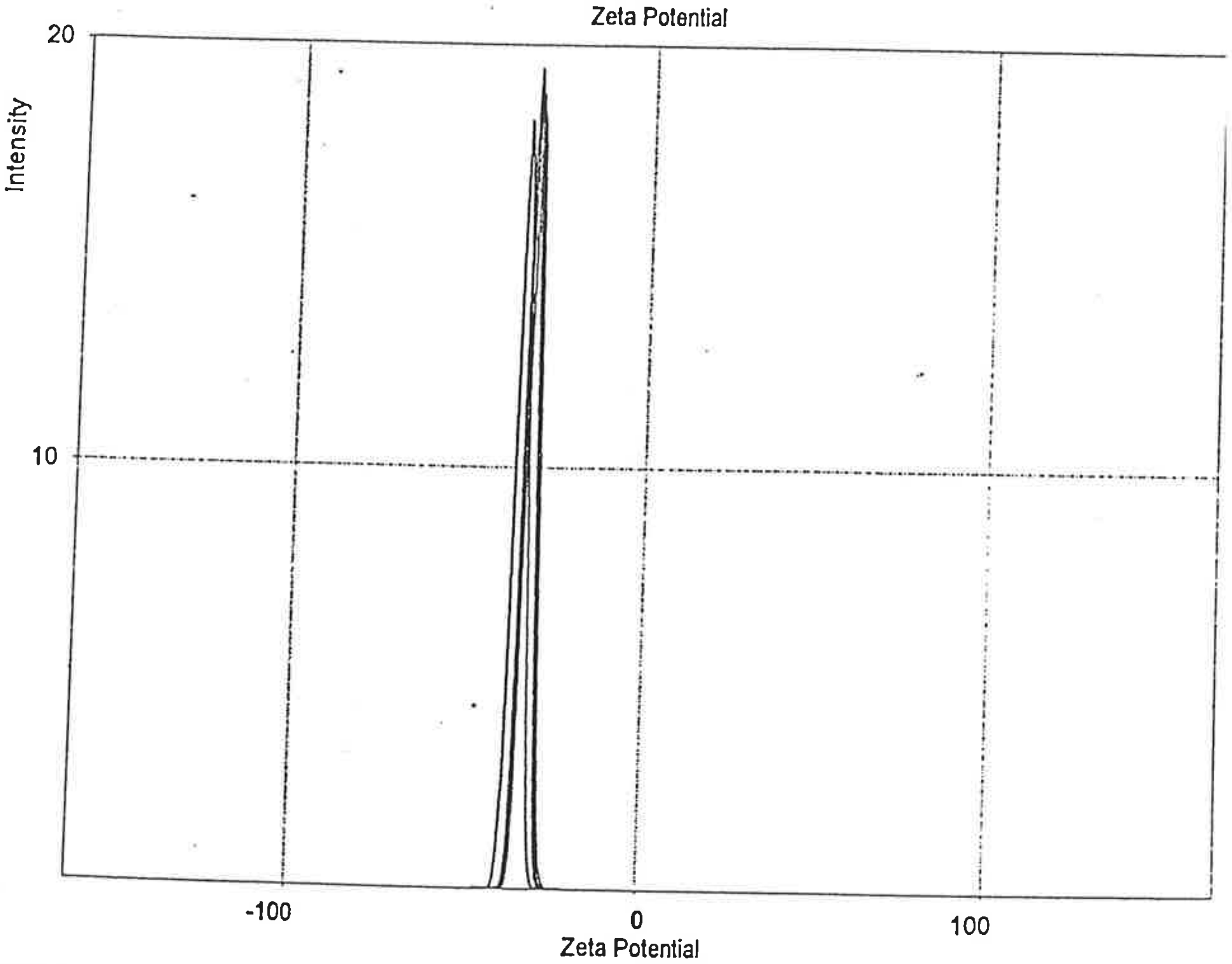
16

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2033.3	-2.585	-35.3	1.7	00:00:24
2	17.0	2034.7	-2.402	-33.2	1.6	00:00:54
3	17.0	2034.0	-2.378	-32.7	1.6	00:01:24
4	17.0	2062.2	-2.351	-32.1	1.7	00:01:55
5	17.0	2045.0	-2.410	-33.1	1.6	00:02:25
Average		2041.8	-2.425	-33.3	1.6	
+/-		12.4	0.092	1.2	0.0	



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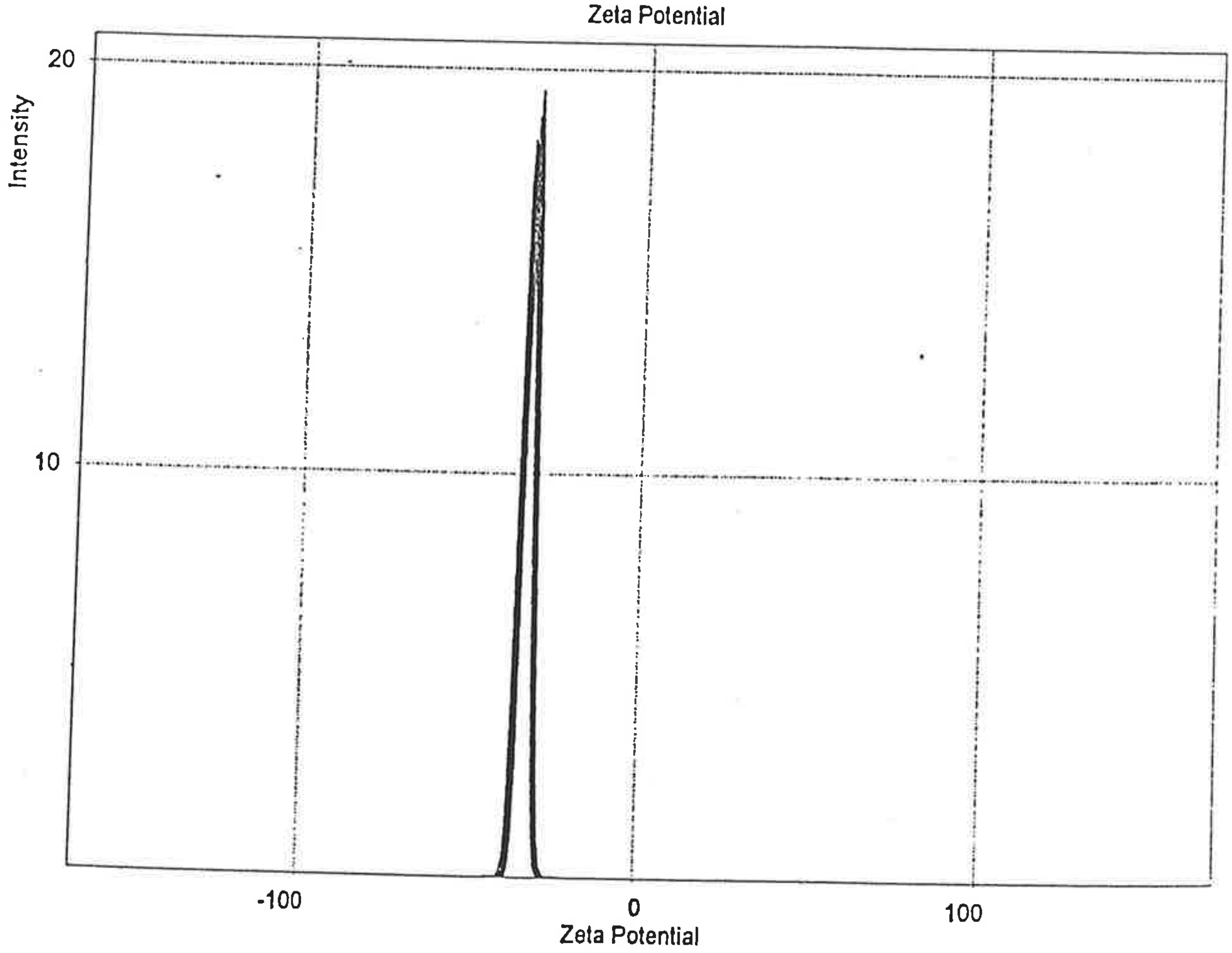
17

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2237.8	-2.410	-32.9	1.6	00:11:45
2	17.0	2240.1	-2.388	-32.4	1.6	00:12:16
3	17.0	2265.7	-2.391	-32.4	1.6	00:12:46
4	17.0	2323.0	-2.435	-33.5	1.7	00:13:17
5	17.0	2216.6	-2.491	-34.1	1.7	00:13:47
Average		2256.7	-2.423	-33.1	1.7	
+/-		41.0	0.042	0.7	0.0	



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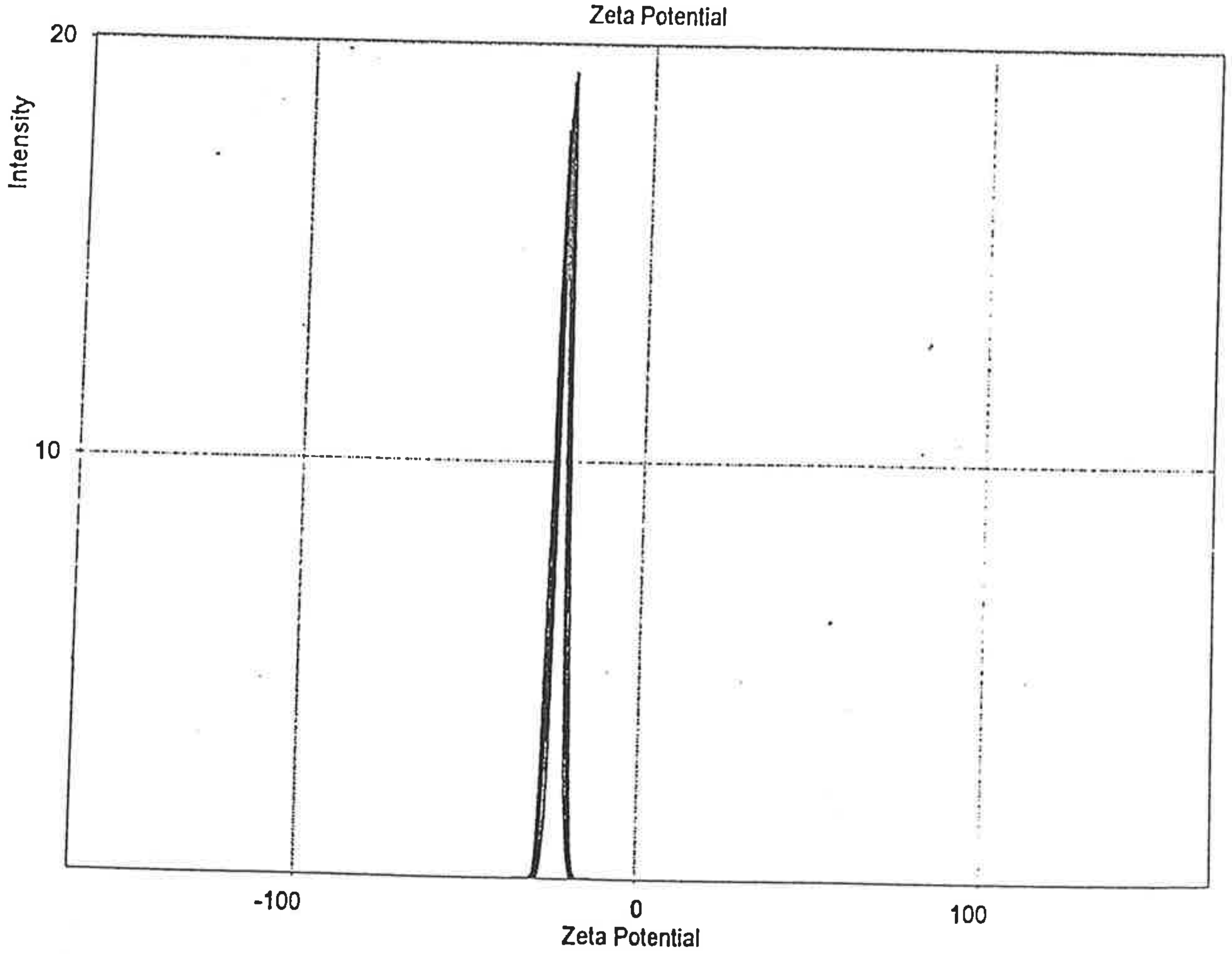
18

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2256.4	-1.777	-24.3	1.7	00:18:30
2	17.0	2234.3	-1.773	-24.0	1.7	00:19:00
3	17.0	2259.6	-1.736	-23.4	1.6	00:19:31
4	17.0	2252.7	-1.785	-24.9	1.7	00:20:01
5	17.0	2291.4	-1.701	-23.2	1.6	00:20:32
Average		2258.9	-1.755	-24.0	1.7	
+/-		20.7	0.035	0.7	0.0	



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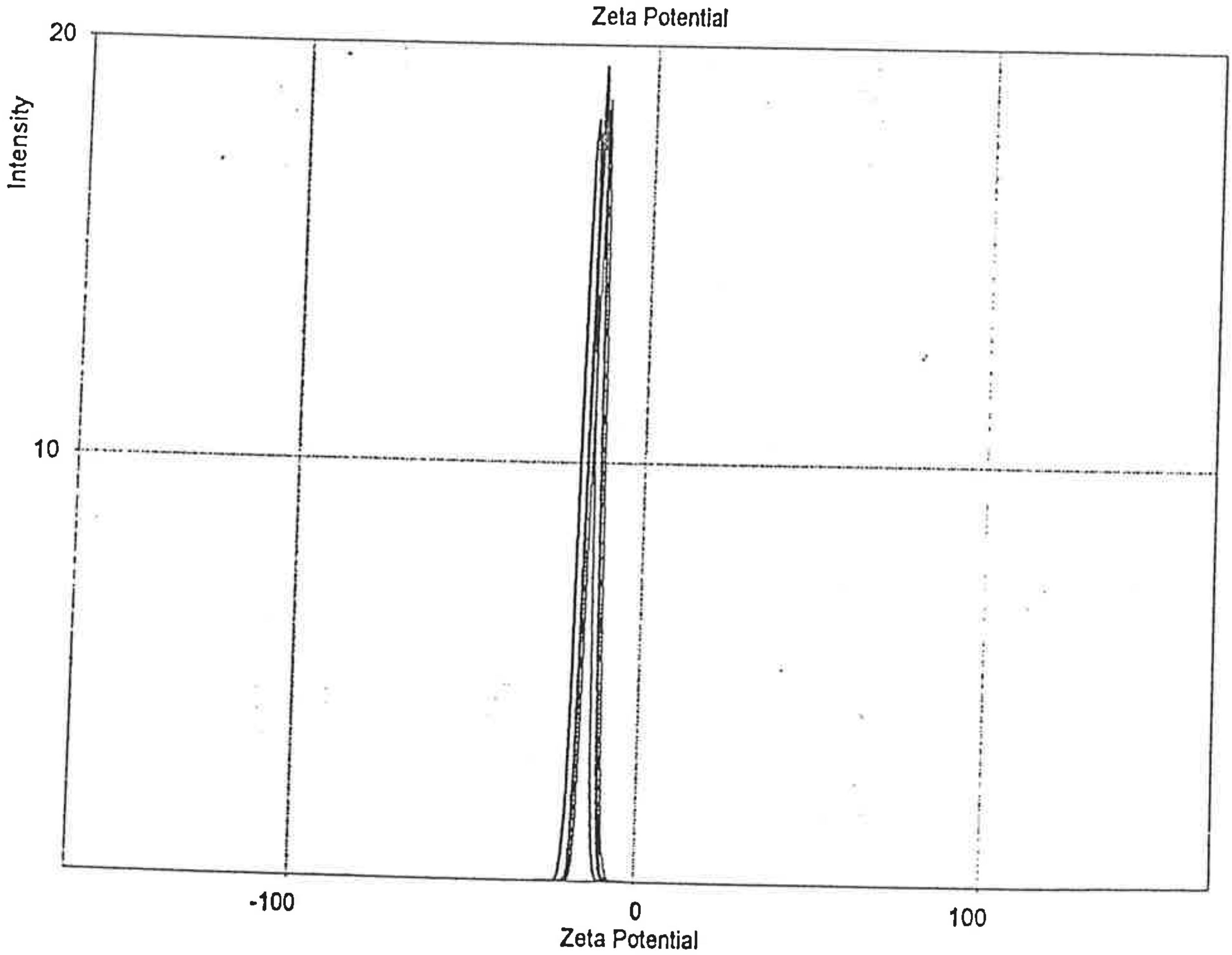
19

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	1979.9	-1.236	-16.9	1.7	00:36:06
2	17.0	1944.6	-1.105	-15.1	1.6	00:36:36
3	17.0	1958.3	-1.074	-14.7	1.7	00:37:07
4	17.0	1915.9	-1.004	-13.8	1.7	00:37:37
5	17.0	1919.6	-1.094	-14.9	1.6	00:38:39
Average		1943.7	-1.103	-15.1	1.7	
+/-		26.8	0.084	1.2	0.0	



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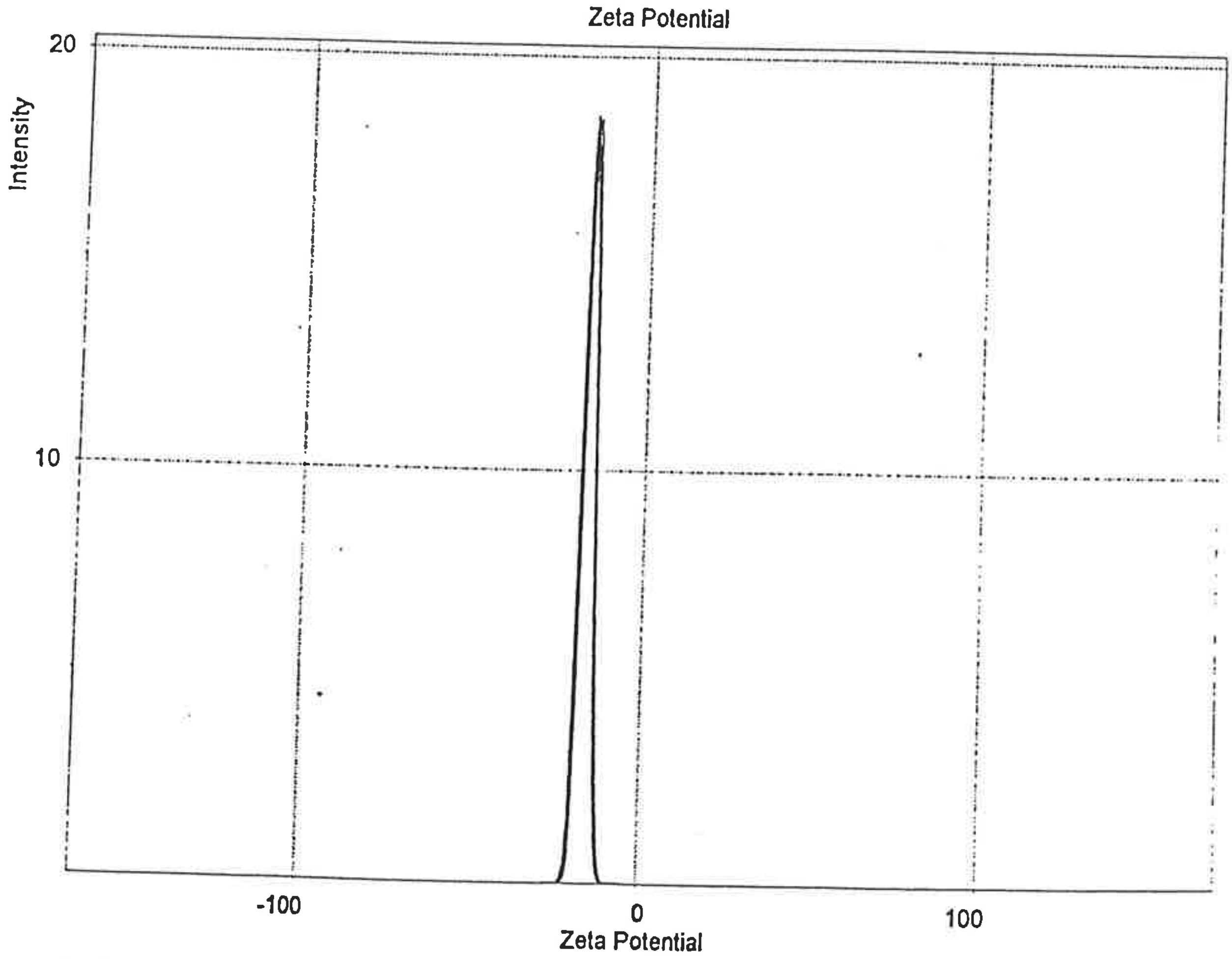
20

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2618.0	-1.181	-16.1	1.7	21:36:34
2	17.0	2177.6	-1.150	-16.1	1.7	21:37:04
3	17.0	2302.2	-1.118	-15.4	1.7	21:37:35
4	17.0	2653.6	-1.162	-15.9	1.7	21:38:05
5	17.0	2433.3	-1.139	-15.6	1.7	21:38:36
Average		2436.9	-1.150	-15.8	1.7	
+/-		203.2	0.024	0.3	0.0	



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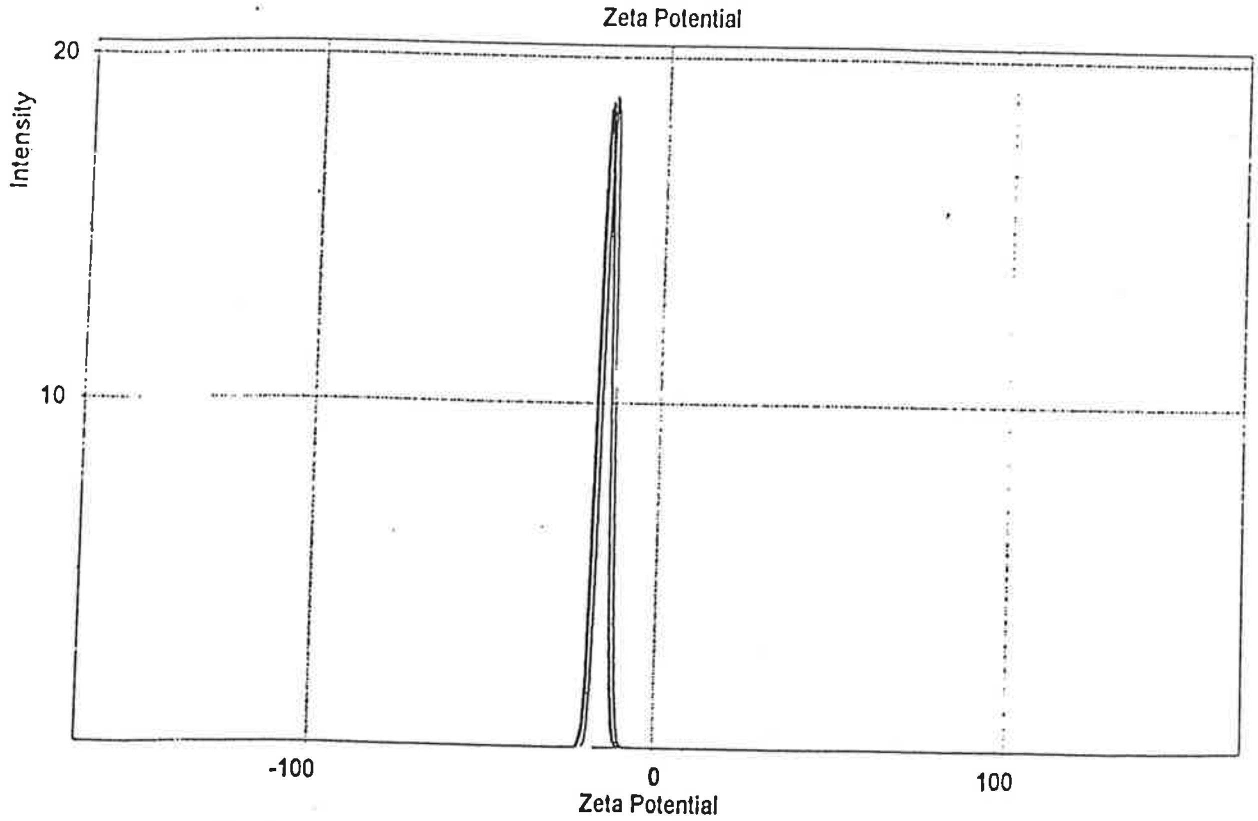
21

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2003.8	-0.973	-13.3	1.7	00:44:44
2	17.0	2207.4	-1.097	-14.8	1.6	00:45:15
3	17.0	2081.8	-0.828	-11.2	1.7	00:45:45
4	17.0	2042.1	-1.190	-16.2	1.7	00:46:15
5	17.0	1923.2	-1.068	-16.4	1.7	00:46:46
6	17.0	2003.8	-0.975	-13.3	1.7	00:44:44
7	17.0	2207.4	-1.022	-14.8	1.6	00:45:15
8	17.0	2081.8	-1.043	-11.2	1.7	00:45:45
9	17.0	2042.1	-1.035	-16.2	1.7	00:46:15
10	17.0	1923.2	-1.029	-16.4	1.7	00:46:46
Average		2051.7	-1.055	-14.4	1.7	
+/-		98.9	0.146	2.0	0.0	



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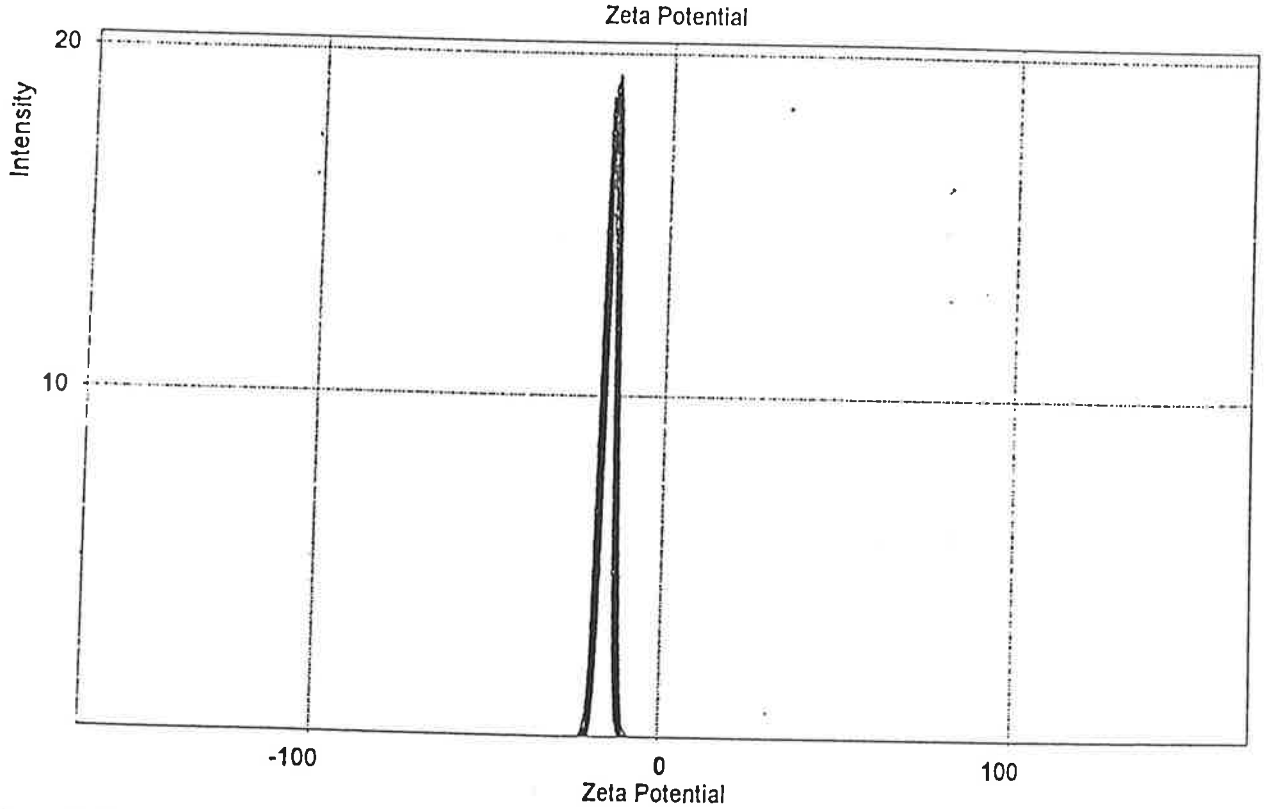
22

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2236.0	-1.096	-15.1	1.7	16:15:57
2	17.0	2076.7	-1.137	-15.6	1.6	16:16:27
3	17.0	2032.8	-1.082	-14.8	1.6	16:16:58
4	17.0	2125.0	-1.040	-14.4	1.7	16:17:28
5	17.0	1902.2	-1.131	-15.5	1.7	16:17:58
6	17.0	3814.4	-1.145	-15,6	1.6	16:19:55
7	17.0	3815.1	-1.146	-15.7	1.6	16:20:25
8	17.0	3744.8	-1.216	-16.7	1.7	16:20:55
9	17.0	4151.2	-1.131	-15.4	1.6	16:21:25
10	17.0	4469.0	-1.187	-16.4	1.6	16:21:56
Average		3036.7	-1.131	-15.5	1.7	
+/-		1037.9	0.050	0.7	0.0	



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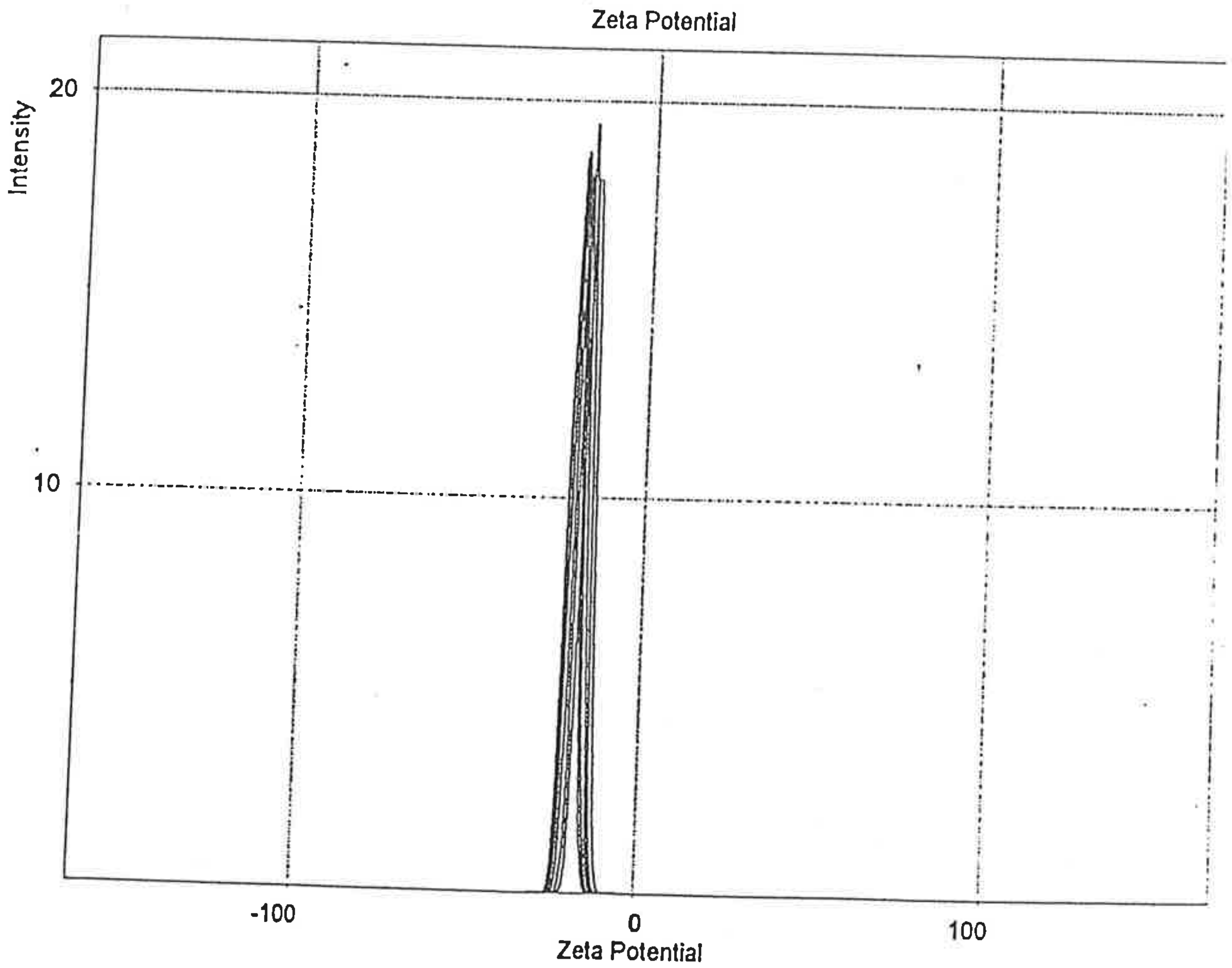
23

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	1931.6	-1.068	-14.2	1.6	01:04:09
2	17.0	1936.4	-0.975	-14.0	1.7	01:04:39
3	17.0	1892.5	-1.022	-13.7	1.7	01:05:09
4	17.0	1965.5	-1.043	-14.4	1.7	01:05:40
5	17.0	1868.9	-1.035	-14.4	1.7	01:06:10
Average		1919.0	-1.029	-14.1	1.7	
+/-		38.2	0.034	0.3	0.0	



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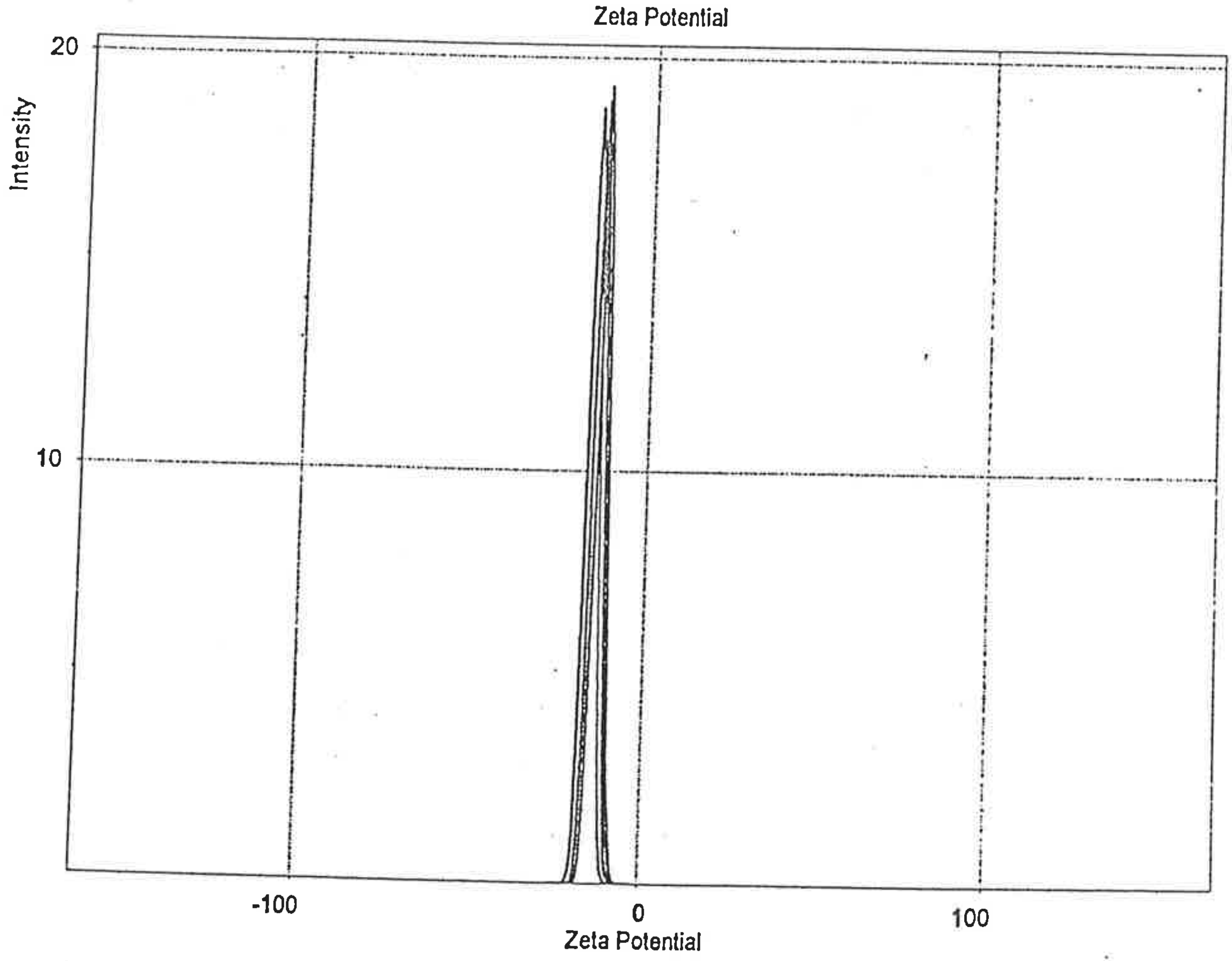
24

Cell type ZEM010 Ref. Beam Mode F(ka) = 1.50 (Smoluchowsky)

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	2242.5	-1.047	-14.2	1.7	01:11:48
2	17.0	2114.6	-0.946	-13.0	1.7	01:14:15
3	17.0	1926.7	-0.978	-13.4	1.6	01:15:20
4	17.0	2024.0	-1.059	-14.5	1.6	01:15:51
5	17.0	1963.5	-1.176	-15.9	1.7	01:16:21
Average		2054.3	-1.041	-14.2	1.7	
+/-		127.0	0.089	1.1	0.0	



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ZetaMaster Version PCS: v1.24

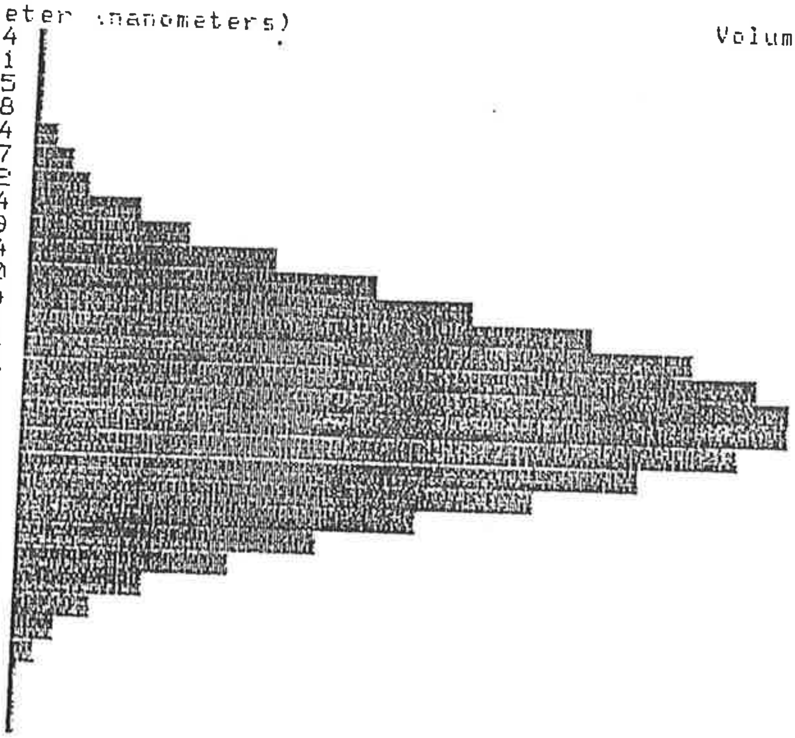
Wednesday 16 August 1995

Appendix 2

Sub-micron Particle Sizes as Determined by the Nicom Analyzer

1

```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter   = 787.7 nm
Stnd. Deviation = 514.8 nm (65.4 %)     Chi Squared          = 116.021
Coeff. of Var'n = 0.654                  Baseline Adj.        = 0.078 %
                                         Mean Diff. Coeff.    = 5.44E-09 cm2/s
```

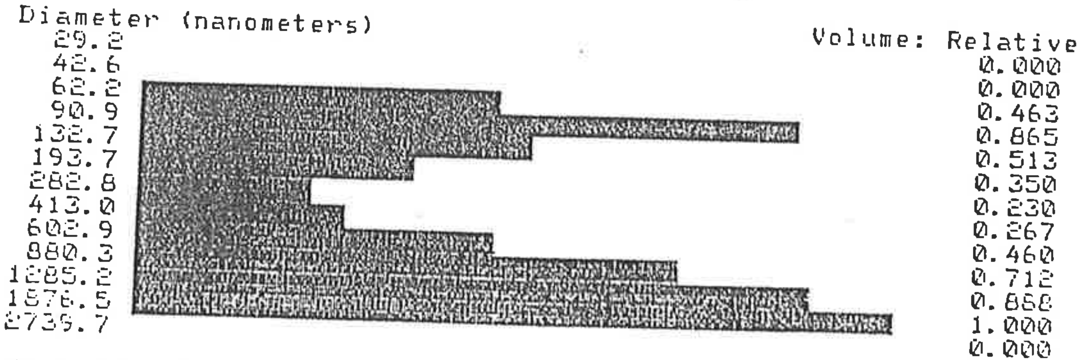


```
Diameter (nanometers)
  56.4                                     Volume: Relative  Percent
  66.1                                             0.001     0.010
  77.5                                             0.002     0.024
  90.8                                             0.006     0.054
 106.4                                             0.012     0.115
 124.7                                             0.024     0.230
 146.2                                             0.045     0.434
 171.4                                             0.080     0.772
 200.9                                             0.134     1.294
 235.4                                             0.211     2.046
 276.0                                             0.315     3.050
 323.4                                             0.443     4.285
 379.1                                             0.586     5.675
 444.4                                             0.732     7.086
 520.8                                             0.862     8.339
 610.5                                             0.956     9.253
 715.5                                             1.000     9.677
 838.7                                             0.986     9.541
 983.0                                             0.916     8.867
1152.2                                             0.803     7.769
1350.5                                             0.663     6.416
1582.9                                             0.516     4.995
1855.3                                             0.379     3.668
2174.6                                             0.262     2.536
2548.9                                             0.171     1.654
2987.6                                             0.105     1.017
3501.7                                             0.061     0.589
4104.4                                             0.033     0.322
4810.8                                             0.017     0.166
5638.7                                             0.008     0.081
                                                   0.004     0.037

Cumulative Results:
25 % of distribution < 378.49 nm
50 % of distribution < 587.45 nm
75 % of distribution < 914.78 nm
99 % of distribution < 2686.14 nm

Run Time       = 0  Hr  7 Min  6 Sec
Count Rate     = 413    Khz          Wavelength     = 632.8  nm
Channel #1     = 3158.9 K            Temperature    = 20     deg C
Channel Width  = 76.4   uSec         Viscosity      = 1.002  cp
                                     Index of Ref.  = 1.333
```

1

VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)

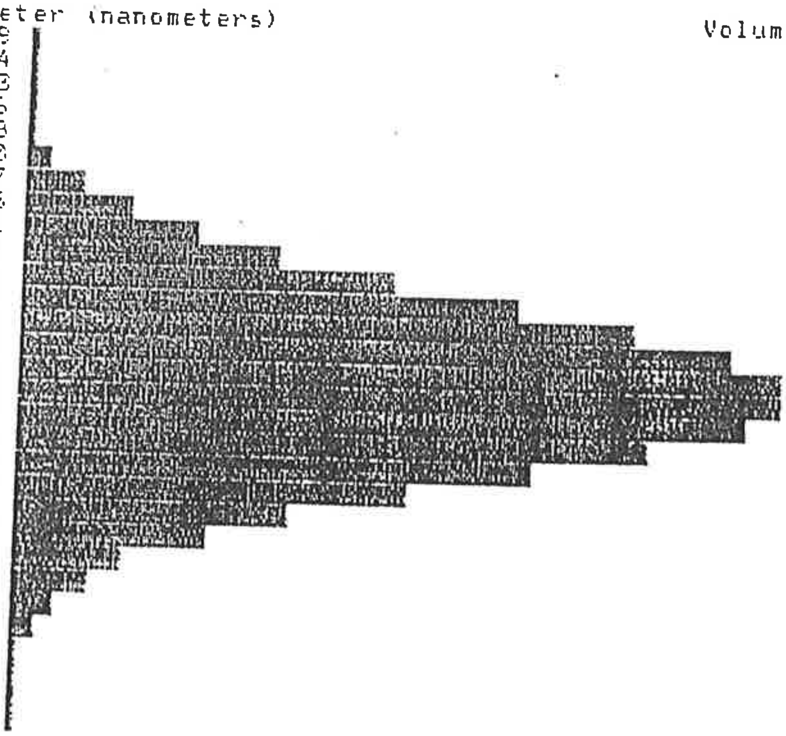
```
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 111.1 nm      Volume:   46.39 %
Peak Number 2:  Mean Diameter = 1401.8 nm      Volume:   53.61 %
```



```
Mean Diameter = 755.1 nm   Fit Error = 42.571    Residual = 18.951

NICOMP SCALE PARAMETERS:
Min. Diam. = 20.0 nm          Plot Size  = 15
Smoothing  = 5                Plot Range = 200

Run Time        = 0  Hr  6 Min 16 Sec     Wavelength     = 632.8  nm
Count Rate      = 375     Khz             Temperature    = 20     deg C
Channel #1      = 3607.2  K               Viscosity      = 1.002  cp
Channel Width   = 76.4    uSec            Index of Ref.  = 1.333

GAUSSIAN SUMMARY:
Mean Diameter    = 770.5 nm               Chi Squared          = 115.992
Stnd. Deviation  = 500.9 nm  (65.0 %)     Baseline Adj.        = 0.033 %
Coeff. of Var'n  = 0.650                  Mean Diff. Coeff.    = 5.56E-09 cm2/s
```

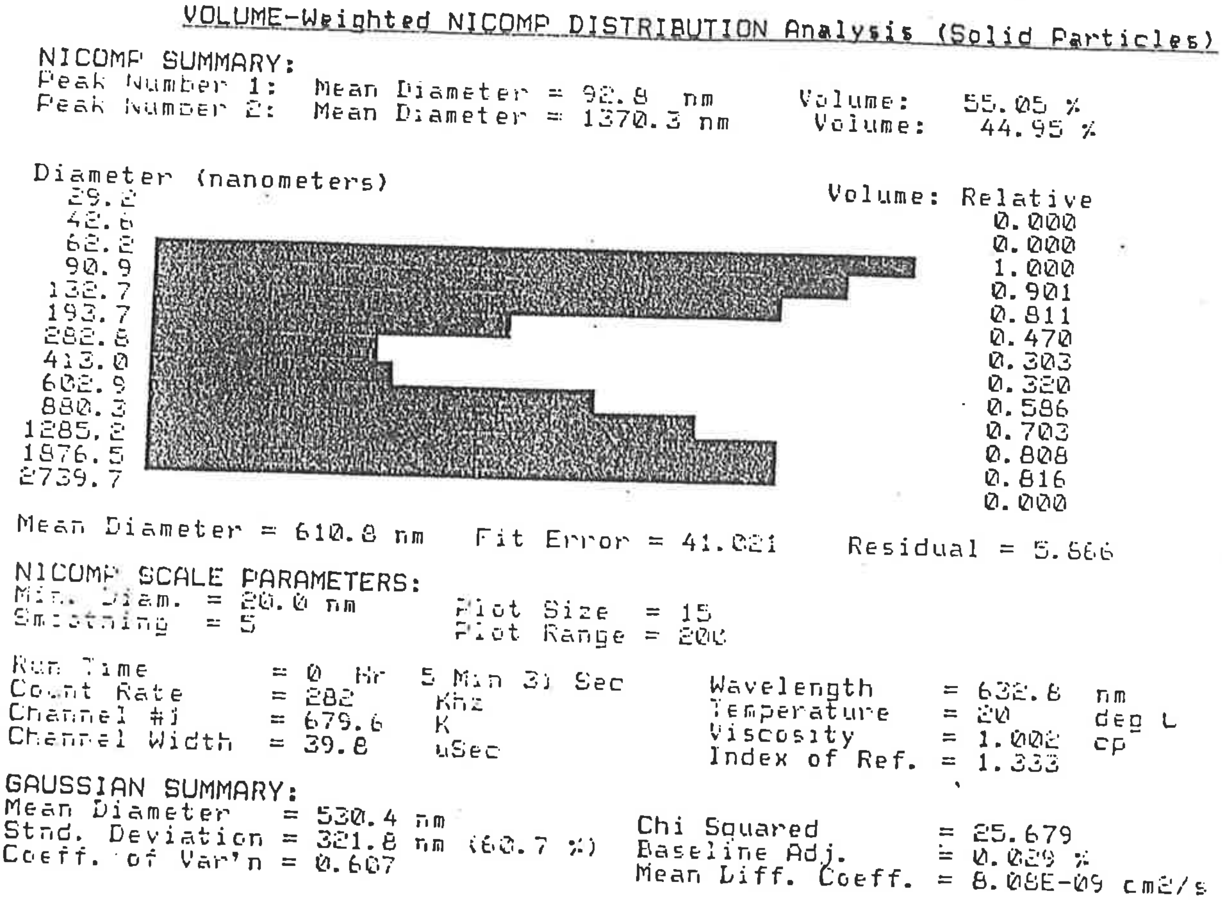
2

```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter    = 533.3 nm                    Chi Squared          = 24.312
Stnd. Deviation = 323.1 nm  (60.6 %)           Baseline Adj.        = 0.014 %
Coeff. of Var'n = 0.606                        Mean Diff. Coeff.    = 8.03E-09 cm2/s
```



```
Diameter (nanometers)                  Volume: Relative   Percent
   43.9                                        0.001      0.007
   51.4                                        0.002      0.019
   60.3                                        0.004      0.046
   70.6                                        0.010      0.105
   82.8                                        0.022      0.224
   97.0                                        0.043      0.448
  113.7                                        0.080      0.836
  133.3                                        0.140      1.457
  156.2                                        0.228      2.368
  183.1                                        0.346      3.595
  214.6                                        0.490      5.095
  251.6                                        0.649      6.741
  294.9                                        0.801      8.327
  345.6                                        0.924      9.603
  405.1                                        0.995     10.339
  474.8                                        1.000     10.393
  556.6                                        0.938      9.753
  652.4                                        0.822      8.545
  764.6                                        0.673      6.989
  896.2                                        0.514      5.337
 1050.5                                        0.366      3.805
 1231.2                                        0.244      2.533
 1443.1                                        0.151      1.574
 1691.5                                        0.088      0.913
 1982.6                                        0.048      0.495
 2323.8                                        0.024      0.250
 2723.8                                        0.011      0.118
 3192.5                                        0.005      0.052
 3742.0                                        0.002      0.021
 4386.0                                        0.001      0.006

Cumulative Results:
25 % of distribution < 271.83 nm
50 % of distribution < 410.03 nm
75 % of distribution < 616.09 nm
99 % of distribution < 1675.26 nm

Run Time        = 0  Hr   4 Min 36 Sec      Wavelength      = 632.8  nm
Count Rate      = 289      Khz              Temperature     = 20     deg C
Channel #1      = 573.0    K                Viscosity       = 1.002  cp
Channel Width   = 39.8     uSec             Index of Ref.   = 1.333
```

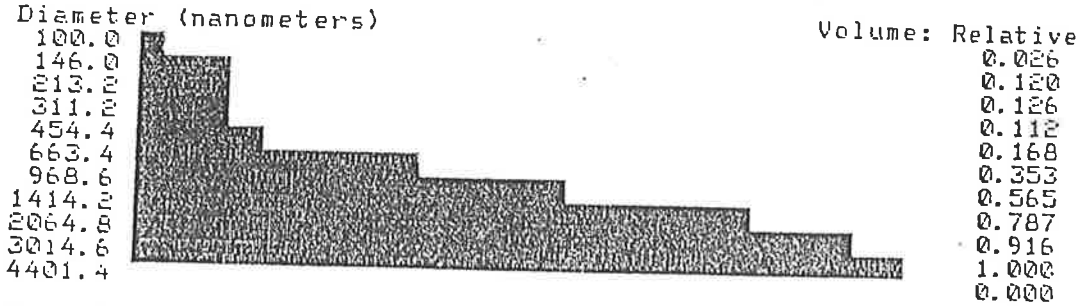
2



```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:   Mean Diameter = 92.8   nm      Volume:   55.05 %
Peak Number 2:   Mean Diameter = 1370.3 nm      Volume:   44.95 %

Diameter (nanometers)
   29.2                                        Volume: Relative
   42.6                                                 0.000
   62.2                                                 0.000
   90.9                                                 1.000
  132.7                                                 0.901
  193.7                                                 0.811
  282.8                                                 0.470
  413.0                                                 0.303
  602.9                                                 0.320
  880.3                                                 0.586
 1285.2                                                 0.703
 1876.5                                                 0.808
 2739.7                                                 0.816
                                                        0.000
Mean Diameter = 610.8 nm   Fit Error = 41.021   Residual = 5.666
NICOMP SCALE PARAMETERS:
Min. Diam. = 20.0 nm        Plot Size  = 15
Smoothing  = 5              Plot Range = 200

Run Time        = 0  Hr  5 Min 31 Sec    Wavelength    = 632.8  nm
Count Rate      = 282     Khz            Temperature   = 20     deg C
Channel #1      = 679.6   K              Viscosity     = 1.002  cp
Channel Width   = 39.8    uSec           Index of Ref. = 1.333
GAUSSIAN SUMMARY:
Mean Diameter   = 530.4 nm              Chi Squared       = 25.679
Stnd. Deviation = 321.8 nm (60.7 %)     Baseline Adj.     = 0.029 %
Coeff. of Var'n = 0.607                 Mean Diff. Coeff. = 8.08E-09 cm2/s
```

4

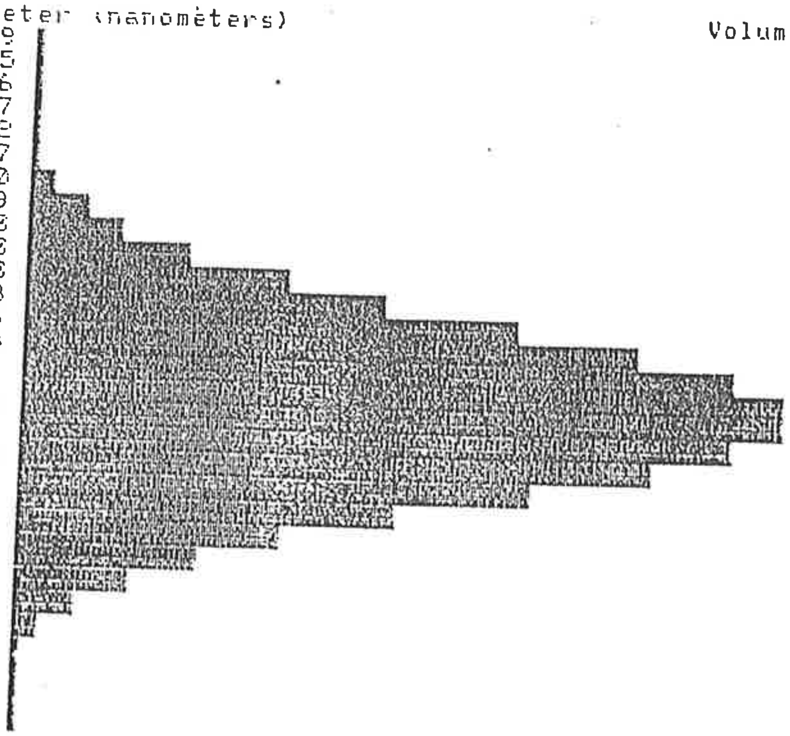
```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 2226.6 nm      Volume:   100.00 %
```



```
Mean Diameter = 1667.7 nm   Fit Error = 71.661    Residual = 12.244

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm          Plot Size  = 15
Smoothing  = 5                Plot Range = 200

Run Time          = 0  Hr 12 Min  6 Sec     Wavelength      = 632.8  nm
Count Rate        = 273       Khz           Temperature     = 20     deg C
Channel #1        = 1178.3  K               Viscosity       = 1.002  cp
Channel Width     = 100.0   uSec            Index of Ref.   = 1.333

GAUSSIAN SUMMARY:
Mean Diameter    = 1189.3 nm
Stnd. Deviation = 696.2 nm (58.5 %)   Chi Squared         = 35.073
Coeff. of Var'n = 0.585               Baseline Adj.      = 0.000 %
                                      Mean Diff. Coeff.  = 3.85E-09 cm2/s
```

4

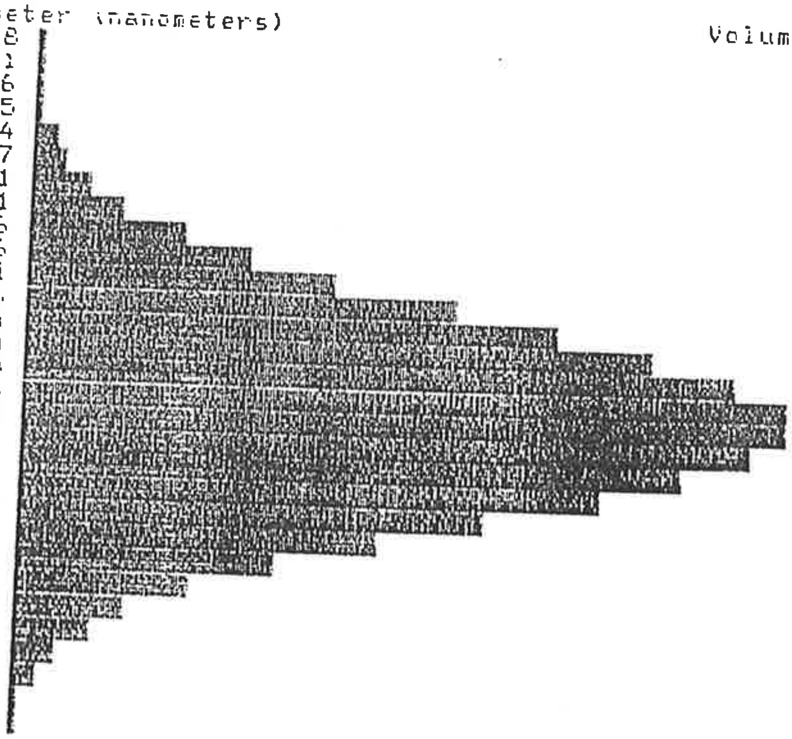
```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter    = 1191.6 nm
Stnd. Deviation = 699.9 nm (58.7 %)   Chi Squared         = 34.292
Coeff. of Var'n = 0.587                Baseline Adj.       = 0.000 %
                                       Mean Diff. Coeff.  = 3.59E-09 cm2/s
```



```
Diameter (nanometers)
  84.9                              Volume: Relative  Percent
  99.5                                       0.000     0.002
 116.6                                       0.000     0.005
 136.7                                       0.001     0.013
 160.2                                       0.003     0.034
 187.7                                       0.008     0.082
 220.0                                       0.017     0.184
 257.9                                       0.036     0.384
 302.3                                       0.069     0.744
 354.3                                       0.125     1.340
 415.3                                       0.210     2.245
 486.8                                       0.326     3.495
 570.6                                       0.472     5.057
 668.8                                       0.635     6.801
 783.9                                       0.794     8.502
 918.6                                       0.922     9.879
1076.9                                       0.996    10.669
1262.2                                       1.000    10.710
1479.5                                       0.933     9.993
1734.1                                       0.809     8.667
2032.5                                       0.652     6.986
2382.3                                       0.489     5.235
2792.3                                       0.340     3.646
3272.9                                       0.220     2.360
3836.1                                       0.133     1.420
4496.4                                       0.074     0.794
5270.2                                       0.039     0.413
6177.2                                       0.019     0.199
7240.3                                       0.008     0.090
8486.4                                       0.003     0.037
                                             0.001     0.015

Cumulative Results:
25 % of distribution < 621.93 nm
50 % of distribution < 926.49 nm
75 % of distribution < 1375.61 nm
99 % of distribution < 3651.79 nm

Run Time        = 0  Hr 12 Min 33 Sec
Count Rate      = 267      Khz          Wavelength     = 632.8  nm
Channel #1      = 1217.9   K            Temperature    = 20     deg C
Channel width   = 100.0    uSec         Viscosity      = 1.002  cp
                                        Index of Ref.  = 1.333
```

5

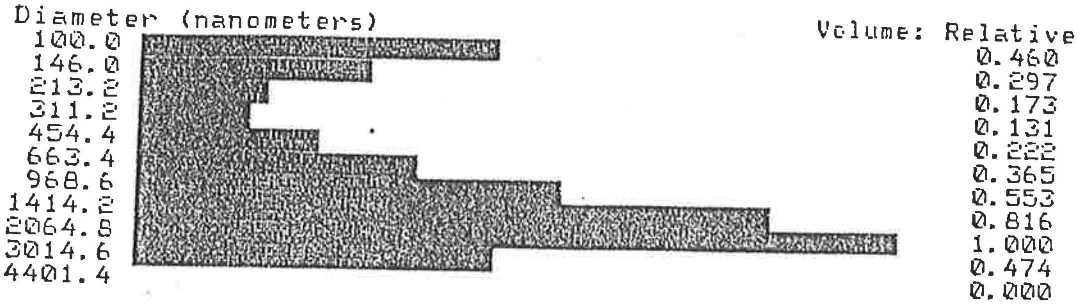
```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter    = 1089.6 nm
Stnd. Deviation = 738.0 nm (67.7 %)     Chi Squared          = 209.404
Coeff. of Var'n = 0.677                 Baseline Adj.        = 0.227 %
                                        Mean Diff. Coeff.    = 3.93E-09 cm2/s
```



```
Diameter (nanometers)
   71.8                                        Volume: Relative   Percent
   84.1                                                 0.001      0.011
   98.6                                                 0.003      0.025
  115.5                                                 0.006      0.054
  135.4                                                 0.012      0.112
  158.7                                                 0.024      0.219
  186.1                                                 0.043      0.406
  218.1                                                 0.076      0.710
  255.6                                                 0.126      1.177
  299.6                                                 0.198      1.846
  351.1                                                 0.294      2.740
  411.6                                                 0.412      3.849
  482.4                                                 0.548      5.119
  565.4                                                 0.690      6.443
  662.8                                                 0.822      7.676
  776.8                                                 0.927      8.656
  910.5                                                 0.990      9.239
 1067.2                                                 1.000      9.334
 1250.9                                                 0.956      8.925
 1466.2                                                 0.865      8.076
 1718.5                                                 0.741      6.921
 2014.2                                                 0.601      5.612
 2360.9                                                 0.461      4.307
 2767.2                                                 0.335      3.125
 3243.5                                                 0.231      2.152
 3801.7                                                 0.150      1.400
 4455.9                                                 0.092      0.863
 5222.8                                                 0.054      0.503
 6121.7                                                 0.030      0.278
 7175.2                                                 0.016      0.145
                                                        0.008      0.072

Cumulative Results:
25 % of distribution < 505.80 nm
50 % of distribution < 799.85 nm
75 % of distribution < 1261.84 nm
99 % of distribution < 3799.77 nm

Run Time        = 0  Hr 10 Min 30 Sec
Count Rate      = 217     KHz        Wavelength      = 632.8   nm
Channel #1      = 1095.6  K          Temperature     = 20      deg C
Channel Width   = 106.7   uSec       Viscosity       = 1.002   cp
                                     Index of Ref.   = 1.333
```

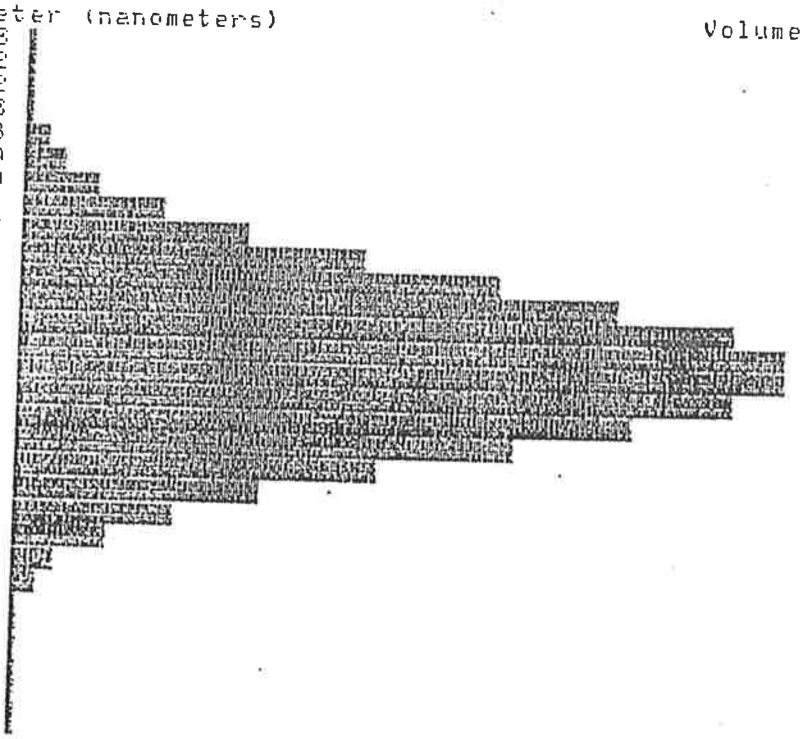
5

```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 135.7 nm      Volume:   31.51 %
Peak Number 2:  Mean Diameter = 1823.0 nm      Volume:   68.49 %
```



```
Mean Diameter = 1267.4 nm   Fit Error = 34.633   Residual = 24.043

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm        Plot Size  = 15
Smoothing  = 5              Plot Range = 200

Run Time         = 0  Hr 11 Min 14 Sec      Wavelength     = 632.8  nm
Count Rate       = 226     KHz              Temperature    = 20     deg C
Channel #1       = 1169.3  k                Viscosity      = 1.002  cp
Channel Width    = 106.7   uSec             Index of Ref.  = 1.333

GAUSSIAN SUMMARY:
Mean Diameter    = 1100.2 nm              Chi Squared        = 219.697
Stnd. Deviation = 751.5 nm (68.3 %)     Baseline Adj.      = 0.013 %
Coeff. of Var'n = 0.683                 Mean Diff. Coeff. = 3.89E-09 cm2/s
```

6



```
            VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter    = 347.5 nm                    Chi Squared          = 90.519
Stnd. Deviation = 196.4 nm (56.5 %)            Baseline Adj.        = 0.038 %
Coeff. of Var'n = 0.565                        Mean Diff. Coeff.    = 1.23E-08 cm2/s

Diameter (nanometers)
   34.3                                          Volume: Relative   Percent
   40.2                                                   0.001      0.008
   47.2                                                   0.002      0.022
   55.3                                                   0.005      0.057
   64.8                                                   0.012      0.136
   76.0                                                   0.027      0.301
   89.0                                                   0.055      0.617
  104.4                                                   0.105      1.167
  122.3                                                   0.183      2.039
  143.4                                                   0.296      3.293
  168.1                                                   0.442      4.915
  197.0                                                   0.609      6.778
  230.9                                                   0.776      8.637
  270.6                                                   0.914     10.172
  317.2                                                   0.994     11.069
  371.8                                                   1.000     11.130
  435.8                                                   0.929     10.342
  510.7                                                   0.798      8.880
  598.7                                                   0.633      7.046
  701.7                                                   0.464      5.166
  822.4                                                   0.314      3.500
  964.0                                                   0.197      2.191
 1129.9                                                   0.114      1.268
 1324.3                                                   0.061      0.678
 1552.3                                                   0.030      0.335
 1819.4                                                   0.014      0.153
 2132.5                                                   0.006      0.064
 2499.6                                                   0.002      0.025
 2929.7                                                   0.001      0.009
 3434.0                                                   0.000      0.003
                                                          0.000      0.001

Cumulative Results:
25 % of distribution < 186.51 nm
50 % of distribution < 273.68 nm
75 % of distribution < 401.62 nm
99 % of distribution < 1026.44 nm

Run Time          = 0  Hr  6 Min 46 Sec
Count Rate        = 306     Khz              Wavelength      = 632.8   nm
Channel #1        = 1013.4  K                Temperature     = 20      deg C
Channel Width     = 43.9    uSec             Viscosity       = 1.002   cp
                                             Index of Ref.   = 1.333
```

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```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 130.7 nm      Volume:   75.67 %
Peak Number 2:  Mean Diameter = 1034.8 nm      Volume:   24.33 %

Diameter (nanometers)
  100.0                                     Volume: Relative
  146.0                                              1.000
  213.2                                              0.528
  311.2                                              0.273
  454.4                                              0.192
  663.4                                              0.240
  968.6                                              0.273
 1414.2                                              0.311
 2064.8                                              0.322
                                                     0.000
Mean Diameter = 427.3 nm   Fit Error = 130.949   Residual = 6.445

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm        Plot Size  = 15
Smoothing  = 5              Plot Range = 200

Run Time        = 0  Hr  7 Min 40 Sec     Wavelength      = 632.8  nm
Count Rate      = 302     Khz             Temperature     = 20     deg C
Channel #1      = 1154.9  K               Viscosity       = 1.002  cp
Channel Width   = 43.9    uSec            Index of Ref.   = 1.333

GAUSSIAN SUMMARY:
Mean Diameter    = 342.7 nm             Chi Squared          = 97.343
Stnd. Deviation = 196.8 nm (57.4 %)     Baseline Adj.        = 0.038 %
Coeff. of Var'n = 0.574                 Mean Diff. Coeff.    = 1.25E-08 cm2/s
```

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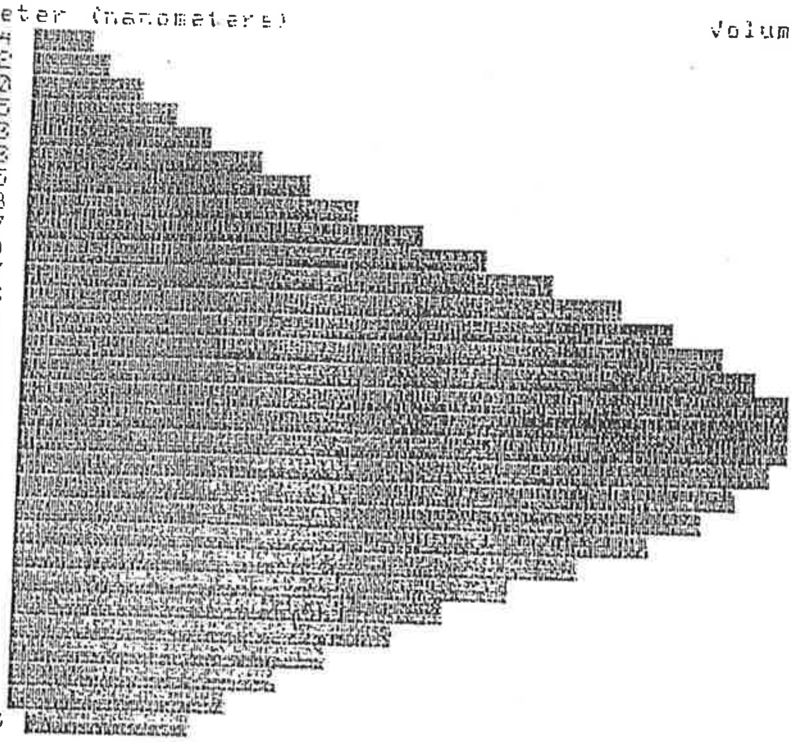

```
Diameter (nanometers)                                  Volume: Relative  Percent
  1114.4                                                        0.077     0.446
  1306.2                                                        0.104     0.604
  1531.0                                                        0.139     0.804
  1794.5                                                        0.181     1.049
  2103.3                                                        0.232     1.344
  2465.3                                                        0.292     1.688
  2889.5                                                        0.359     2.080
  3386.8                                                        0.434     2.513
  3969.7                                                        0.515     2.979
  4652.9                                                        0.598     3.464
  5453.7                                                        0.682     3.950
  6392.3                                                        0.763     4.419
  7492.4                                                        0.837     4.848
  8781.9                                                        0.901     5.217
 10293.3                                                        0.951     5.507
 12064.8                                                        0.985     5.701
 14141.2                                                        1.000     5.790
 16574.9                                                        0.996     5.767
 19427.5                                                        0.973     5.635
 22771.0                                                        0.933     5.400
 26689.9                                                        0.877     5.075
 31283.3                                                        0.808     4.679
 36667.2                                                        0.731     4.231
 42977.7                                                        0.648     3.753
 50374.3                                                        0.564     3.265
 59043.8                                                        0.481     2.786
 69205.4                                                        0.403     2.332
 81115.8                                                        0.331     1.915
 95076.1                                                        0.266     1.542
111438.8                                                        0.210     1.218

Cumulative Results:
25 % of distribution \ 6315.17 nm
50 % of distribution : 13239.96 nm
75 % of distribution . 27352.31 nm
99 % of distribution . 77316.82 nm

Run Time          = 0  Hr 15 Min 51 Sec        Wavelength      = 632.8   nm
Count Rate        = 40      Khz                Temperature     = 20      deg C
Channel #1        = 64.0    K                  Viscosity       = 1.002   cp
Channel Width     = 500.0   uSec               Index of Ref.   = 1.333
```

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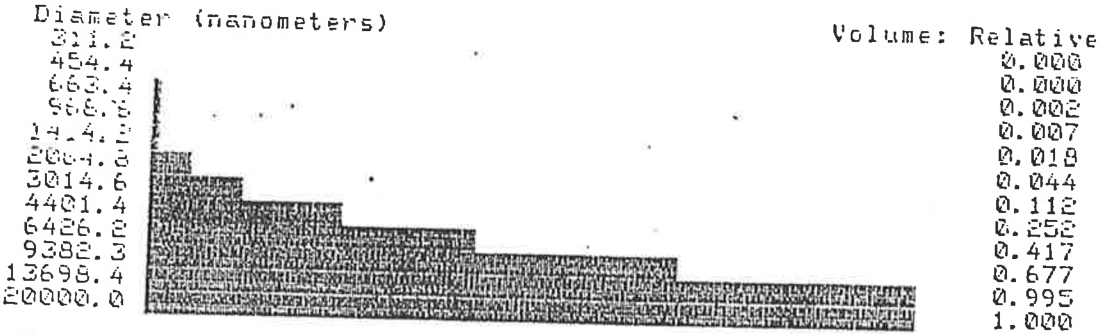
```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 14962.6 nm      Volume:   100.00 %
```



```
Mean Diameter = 12546.4 nm    Fit Error = 24.411     Residual = 73.796

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm
Smoothing  = 5              Plot Size  = 15
                           Plot Range = 200

Run Time        = 0  Hr 17 Min 46 Sec      Wavelength     = 632.8  nm
Count Rate      = 46       Khz             Temperature    = 20     deg C
Channel #1      = 66.7     K               Viscosity      = 1.002  cp
Channel Width   = 500.0    uSec            Index of Ref.  = 1.333

GAUSSIAN SUMMARY:
Mean Diameter    = 28496.3 nm              Chi Squared        = 67.562
Stnd. Deviation = 32854.2 nm (115.3 %)    Baseline Adj.       = 0.010 %
Coeff. of Var'n = 1.153                 Mean Diff. Coeff. = 1.50E-10 cm2/s
```

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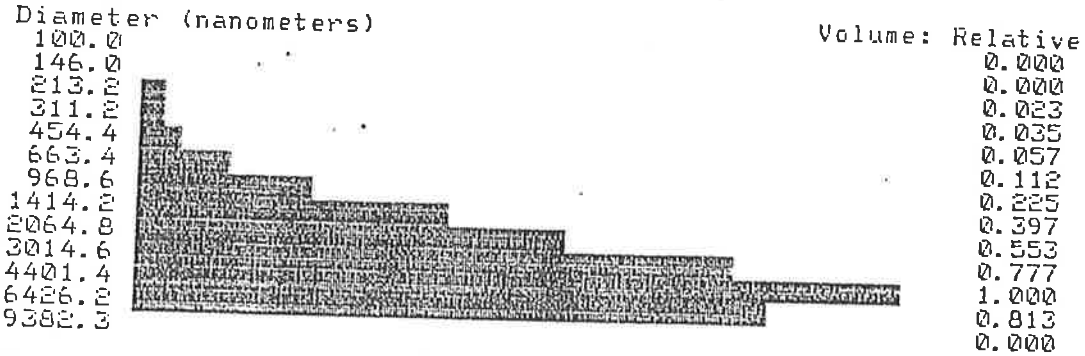
```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 4171.0 nm      Volume:   100.00 %
```



```
Mean Diameter = 3508.5 nm   Fit Error = 43.645    Residual = 110.159
NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm       Plot Size  = 15
Smoothing  = 5             Plot Range = 200

Run Time        = 0  Hr 11 Min 49 Sec     Wavelength     = 632.8  nm
Count Rate      = 164     Khz             Temperature    = 20     deg C
Channel #1      = 1163.3  K               Viscosity      = 1.002  cp
Channel Width   = 355.3   uSec            Index of Ref.  = 1.333

GAUSSIAN SUMMARY:
Mean Diameter   = 21284.0 nm               Chi Squared        = 43.627
Stnd. Deviation = 31278.8 nm (147.0 %)   Baseline Adj.      = 0.021 %
Coeff. of Var'n = 1.470               Mean Diff. Coeff. = 2.01E-10 cm2/s
```

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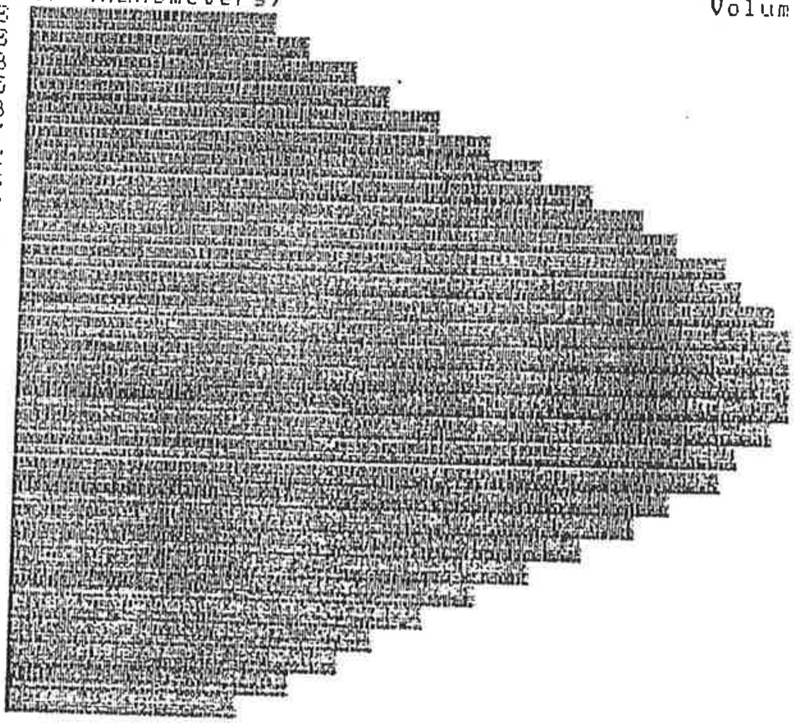

```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter    = 22094.8 nm
Stnd. Deviation = 32966.0 nm (149.2 %)  Chi Squared          = 44.878
Coeff. of Var'n = 1.492                  Baseline Adj.        = 0.009 %
                                        Mean Diff. Coeff. = 1.94E-10 cm2/s

Diameter (nanometers)
                                         Volume: Relative   Percent
  726.3                                          0.305      1.451
  851.3                                          0.357      1.701
  997.8                                          0.413      1.970
 1169.5                                          0.474      2.257
 1370.8                                          0.537      2.557
 1606.7                                          0.601      2.863
 1883.2                                          0.665      3.170
 2207.3                                          0.728      3.471
 2587.2                                          0.788      3.757
 3032.5                                          0.844      4.021
 3554.4                                          0.893      4.256
 4166.1                                          0.934      4.453
 4883.1                                          0.967      4.606
 5723.5                                          0.989      4.712
 6708.5                                          1.000      4.765
 7863.0                                          1.000      4.765
 9216.3                                          0.989      4.711
10802.4                                          0.966      4.606
12661.5                                          0.934      4.452
14840.6                                          0.893      4.254
17394.7                                          0.844      4.020
20388.4                                          0.788      3.756
23897.3                                          0.728      3.469
28010.1                                          0.665      3.168
32830.7                                          0.600      2.861
38480.9                                          0.536      2.555
45103.6                                          0.473      2.255
52866.0                                          0.413      1.969
61964.4                                          0.357      1.699
72628.5                                          0.304      1.450

Cumulative Results:
25 % of distribution < 2778.04 nm
50 % of distribution < 6706.07 nm
75 % of distribution < 16189.10 nm
99 % of distribution < [illegible] nm

Run Time        = 0  Hr 10 Min 49 Sec      Wavelength      = 632.8  nm
Count Rate      = 161       kHz            Temperature     = 20     deg C
Channel #1      = 1086.1    K              Viscosity       = 1.002  cp
Channel width   = [illegible]   usec       Index of Ref.   = 1.333
```

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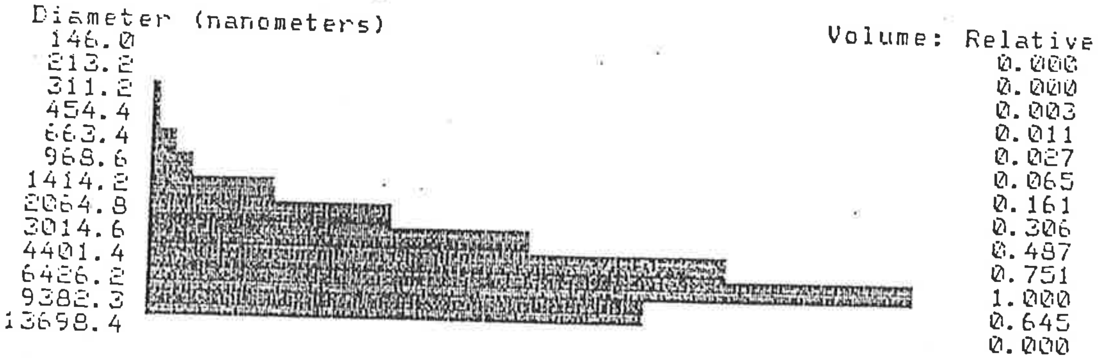
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)

```
NICOMP SUMMARY:
Peak Number 1:   Mean Diameter = 5983.8 nm      Volume:   100.00 %
```

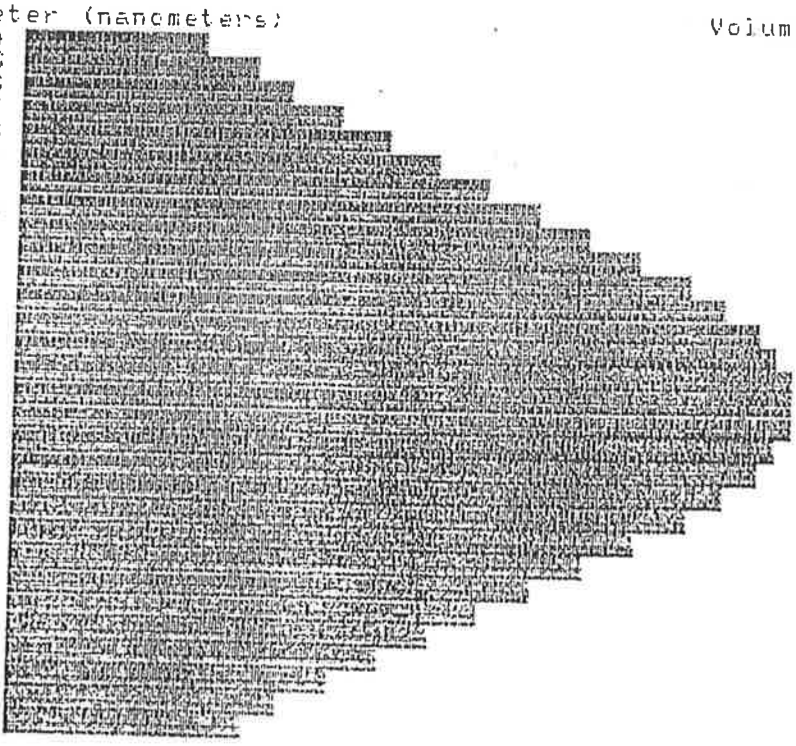


```
Diameter (nanometers)
  146.0                                          Volume: Relative
  213.2                                                    0.000
  311.2                                                    0.000
  454.4                                                    0.003
  663.4                                                    0.011
  968.6                                                    0.027
 1414.2                                                    0.065
 2064.8                                                    0.161
 3014.6                                                    0.306
 4401.4                                                    0.487
 6426.2                                                    0.751
 9382.3                                                    1.000
13698.4                                                    0.645
                                                           0.000
```

```
Mean Diameter = 5266.1 nm    Fit Error = 21.695     Residual = 94.008

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm          Plot Size  = 15
Smoothing  = 5                Plot Range = 200

Run Time        = 0  Hr 11 Min 49 Sec       Wavelength      = 632.8  nm
Count Rate      = 24       Khz               Temperature     = 20     deg C
Channel #1      = 43.6     K                 Viscosity       = 1.002  cp
Channel Width   = 266.0    uSec              Index of Ref.   = 1.333

GAUSSIAN SUMMARY:
Mean Diameter   = 19014.8 nm                Chi Squared         = 1.409
Stnd. Deviation = 26829.1 nm (141.1 %)       Baseline Adj.       = 0.000 %
Coeff. of Var'n = 1.411                    Mean Diff. Coeff. = 2.25E-10 cm2/s
```

9

```
            VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
 GAUSSIAN SUMMARY:
 Mean Diameter  = 19014.8 nm                  Chi Squared        = 1.409
 Stnd. Deviation = 26829.1 nm (141.1 %)   Baseline Adj.        = 0.000 %
 Coeff. of Var'n = 1.411                 Mean Diff. Coeff. = 2.25E-10 cm2/s
```



```
 Diameter (nanometers)                          Volume: Relative   Percent
   644.4                                                 0.238      1.179
   755.3                                                 0.287      1.417
   885.3                                                 0.340      1.682
  1037.7                                                 0.399      1.972
  1216.3                                                 0.462      2.283
  1425.6                                                 0.528      2.609
  1670.9                                                 0.596      2.944
  1958.5                                                 0.664      3.281
  2295.6                                                 0.730      3.610
  2690.6                                                 0.793      3.922
  3153.7                                                 0.851      4.208
  3696.4                                                 0.902      4.457
  4332.6                                                 0.943      4.662
  5078.3                                                 0.974      4.815
  5952.2                                                 0.993      4.910
  6976.6                                                 1.000      4.944
  8177.3                                                 0.994      4.915
  9584.7                                                 0.976      4.826
 11234.2                                                 0.946      4.678
 13167.7                                                 0.906      4.478
 15433.8                                                 0.856      4.232
 18090.0                                                 0.799      3.950
 21203.4                                                 0.736      3.640
 24852.5                                                 0.670      3.312
 29129.7                                                 0.602      2.975
 34143.0                                                 0.534      2.639
 40019.1                                                 0.468      2.312
 46906.4                                                 0.405      2.000
 54979.2                                                 0.345      1.708
 64441.2                                                 0.291      1.440

 Cumulative Results:
 25 % of distribution ( 2700.74 nm
 50 % of distribution ( 6357.09 nm
 75 % of distribution ( 14851.92 nm
 99 % of distribution ( 37714.17 nm

 Run Time        = 0  Hr 11 Min 45 Sec      Wavelength     = 632.8  nm
 Count Rate      = 24       kHz             Temperature    = 20     deg C
 Channel #1      = 43.6     K               Viscosity      = 1.002  cp
 Channel Width   = 262.0    uSec            Index of Ref.  = 1.333
```

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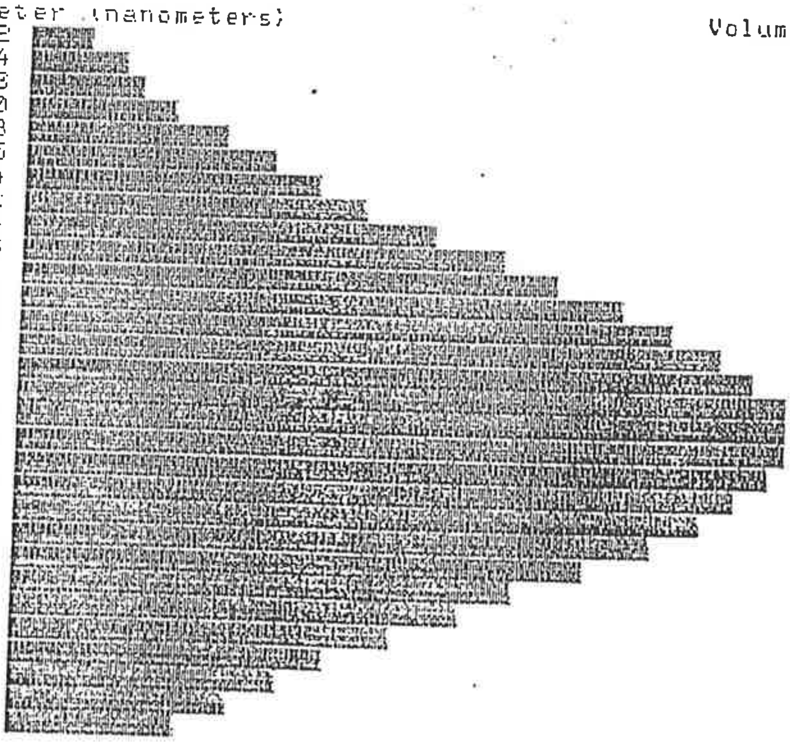


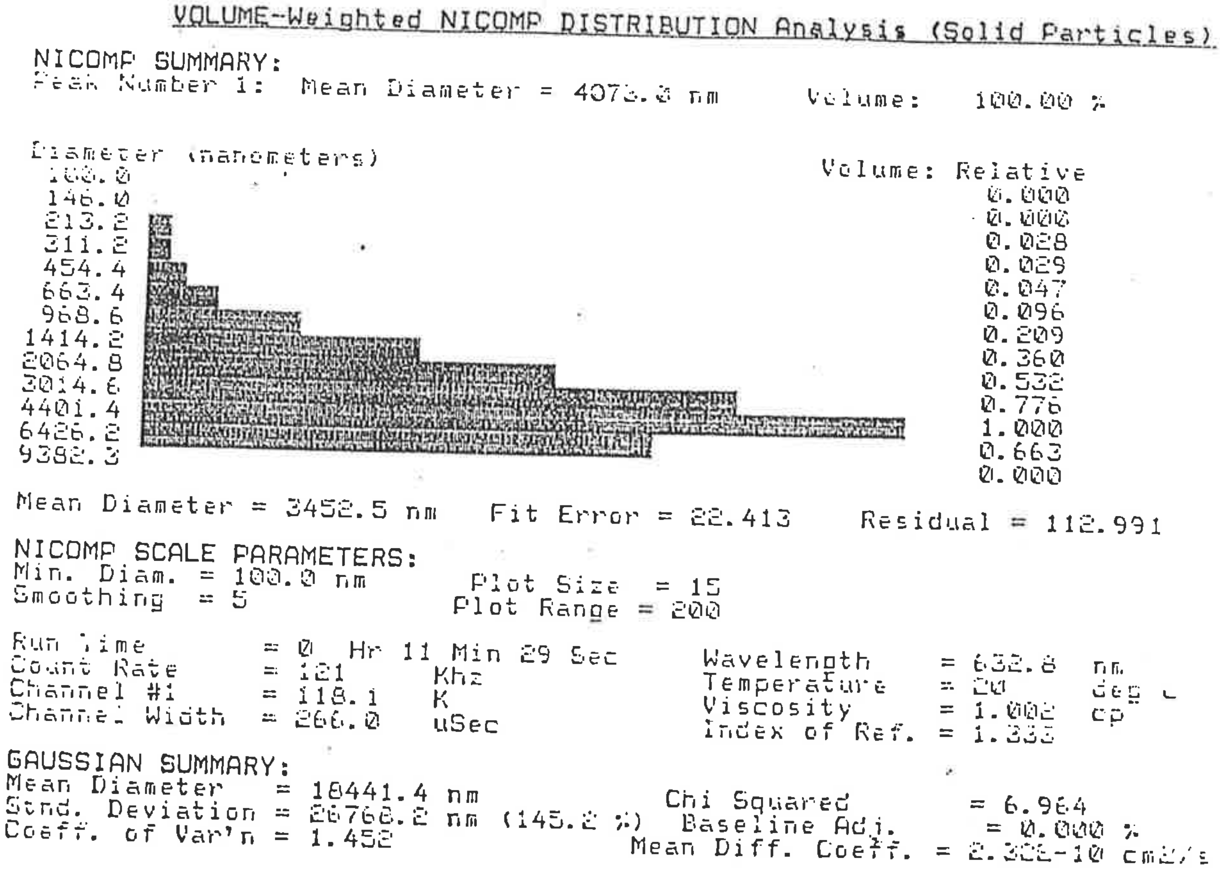
```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter      = 10229.1 nm
Stnd. Deviation'= 11845.3 nm (115.8 %)   Chi Squared          = 0.215
Coeff. of Var'n = 1.158                   Baseline Adj.         = 0.036 %
                                      Mean Diff. Coeff.  = 4.19E-10 cm2/s

Diameter (nanometers)
396.2                                              Volume: Relative  Percent
464.4                                                       0.084     0.479
544.3                                                       0.112     0.644
638.0                                                       0.148     0.849
747.8                                                       0.192     1.100
876.5                                                       0.244     1.398
1027.4                                                      0.304     1.743
1204.2                                                      0.373     2.134
1411.4                                                      0.448     2.563
1654.3                                                      0.528     3.022
1939.1                                                      0.610     3.496
2272.8                                                      0.693     3.969
2663.9                                                      0.772     4.422
3122.4                                                      0.844     4.835
3659.8                                                      0.906     5.188
4289.6                                                      0.954     5.464
5027.9                                                      0.986     5.646
5893.2                                                      1.000     5.727
6907.4                                                      0.995     5.700
8096.2                                                      0.972     5.567
9489.6                                                      0.932     5.337
11122.8                                                     0.877     5.020
13037.0                                                     0.809     4.635
15280.7                                                     0.733     4.199
17910.6                                                     0.652     3.733
20993.1                                                     0.569     3.258
24606.0                                                     0.487     2.789
28840.8                                                     0.409     2.344
33804.3                                                     0.338     1.933
39622.1                                                     0.273     1.565
                                                            0.217     1.243

Cumulative Results:
25 % of distribution < 2207.00 nm
50 % of distribution < 4668.10 nm
75 % of distribution < 9719.56 nm
95 % of distribution < 24626.27 nm

Run Time        = 0  Hr  9 Min 34 Sec      Wavelength     = 632.8  nm
Count Rate      = 56      khz              Temperature    = 20     deg C
Channel #1      = 72.4    K                Viscosity      = 1.002  cp
Channel width   = 266.0   uSec             Index of Ref.  = 1.333
```

11



```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 4073.0 nm      Volume:   100.00 %

Diameter (nanometers)
  100.0                                           Volume: Relative
  146.0                                                     0.000
  213.2                                                     0.000
  311.2                                                     0.028
  454.4                                                     0.029
  663.4                                                     0.047
  968.6                                                     0.096
 1414.2                                                     0.209
 2064.8                                                     0.360
 3014.6                                                     0.532
 4401.4                                                     0.776
 6426.2                                                     1.000
 9382.3                                                     0.663
                                                            0.000
Mean Diameter = 3452.5 nm   Fit Error = 22.413    Residual = 112.991

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm          Plot Size  = 15
Smoothing  = 5                Plot Range = 200

Run Time        = 0  Hr 11 Min 29 Sec     Wavelength     = 632.8  nm
Count Rate      = 121     Khz             Temperature    = 20     deg C
Channel #1      = 118.1   K               Viscosity      = 1.002  cp
Channel Width   = 266.0   uSec            Index of Ref.  = 1.333

GAUSSIAN SUMMARY:
Mean Diameter    = 18441.4 nm              Chi Squared         = 6.964
Stnd. Deviation = 26768.2 nm (145.2 %)   Baseline Adj.        = 0.000 %
Coeff. of Var'n = 1.452                 Mean Diff. Coeff. = 2.32E-10 cm2/s
```

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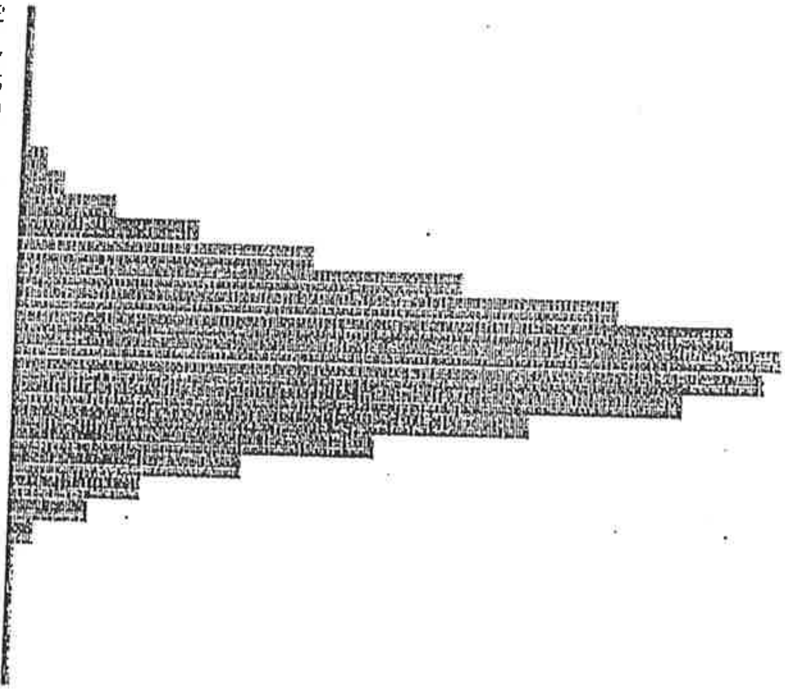
```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)

GAUSSIAN SUMMARY:
Mean Diameter    = 995.9 nm                   Chi Squared          = 2753.531
Stnd. Deviation. = 485.1 nm (48.7 %)          Baseline Adj.        = 0.024 %
Coeff. of Var'n  = 0.487                      Mean Diff. Coeff.    = 4.30E-09 cm2/s
```



```
Diameter (nanometers)
   78.7                                    Volume: Relative   Percent
   92.2                                             0.000      0.000
  108.1                                             0.000      0.000
  126.7                                             0.000      0.001
  148.5                                             0.000      0.005
  174.0                                             0.001      0.016
  204.0                                             0.004      0.050
  239.1                                             0.011      0.139
  280.2                                             0.027      0.353
  328.4                                             0.062      0.803
  384.9                                             0.127      1.644
  451.2                                             0.233      3.025
  528.8                                             0.386      5.005
  619.9                                             0.574      7.448
  726.5                                             0.768      9.964
  851.6                                             0.924     11.987
  998.1                                             1.000     12.966
 1169.9                                             0.973     12.612
 1371.3                                             0.851     11.030
 1607.3                                             0.669      8.674
 1883.9                                             0.473      6.133
 2208.1                                             0.301      3.900
 2588.1                                             0.172      2.229
 3033.6                                             0.088      1.146
 3555.6                                             0.041      0.530
 4167.6                                             0.017      0.220
 4884.8                                             0.006      0.082
 5725.5                                             0.002      0.028
 6710.9                                             0.001      0.008
 7865.9                                             0.000      0.002
                                                    0.000      0.001

Cumulative Results:
25 % of distribution < 586.68 nm
50 % of distribution < 816.80 nm
75 % of distribution < 1135.95 nm
99 % of distribution < 2542.29 nm

Run Time           = 0  Hr 10 Min 35 Sec      Wavelength       = 632.8   nm
Count Rate         = 285      Khz             Temperature      = 20      deg C
Channel #1         = 2729.2   K               Viscosity        = 1.002   cp
Channel Width      = 561.0    uSec            Index of Ref.    = 1.333
```

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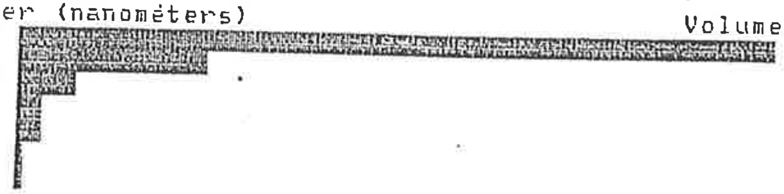

```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 115.6 nm      Volume:   100.00 %

Diameter (nanometers)
                                                      Volume: Relative
 100.0                                                         1.000
 146.0                                                         0.260
 213.2                                                         0.079
 311.2                                                         0.028
 454.4                                                         0.022
 663.4                                                         0.012
 968.6                                                         0.007
1414.2                                                         0.000

Mean Diameter = 133.8 nm   Fit Error = 2386.618   Residual = 44.956

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm        Plot Size  = 15
Smoothing  = 5              Plot Range = 200

Run Time        = 0  Hr 11 Min 17 Sec     Wavelength      = 632.8  nm
Count Rate      = 285      Khz            Temperature     = 20     deg C
Channel #1      = 2904.6   K              Viscosity       = 1.002  cp
Channel Width   = 561.0    uSec           Index of Ref.   = 1.333

GAUSSIAN SUMMARY:
Mean Diameter    = 988.7 nm               Chi Squared          = 2968.555
Stnd. Deviation = 484.1 nm (49.0 %)      Baseline Adj.        = 0.018 %
Coeff. of Var'n = 0.490                  Mean Diff. Coeff.    = 4.33E-09 cm2/s
```

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```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 129.0 nm     Volume:   100.00 %
```

```
Diameter (nanometers)                                  Volume: Relative
 100.0                                                          1.000
 146.0                                                          0.467
 213.2                                                          0.250
 311.2                                                          0.126
 454.4                                                          0.127
 663.4                                                          0.116
 968.6                                                          0.108
1414.2                                                          0.000

Mean Diameter = 227.7 nm   Fit Error = 378.657   Residual = 2.009

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm        Plot Size  = 15
Smoothing  = 5              Plot Range = 200

Run Time         = 0  Hr 37 Min 25 Sec     Wavelength     = 632.8  nm
Count Rate       = 281       Khz           Temperature    = 20     deg C
Channel #1       = 2588.1   K              Viscosity      = 1.002  cp
Channel Width    = 22.7      uSec          Index of Ref.  = 1.333

GAUSSIAN SUMMARY:
Mean Diameter    = 164.1 nm
Stnd. Deviation  = 74.2  nm (45.2 %)    Chi Squared         = 15.619
Coeff. of Var'n  = 0.452                Baseline Adj.       = 0.000 %
                                        Mean Diff. Coeff. = 2.61E-08 cm2/s
```

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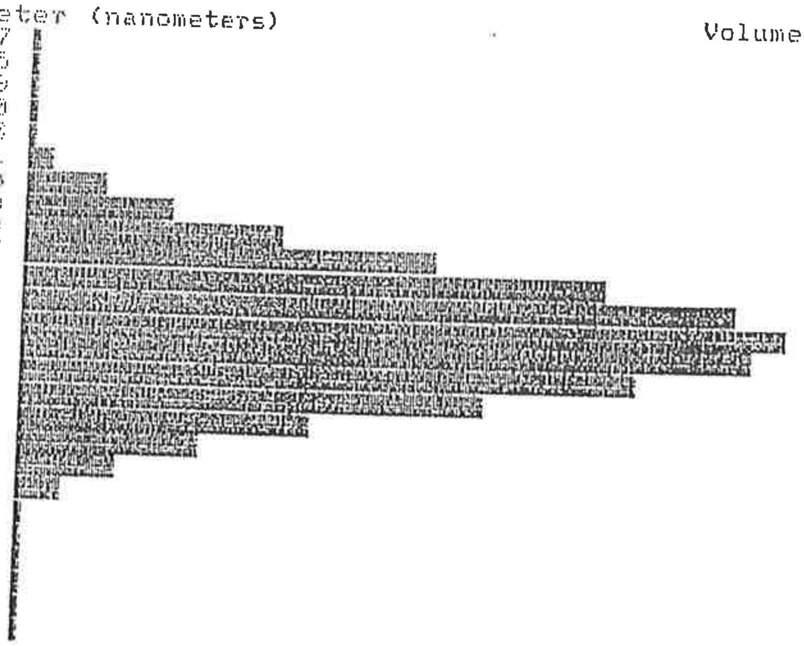

```
          VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter    = 164.9 nm
Stnd. Deviation = 74.0   nm  (44.9 %)     Chi Squared          = 9.224
Coeff. of Var'n = 0.449                   Baseline Adj.        = 0.000 %
                                          Mean Diff. Coeff.    = 2.60E-08 cm2/s

Diameter (nanometers)
                                                   Volume: Relative   Percent
  21.7                                                      0.000      0.001
  25.5                                                      0.000      0.006
  29.9                                                      0.002      0.023
  35.0                                                      0.005      0.077
  41.0                                                      0.016      0.226
  48.1                                                      0.042      0.587
  56.3                                                      0.095      1.346
  66.0                                                      0.193      2.723
  77.4                                                      0.345      4.861
  90.7                                                      0.543      7.655
 106.4                                                      0.754     10.636
 124.7                                                      0.925     13.039
 146.1                                                      1.000     14.103
 171.3                                                      0.954     13.459
 200.7                                                      0.804     11.332
 235.3                                                      0.597      8.419
 275.8                                                      0.391      5.518
 323.2                                                      0.226      3.191
 378.8                                                      0.115      1.628
 444.0                                                      0.052      0.733
 520.5                                                      0.021      0.291
 610.0                                                      0.007      0.102
 715.0                                                      0.002      0.032
 838.1                                                      0.001      0.009
 982.3                                                      0.000      0.002
1151.4                                                      0.000      0.000
1349.5                                                      0.000      0.000
1581.6                                                      0.000      0.000

Cumulative Results:
25 % of distribution < 101.48 nm
50 % of distribution < 137.67 nm
75 % of distribution < 186.95 nm
95 % of distribution < 392.96 nm

Run Time          = 0  Hr 23 Min 34 Sec
Count Rate        = 285     Khz            Wavelength       = 632.8   nm
Channel #1        = 1650.4  K              Temperature      = 20      deg C
Channel Width     = 22.7    uSec           Viscosity        = 1.002   cp
                                           Index of Ref.    = 1.333
```

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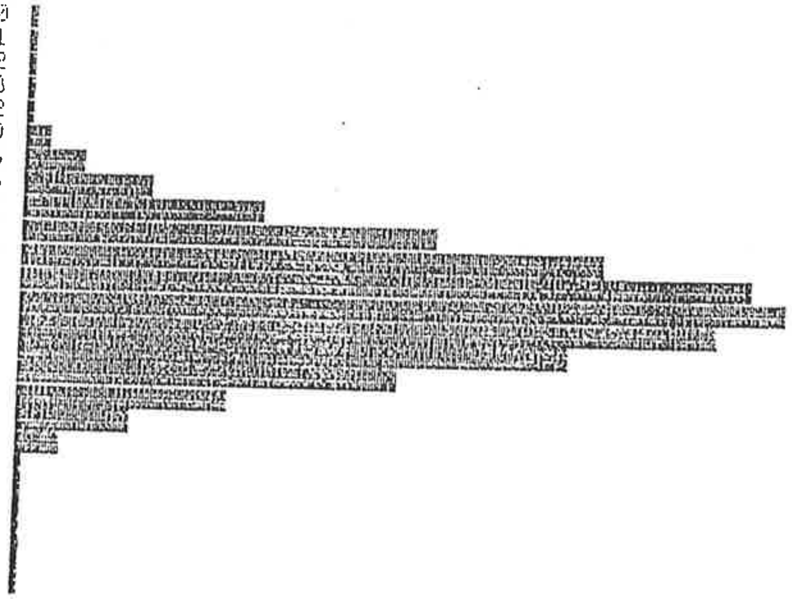
```
           VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter    = 503.2 nm
Stnd. Deviation = 204.1 nm  (40.6 %)      Chi Squared          = 27.085
Coeff. of Var'n = 0.406                   Baseline Adj.        = 0.000 %
                                          Mean Diff. Coeff.    = 8.51E-09 cm2/s
```



```
Diameter (nanometers)
  43.5                                         Volume: Relative  Percent
  51.0                                                  0.000     0.000
  59.7                                                  0.000     0.000
  70.0                                                  0.000     0.000
  82.1                                                  0.000     0.000
  96.2                                                  0.000     0.002
 112.8                                                  0.001     0.009
 132.2                                                  0.002     0.036
 154.9                                                  0.008     0.131
 181.6                                                  0.026     0.406
 212.8                                                  0.069     1.084
 249.4                                                  0.159     2.479
 292.4                                                  0.312     4.866
 342.7                                                  0.525     8.195
 401.7                                                  0.759    11.840
 470.8                                                  0.940    14.675
 551.8                                                  1.000    15.685
 646.8                                                  0.912    14.237
 758.1                                                  0.714    11.143
 888.6                                                  0.479     7.402
1041.5                                                  0.276     4.310
1220.7                                                  0.137     2.130
1430.8                                                  0.056     0.903
1677.1                                                  0.021     0.329
1965.7                                                  0.007     0.103
2304.0                                                  0.002     0.027
2700.5                                                  0.000     0.006
3165.3                                                  0.000     0.001
3710.1                                                  0.000     0.000
4348.6                                                  0.000     0.000
                                                        0.000     0.000

Cumulative Results:
25 % of distribution < 324.58 nm
50 % of distribution < 428.16 nm
75 % of distribution < 563.23 nm
99 % of distribution < 1111.44 nm

Run Time         = 0  Hr 13 Min 42 Sec
Count Rate       = 316      Khz             Wavelength      = 632.8   nm
Channel #1       = 2540.4   K               Temperature     = 20      deg C
Channel Width    = 53.7     uSec            Viscosity       = 1.002   cp
                                            Index of Ref.   = 1.333
```

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```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:   Mean Diameter = 133.3 nm      Volume:   68.85 %
Peak Number 2:   Mean Diameter = 1287.3 nm      Volume:   31.15 %
```

```
Diameter (nanometers)
  100.0                                              Volume: Relative
  146.0                                                        1.000
  213.2                                                        0.608
  311.2                                                        0.321
  454.4                                                        0.209
  663.4                                                        0.300
  968.6                                                        0.368
 1414.2                                                        0.421
 2064.8                                                        0.452
 3014.6                                                        0.394
                                                               0.000
Mean Diameter = 629.4 nm    Fit Error = 169.311    Residual = 1.257
NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm         Plot Size  = 15
Smoothing  = 5               Plot Range = 200

Run Time        = 0  Hr 15 Min 18 Sec      Wavelength     = 632.8   nm
Count Rate      = 308     Khz              Temperature    = 20      deg C
Channel #1      = 2854.8  K                Viscosity      = 1.002   cp
Channel Width   = 53.7    uSec             Index of Ref.  = 1.333
GAUSSIAN SUMMARY:
Mean Diameter    = 504.6 nm                Chi Squared        = 22.528
Stnd. Deviation  = 208.6 nm (41.3 %)       Baseline Adj.      = 0.000 %
Coeff. of Var'n  = 0.413                   Mean Diff. Coeff.  = 8.49E-09 cm2/s
```

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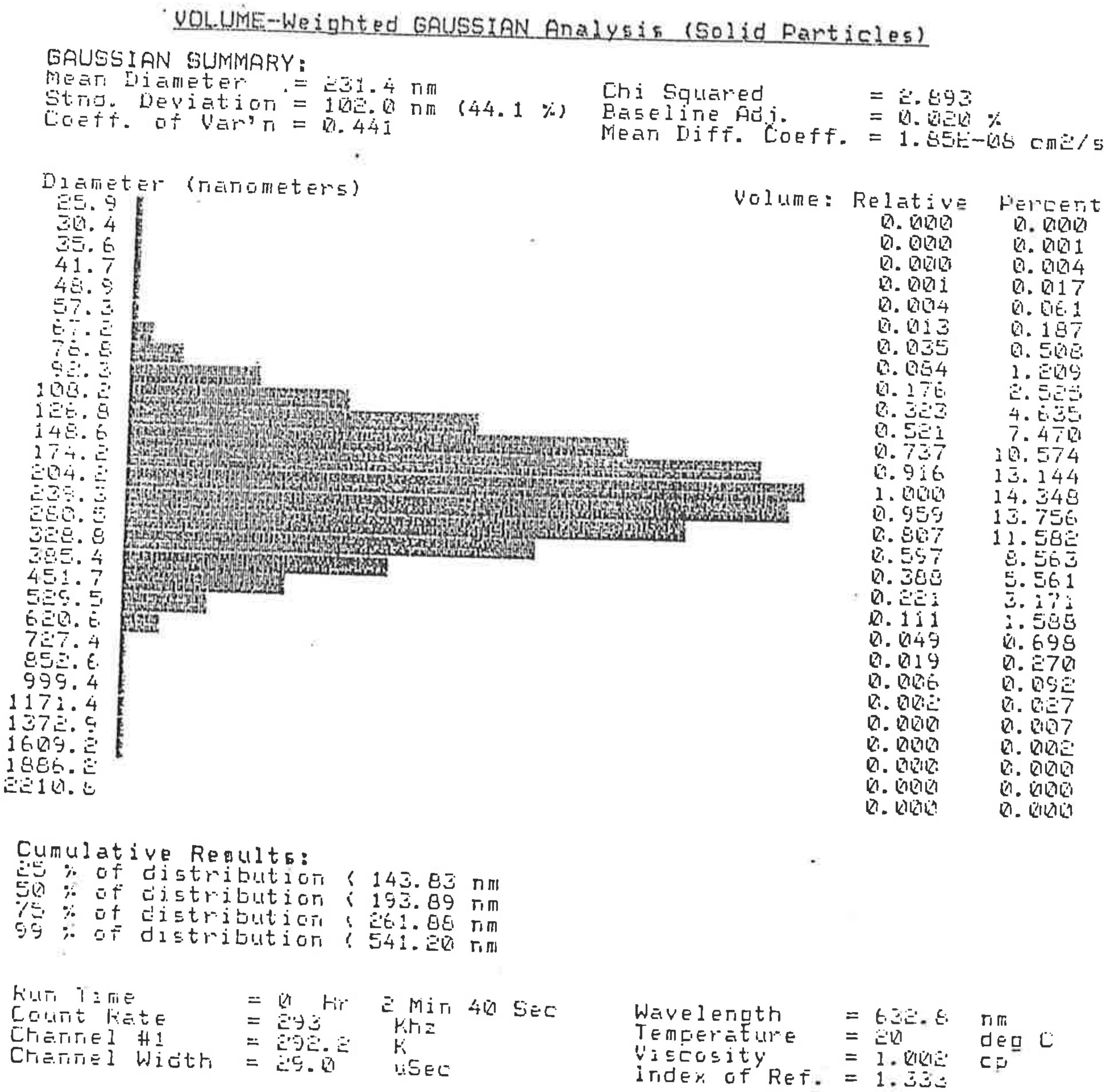

```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter   .= 231.4 nm                        Chi Squared        = 2.893
Stnd. Deviation = 102.0 nm  (44.1 %)               Baseline Adj.      = 0.020 %
Coeff. of Var'n = 0.441                            Mean Diff. Coeff.  = 1.85E-08 cm2/s

Diameter (nanometers)
   25.9                                  Volume: Relative  Percent
   30.4                                            0.000     0.000
   35.6                                            0.000     0.001
   41.7                                            0.000     0.004
   48.9                                            0.001     0.017
   57.3                                            0.004     0.061
   67.2                                            0.013     0.187
   78.8                                            0.035     0.508
   92.3                                            0.084     1.209
  108.2                                            0.176     2.525
  126.8                                            0.323     4.635
  148.6                                            0.521     7.470
  174.2                                            0.737    10.574
  204.2                                            0.916    13.144
  239.3                                            1.000    14.348
  280.5                                            0.959    13.756
  328.8                                            0.807    11.582
  385.4                                            0.597     8.563
  451.7                                            0.388     5.561
  529.5                                            0.221     3.171
  620.6                                            0.111     1.588
  727.4                                            0.049     0.698
  852.6                                            0.019     0.270
  999.4                                            0.006     0.092
 1171.4                                            0.002     0.027
 1372.9                                            0.000     0.007
 1609.2                                            0.000     0.002
 1886.2                                            0.000     0.000
 2210.6                                            0.000     0.000
                                                   0.000     0.000

Cumulative Results:
25 % of distribution < 143.83 nm
50 % of distribution < 193.89 nm
75 % of distribution < 261.88 nm
99 % of distribution < 541.20 nm

Run Time         = 0  Hr  2 Min 40 Sec      Wavelength     = 632.8  nm
Count Rate       = 293     Khz              Temperature    = 20     deg C
Channel #1       = 292.2   K                Viscosity      = 1.002  cp
Channel Width    = 29.0    uSec             Index of Ref.  = 1.333
```

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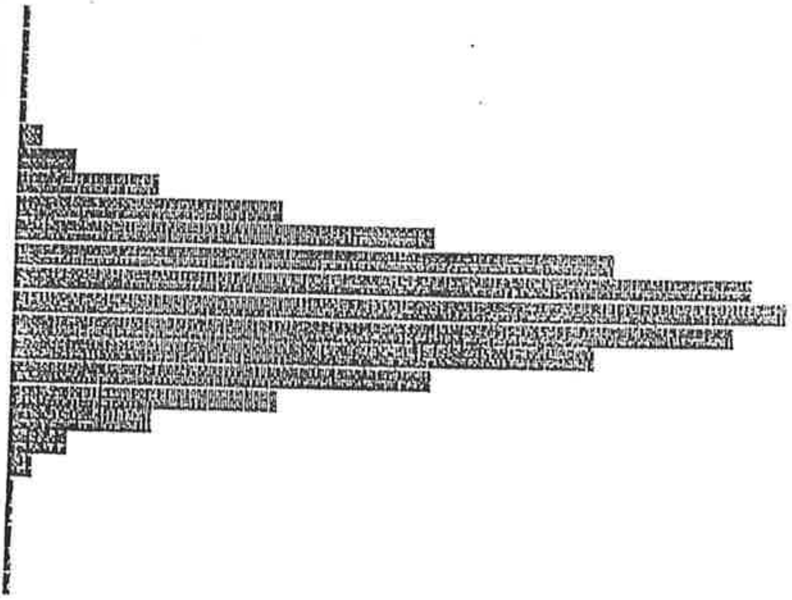
```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter    = 562.1 nm                Chi Squared          = 152.400
Stnd. Deviation = 240.4  nm  (42.8 %)     Baseline Adj.        = 0.000 %
Coeff. of Var'n = 0.428                    Mean Diff. Coeff.    = 7.62E-09 cm2/s

Diameter (nanometers)
                                          Volume: Relative   Percent
  47.6                                            0.000      0.000
  55.8                                            0.000      0.000
  65.3                                            0.000      0.000
  76.6                                            0.000      0.001
  89.8                                            0.000      0.004
 105.2                                            0.001      0.016
 123.3                                            0.004      0.057
 144.6                                            0.012      0.185
 169.4                                            0.035      0.517
 198.6                                            0.085      1.263
 232.8                                            0.181      2.680
 272.8                                            0.336      4.983
 319.8                                            0.543      8.046
 374.8                                            0.764     11.319
 439.3                                            0.937     13.673
 515.0                                            1.000     14.814
 603.6                                            0.930     13.780
 707.5                                            0.754     11.137
 829.2                                            0.532      7.684
 971.9                                            0.327      4.850
1139.2                                            0.175      2.599
1335.2                                            0.082      1.213
1565.0                                            0.033      0.493
1834.4                                            0.012      0.175
2150.1                                            0.004      0.054
2520.1                                            0.001      0.015
2953.8                                            0.000      0.003
3462.2                                            0.000      0.001
4058.1                                            0.000      0.000
4756.5                                            0.000      0.000
```



```
Cumulative Results:
25 % of distribution < 353.99 nm
50 % of distribution < 473.82 nm
75 % of distribution < 633.96 nm
99 % of distribution < 1290.72 nm

Run Time        = 0   Hr   5 Min 48 Sec      Wavelength    = 632.8   nm
Count Rate      = 282      Khz               Temperature   = 20      deg C
Channel #1      = 1154.1   K                 Viscosity     = 1.002   cp
Channel Width   = 53.7     uSec              Index of Ref. = 1.333
```

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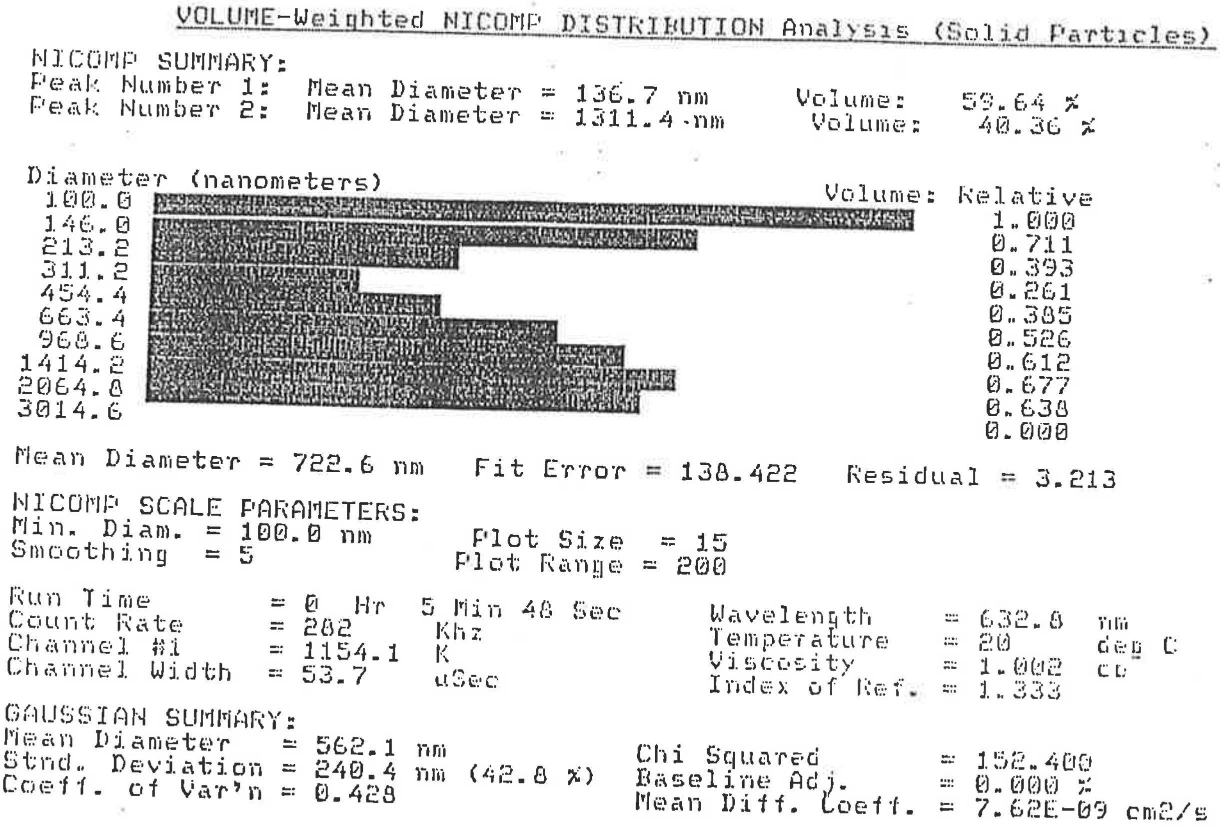

```
          VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:  Mean Diameter = 136.7 nm      Volume:   59.64 %
Peak Number 2:  Mean Diameter = 1311.4 nm      Volume:   40.36 %

Diameter (nanometers)                                   Volume: Relative
  100.0                                                           1.000
  146.0                                                           0.711
  213.2                                                           0.393
  311.2                                                           0.261
  454.4                                                           0.385
  663.4                                                           0.526
  968.6                                                           0.612
 1414.2                                                           0.677
 2064.0                                                           0.638
 3014.6                                                           0.000

Mean Diameter = 722.6 nm    Fit Error = 138.422    Residual = 3.213

NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm       Plot Size  = 15
Smoothing  = 5             Plot Range = 200

Run Time        = 0  Hr  5 Min 48 Sec       Wavelength      = 632.8  nm
Count Rate      = 282      Khz              Temperature     = 20     deg C
Channel #1      = 1154.1   K                Viscosity       = 1.002  cp
Channel Width   = 53.7     uSec             Index of Ref.   = 1.333

GAUSSIAN SUMMARY:
Mean Diameter   = 562.1 nm
Stnd. Deviation = 240.4 nm (42.8 %)    Chi Squared        = 152.400
Coeff. of Var'n = 0.428                Baseline Adj.      = 0.000 %
                                       Mean Diff. Coeff.  = 7.62E-09 cm2/s
```

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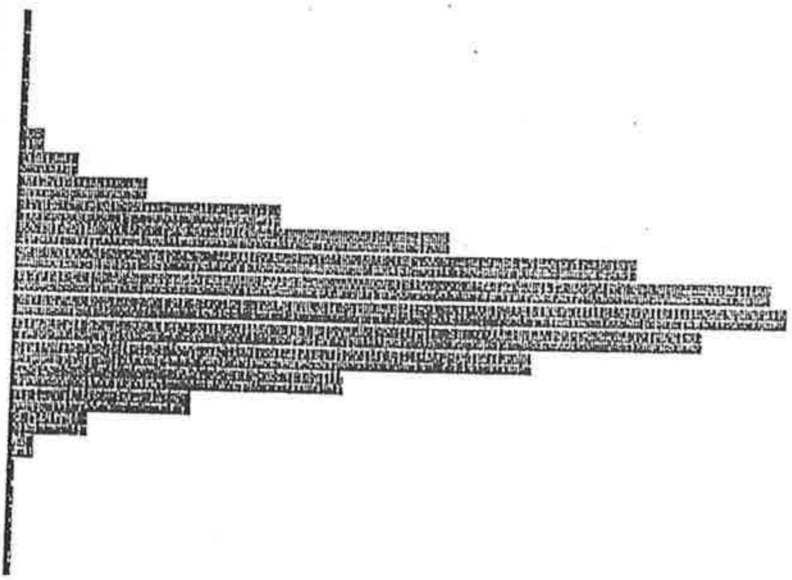
```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)
GAUSSIAN SUMMARY:
Mean Diameter      = 413.8 nm
Stnd. Deviation = 163.0 nm (39.4 %)     Chi Squared          = 44.247
Coeff. of Var'n = 0.394                 Baseline Adj.        = 0.000 %
                                        Mean Diff. Coeff.  = 1.04E-08 cm2/s
```



```
Diameter (nanometers)
   37.0                                     Volume: Relative   Percent
   43.4                                             0.000      0.000
   50.9                                             0.000      0.000
   59.6                                             0.000      0.000
   69.9                                             0.000      0.000
   81.9                                             0.000      0.001
   96.0                                             0.000      0.008
  112.6                                             0.002      0.034
  131.9                                             0.008      0.128
  154.7                                             0.026      0.414
  181.3                                             0.071      1.137
  212.5                                             0.166      2.652
  249.0                                             0.329      5.256
  291.9                                             0.554      8.857
  342.1                                             0.794     12.684
  401.0                                             0.967     15.440
  470.0                                             1.000     15.575
  550.9                                             0.879     14.048
  645.7                                             0.657     10.501
  756.8                                             0.418      6.671
  887.1                                             0.226      3.602
 1039.8                                             0.104      1.653
 1218.7                                             0.040      0.645
 1428.5                                             0.013      0.214
 1674.3                                             0.004      0.060
 1962.5                                             0.001      0.014
 2300.2                                             0.000      0.003
 2696.1                                             0.000      0.001
 3160.1                                             0.000      0.000
                                                    0.000      0.000

Cumulative Results:
25 % of distribution < 270.18 nm
50 % of distribution < 353.84 nm
75 % of distribution < 461.41 nm
99 % of distribution < 881.77 nm

Run Time          = 0  Hr   8 Min   5 Sec
Count Rate        = 320     Khz          Wavelength       = 632.8   nm
Channel #1        = 1622.7  K            Temperature      = 20      deg C
Channel Width     = 53.7    uSec         Viscosity        = 1.002   cp
                                         Index of Ref.    = 1.333
```

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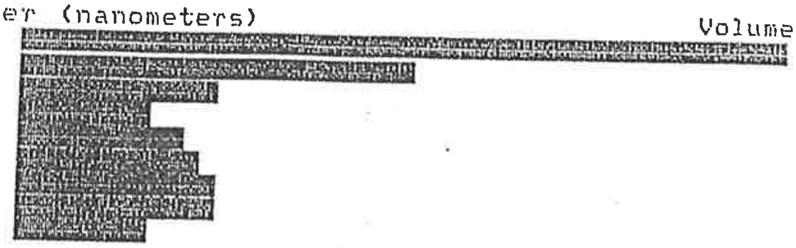
```
VOLUME-Weighted NICOMP DISTRIBUTION Analysis (Solid Particles)
NICOMP SUMMARY:
Peak Number 1:   Mean Diameter = 129.5 nm      Volume:   80.45 %
Peak Number 2:   Mean Diameter = 1227.1 nm      Volume:   19.55 %
```



```
Diameter (nanometers)
  100.0                                        Volume: Relative
  146.0                                                  1.000
  213.2                                                  0.507
  311.2                                                  0.252
  454.4                                                  0.159
  663.4                                                  0.199
  968.6                                                  0.219
 1414.2                                                  0.242
 2064.8                                                  0.243
 3014.6                                                  0.168
                                                         0.000
Mean Diameter = 481.1 nm   Fit Error = 249.257   Residual = 0.000
NICOMP SCALE PARAMETERS:
Min. Diam. = 100.0 nm       Plot Size  = 15
Smoothing  = 5             Plot Range = 200

Run Time          = 0  Hr  8 Min 46 Sec      Wavelength     = 632.8   nm
Count Rate        = 320     Khz              Temperature    = 20      deg C
Channel #1        = 1759.5  K                Viscosity      = 1.002   cp
Channel Width     = 53.7    uSec             Index of Ref.  = 1.333

GAUSSIAN SUMMARY:
Mean Diameter   = 413.4 nm                Chi Squared       = 44.191
Stnd. Deviation = 162.5 nm (39.3 %)       Baseline Adj.     = 0.000 %
Coeff. of Var'n = 0.393                   Mean Diff. Coeff. = 1.04E-08 cm2/s
```

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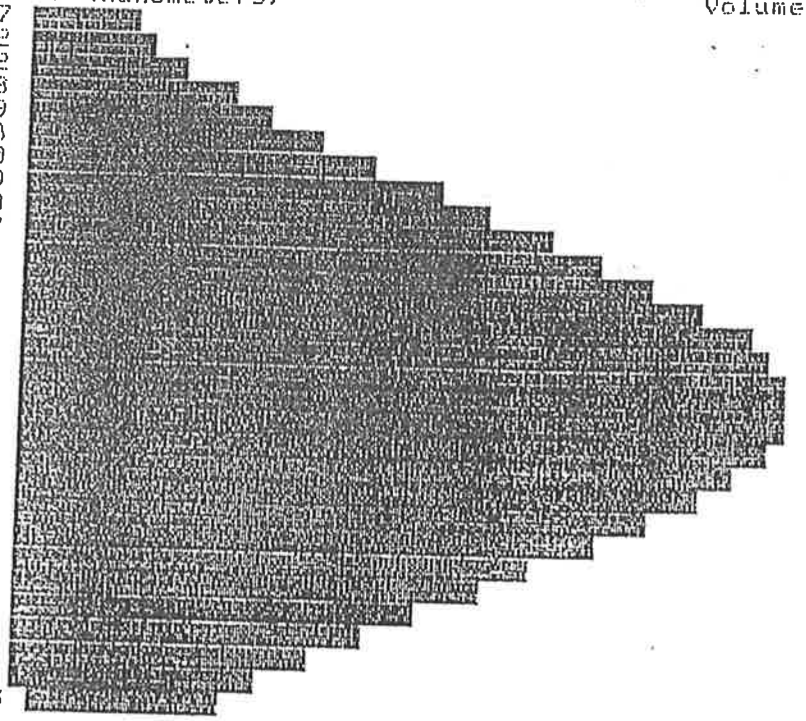
```
VOLUME-Weighted GAUSSIAN Analysis (Solid Particles)

GAUSSIAN SUMMARY:
Mean Diameter   = 29997.8 nm                          Chi Squared          = 2280.275
Stnd. Deviation = 37613.4 nm (125.4 %)                 Baseline Adj.        = 0.248 %
Coeff. of Var'n = 1.254                              Mean Diff. Coeff. = 1.43E-10 cm2/s
```



```
 Diameter (nanometers)                     Volume: Relative   Percent
   1095.7                                             0.132     0.710
   1284.2                                             0.169     0.909
   1505.2                                             0.213     1.145
   1764.3                                             0.264     1.419
   2067.9                                             0.322     1.731
   2423.8                                             0.386     2.078
   2841.0                                             0.456     2.455
   3329.9                                             0.530     2.854
   3903.0                                             0.607     3.266
   4574.7                                             0.683     3.677
   5362.1                                             0.757     4.074
   6284.9                                             0.825     4.442
   7366.5                                             0.886     4.766
   8634.3                                             0.935     5.033
  10120.3                                             0.972     5.229
  11862.1                                             0.994     5.348
  13903.5                                             1.000     5.381
  16296.4                                             0.990     5.329
  19101.0                                             0.965     5.193
  22388.3                                             0.926     4.981
  26241.4                                             0.874     4.701
  30757.6                                             0.811     4.366
  36051.1                                             0.741     3.990
  42255.6                                             0.667     3.589
  49527.9                                             0.590     3.177
  58051.7                                             0.514     2.767
  68042.5                                             0.441     2.372
  79752.8                                             0.372     2.001
  93478.5                                             0.309     1.661
 109566.3                                             0.252     1.357
```

```
Cumulative Results:
25 % of distribution < 5494.31 nm
50 % of distribution < 12168.37 nm
75 % of distribution < 26508.96 nm
99 % of distribution < 97464.68 nm

Run Time        = 0  Hr  5 Min 33 Sec      Wavelength       = 632.8   nm
Count Rate      = 459     Khz              Temperature      = 20      deg C
Channel #1      = 3159.4  K                Viscosity        = 1.002   cp
Channel Width   = 618.7   uSec             Index of Ref.    = 1.333
```